Electrophilicity of aromatic triflones in σ-complexation processes†

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The kinetics of σ-complexation of 2,6-bis(trifluoromethanesulfonyl)-4-nitroanisole (**4**) have been investigated over a large pH range of 2–15.68 in methanol. Two competitive processes have been identified with the initial addition of MeO^- at the unsubstituted 3-position of **4** to give a 1,3-dimethoxy adduct (**4b-Me**) and a subsequent and slow conversion of this species into the 1,1-dimethoxy isomer (**4a-Me**). Both **4a-Me** and **4b-Me** are more stable than the related adducts of 2,6-dinitro-4-trifluromethanesulfonylanisole, *i.e.* **5a-Me** and **5b-Me**, and 2,4,6-trinitroanisole, *i.e.* **6a-Me** and **6b-Me**, the latter compound being a conventional reference aromatic electrophile in Meisenheimer complex chemistry. The high thermodynamic stability of **4a-Me** (pK_a = 10.48) and **4b-Me** (pK_a = 12.23) relative to **5a-Me** (pK_a = 10.68) and **6a-Me** (pK_a = 12.56) or **5b-Me** (pK_a = 15.38) and **6b-Me** (pK_a = 16.46), is shown to derive from an especially high capacity of a *para* or an *ortho* SO_2CF_3 group to stabilize a negative charge through Fπ-type polarization effects. From the kinetic data, it appears that the contribution of a methanol pathway to the formation of **4a-Me** is much weaker than that found to operate in the formation of the 1,1-complex **5a-Me** of 2,6-dinitro-4-trifluromethanesulfonylanisole, the experimental evidence suggesting that the reactivity of **4** and **5** is located just beyond the region defining the boundary between super- and normal-electrophilicity in methanol. Comparison of our results with available literature data show that this boundary corresponds to a pK^{MeOH}_a value of ~ 10, in agreement with our previous finding of a very effective solvent contribution to the σ-complexation of 1,3,5-tris(trifluoromethanesulfonyl)benzene (**13**; pK^{MeOH}_a = 9.12) in methanol. Taking advantage of our observation that pK^{MeOH}_a and $pK^{H_2O}_a$ values for σ-complexation at unsubstituted ring positions are related by a nice linear correlation, an approximate ranking of the electrophilicity of our aromatic triflones on the *E* scale developed by Mayr (*Acc. Chem. Res.* 2003, **36**, 66) can be made.

Introduction

There is current interest in quantitatively assessing the electrophilicities of electron-deficient aromatic and heteroaromatic structures, termed herein as Meisenheimer electrophiles, exhibiting a high reactivity in nucleophilic aromatic substitutions and related σ-complexation processes.[1–8] Using hydration as a simple reference process, it has been shown that heteroaromatics such as nitrobenzofuroxans, nitrobenzofurazans, nitrobenzotriazoles, nitrotetrazolopyridines *etc.* are considerably more electrophilic than 1,3,5-trinitrobenzene (TNB, **1**), the conventional aromatic electrophile in σ-complex chemistry.[1,2,4c,9–12] While TNB only reacts with the strong oxygen base hydroxide ion [eqn (1), Scheme 1], prototype highly electron-deficient structures like 4,6-dinitrobenzofuroxan (DNBF, **2**) and 4,6-dinitrotetrazolopyridine (DNTP, **3**) undergo facile addition of water according to eqn (2) and (3) to give the hydroxide adducts **2-H** and **3-H** which are, respectively, 10^{10} and 10^{13} times thermodynamically more stable than the analogous TNB adduct **1-H**.[10,12] Interestingly, exhaustive kinetic studies of the formation of a large number of hydroxy σ-complexes, notably those shown in eqn (1)–(3) (Scheme 1), have been carried out in aqueous solution.[2,4c,9–12] These studies have revealed that there is a close relationship between the thermodynamic reactivity of Meisenheimer electrophiles, as measured by the related $pK^{H_2O}_a$ values, and an effective contribution of the water pathway ($k^{H_2O}_2$) to the formation of the corresponding σ-adducts.[13] It thus appears that the water pathway contributes to some extent to the formation of hydroxy σ-complexes of all Meisenheimer electrophiles with $pK^{H_2O}_a \leq$ 7–8. This borderline $pK^{H_2O}_a$ value appears to be a useful index to demarcate a superelectrophilic reactivity from a normal electrophilic reactivity for electron-deficient aromatic and heteroaromatic structures.[2,13]

Recently, it has been demonstrated that low $pK^{H_2O}_a$ for formation of hydroxy σ complexes goes along with a high susceptibility of the parent electrophiles to undergo σ-complexation with extremely weak carbon nucleophiles such as benzenoid aromatics (phenols, anilines.)[3a,14,15] or π-excessive heteroaromatics (pyrroles, indoles, thiophenes, furans *etc.*)[16,17] whose carbon basicities are associated with large negative pK^{CH}_a values, *e.g.* 1,3-dimethoxybenzene (pK^{CH}_a = –9),[14] 3-methoxythiophene (pK^{CH}_a = –6.5)[16c] or indole (pK^{CH}_a = –3.46).[16,17] The ease of these carbon–carbon couplings has led to many synthetic, analytical and biological applications.[18–20] It follows that measurement of pK_a values for hydroxy σ complexes of Meisenheimer electrophiles is of great value for predicting the potential reactivity of a given substrate, a feature which is of real benefit for synthetic organic applications.[2,13]

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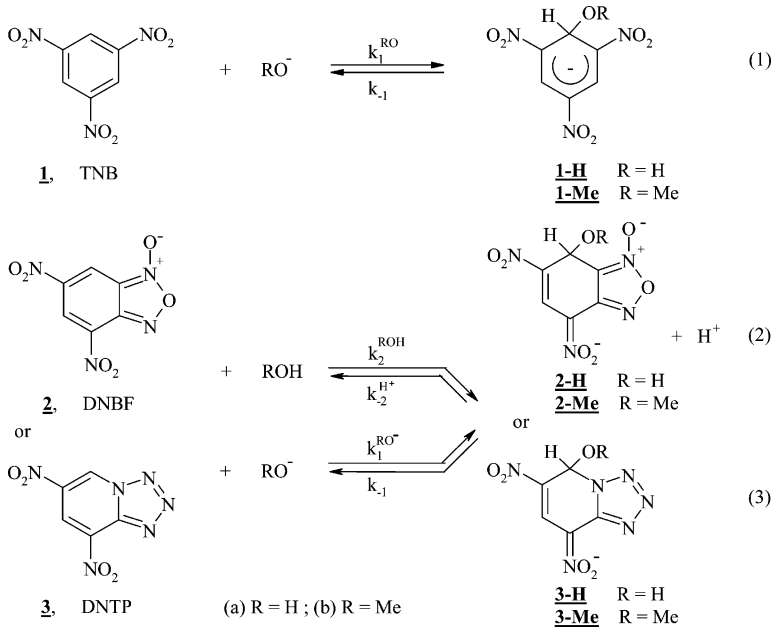


Scheme 1

The above investigations have renewed the interest in using the strong electron-withdrawing influence exerted by a SO_2CF_3 group in many acid–base combinations to broaden the range of Meisenheimer electrophiles exhibiting superelectrophilic properties.[21–31] In this context, a comprehensive kinetic and thermodynamic study of the σ-complexation of 2,6-bis(trifluoromethanesulfonyl)-4-nitroanisole **4** in methanol is reported; use of water as a solvent was precluded for solubility reasons. Combining the results obtained with data previously reported for the interaction of MeO^- with various nitro and/or SO_2CF_3 activated arenes or hetarenes leads to the recognition of a superelectrophilic dimension for some electrophilic triflones in methanol.[2,32,33] Available data also allow an approximate but meaningful positioning of SO_2CF_3-activated substrates on the general electrophilicity scale developed by Mayr and co-workers for cationic electrophiles.[34,35]

Results

All rate and equilibrium measurements pertaining to the interaction of methoxide ion with 2,6-bis(trifluoromethanesulfonyl)-4-nitroanisole **4** were made at 20 °C and constant ionic strength of 0.01 mol dm^{-3} maintained with sodium bromide as needed (see Experimental section). Dilute methanesulfonic acid solutions, various buffer solutions and dilute methoxide solutions were used to cover a pH range of 2–15.68 in methanol. To be noted is that all pH values quoted below have been measured relative to the standard state in pure MeOH. Accordingly, the relationship $[H^+] = 10^{-pH}/\gamma\pm$ holds with $\gamma\pm$ being the mean activity coefficient calculated by using a simplified Debye–Hückel type equation, *i.e.* $\log \gamma \pm = -Bz^2\sqrt{I}$ with $I = 0.01$ mol dm^{-3} and $B = 1.8$ at 20 °C in methanol.[33,36]

The yellow colored 1,1-dimethoxy complex **4a-Me** (λ_{max} = 380 nm), previously identified by NMR spectroscopy by Yagupolskii *et al.*,[37] was found to form rapidly and completely in buffer solutions and dilute methoxide solutions of pH > 12 in methanol. Although **4a-Me** was in all instances the thermodynamically stable product of the interaction, oscilloscope pictures taken in a stopped-flow apparatus showed that this adduct was no longer directly formed in solutions of methoxide ion concentration greater than 10^{-5} mol dm^{-3} (pH ≥ 11.7). As shown in Fig. 1, the appearance of **4a-Me** was then preceded by the much faster formation of a less stable species. Based on previous studies of the interaction of MeO^- with 2,4,6-trinitroanisole **6** and related 4-X-2,6-dinitroanisoles,[38] which have led to the NMR characterization of a 1,3-dimethoxy adduct, *e.g.* **6b-Me**, prior to that of the expected 1,1-adduct, *e.g.* **6a-Me**, there is little doubt that this short lived species is the 1,3-dimethoxy analogue **4b-Me** (λ_{max} = 430 nm). As a matter of fact, carrying out NMR experiments at −30 °C in acetonitrile has allowed the observation of the AX system characteristic of this transient species (see Experimental section). Fig. 2 shows a set of UV-Visible spectra illustrating the conversion of **4b-Me** into **4a-Me**. Taking advantage of the good separation of the two relaxation times corresponding to the formation of

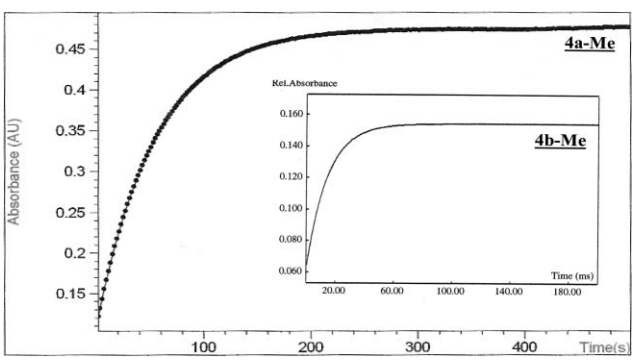
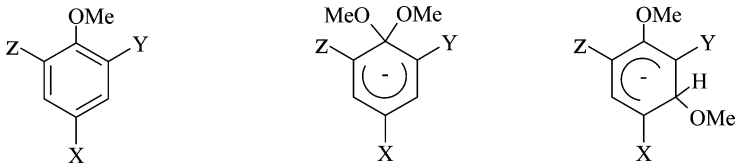


Fig. 1 Oscilloscope traces showing the two relaxation processes pertaining to the 1,3-adduct **4b-Me** at 430 nm and its subsequent conversion into the 1,1-adduct **4a-Me** at 380 nm in a 2-bromophenol buffer (pH = 13.04) at T = 20 °C in methanol.



4 X = NO_2 , Y = Z = SO_2CF_3
5 X = SO_2CF_3 , Y = Z = NO_2
6 X = Y = Z = NO_2

4a-Me **5a-Me** **6a-Me**

4b-Me **5b-Me** **6b-Me**

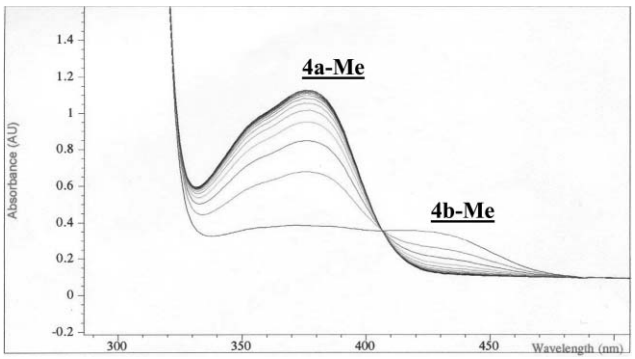


Fig. 2 UV-Visible absorption spectra illustrating the conversion of **4b-Me** (λ_{max} = 430 nm) into **4a-Me** (λ_{max} = 380 nm) in a 0.1 mol dm^{-3} sodium methoxide solution in methanol.

4b-Me and **4a-Me**, a complete kinetic and thermodynamic analysis of the interaction of **4** with MeO^- could be achieved. All kinetic experiments were carried out under pseudo-first-order conditions with a large excess of the acid, base or buffer reagent over the substrate concentration (≈ 3–5 10^{-5} mol dm^{-3}).

Formation of 4a-Me

Addition of methanesulfonic acid to a methanolic solution of the adduct **4a-Me**, previously isolated as a sodium salt,[37] resulted in a full recovery of the parent anisole **4**, pointing to the reversibility of the σ-complexation process. Using a series of 2,4,6-trichlorophenol buffers (see Experimental section), the $pH_{1/2}$ value for half-formation of **4a-Me** according to equilibrium (4) was readily determined from the observed absorbance variations at λ_{max} = 380 nm of this adduct as a function of pH. These actually describe a regular acid–base type of equilibration, as evidenced by the observation of a good straight line with slope close to unity, fitting eqn (6) (Fig. S1). In this equation, A_4 and $A_{4\text{-Me}}$ represent the absorbances of the pure species **4** and **4a-Me** at a given C_o concentration while A represents

$$\mathbf{4} + \mathrm{MeOH} \underset{k_{-2}^{H^+}}{\overset{k_2^{MeOH}}{\rightleftharpoons}} \mathbf{4a\text{-}Me} + H^+ \quad (4)$$

$$\mathbf{4b\text{-}Me} \underset{k_{-3}}{\overset{k_3^{MeO}}{\rightleftharpoons}} \mathbf{4} + MeO^- \underset{k_{-1}}{\overset{k_1^{MeO}}{\rightleftharpoons}} \mathbf{4a\text{-}Me} \quad (5)$$

$$pH = pK_a + \log\frac{[\mathbf{4a\text{-}Me}]}{[\mathbf{4}]} = pK_a + \log\frac{A - A_4}{A_{\mathbf{4a\text{-}Me}} - A} \quad (6)$$

the absorbance of a mixture of these two species (total concentration C_o) at a given pH. From the plot of Fig. S1, we readily obtained : $pH_{1/2} = 10.48 \pm 0.1$. This value corresponds to the pK_a value for formation of **4a-Me** at I = 0.01 mol dm^{-3}. As shown previously,[33] this value is related to the thermodynamic pK°_a at zero ionic strength by eqn (7) with $\gamma\pm = 0.66$, *i.e.* $pK^\circ_a = 10.66 \pm 0.1$.

$$pK^\circ_a = pH_{1/2} - \log \gamma\pm \quad (7)$$

The kinetics of formation and decomposition of the thermodynamically stable 1,1-dimethoxy adduct **4a-Me** were studied in the pH range of 2–15.68. In agreement with a negligible role of the fast preequilibrium leading to the isomeric 1,3-complex **4b-Me** up to pH = 10.7, only one relaxation time corresponding to the direct formation (pH > 9.3) or decomposition (pH < 10.7) of **4a-Me** through the two methanol ($k^{MeOH}{}_2$, $k^{H^+}{}_{-2}$) and methoxide ion ($k^{MeO}{}_1$, k_{-1}) pathways of eqn (4) and (5) was observed in the pH range 2–10.7. Instead, as discussed above, the interaction consisted of two steps at high pH, namely a fast σ-complexation of **4** to give partially (10.7 < pH ≤ 13.3) or totally (pH > 13.3) the 1,3-adduct **4b-Me**, followed by a subsequent slow conversion to **4a-Me**. The variations in the first-order rate constant, k_{obsd}, for the combined processes at 20 °C are plotted in Fig. 3, where the data at pH ≥ 10.7 refer to the isomerization step, as a function of pH. In none of our experiments carried out in buffer solutions, catalysis by buffer species was observed, (Fig. S2). Experimental values of k_{obsd} are given in Table 1.

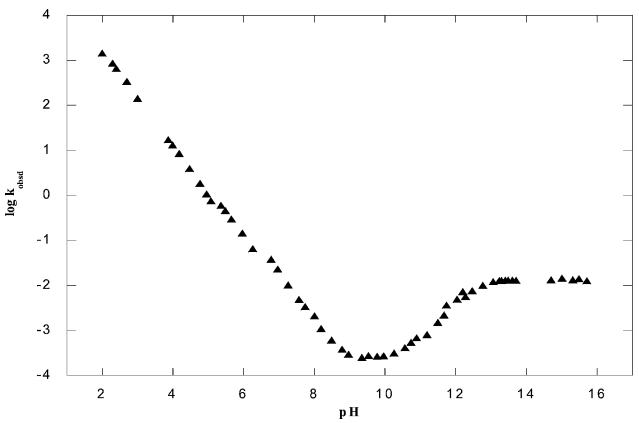


Fig. 3 The pH dependence of the observed first-order rate constant, k_{obsd}, for formation and decomposition of the 1,1-dimethoxy adduct **4a-Me** at T = 20 °C in methanol.

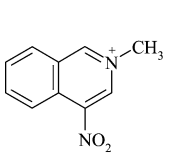
As elaborated in more detail in previous studies of the addition of water or MeOH to a number of highly electrophilic Meisenheimer structures, *e.g.* DNBF,[10,36a] or various heterocyclic cations, *e.g.* the isoquinolinium or naphthyridinium cations **7** and **8**,[39] the observed rate constant, k_{obsd}, can be expressed at each pH as

Table 1 Observed first-order rate constants, k_{obsd}, for formation and/or decomposition of the adduct **4a-Me** in methanol[a]

pH[b]	k_{obsd}/s^{-1}	pH[b]	k_{obsd}/s^{-1}	pH[b]	k_{obsd}/s^{-1}
2[c]	1440	7.26[f]	1.00×10^{-2}	11.66[j]	2.07×10^{-3}
2.3[c]	875	7.56[f]	4.75×10^{-3}	11.72[k]	3.49×10^{-3}
2.4[c]	650	7.74[f]	3.26×10^{-3}	12.02[k]	4.71×10^{-3}
2.7[c]	340	8.00[g]	2.04×10^{-3}	12.18[k]	6.92×10^{-3}
3.0[c]	142	8.18[g]	1.06×10^{-3}	12.45[l]	7.22×10^{-3}
3.87[d]	17.3	8.48[g]	5.92×10^{-4}	12.75[l]	9.52×10^{-3}
3.99[d]	13.1	8.78[g]	3.67×10^{-4}	13.04[l]	1.24×10^{-2}
4.17[d]	8.48	8.96[g]	2.84×10^{-4}	13.22[l]	1.20×10^{-2}
4.47[d]	3.92	9.34[h]	2.39×10^{-4}	13.28[m]	1.21×10^{-2}
4.77[d]	1.82	9.52[h]	2.66×10^{-4}	13.38[m]	1.22×10^{-2}
4.95[d]	1.06	9.77[i]	2.55×10^{-4}	13.46[m]	1.22×10^{-2}
5.07[d]	0.75	9.95[i]	2.61×10^{-4}	13.58[m]	1.22×10^{-2}
5.36[e]	0.59	10.25[i]	3.02×10^{-4}	13.68[m]	1.21×10^{-2}
5.48[e]	0.45	10.55[i]	3.94×10^{-4}	14.68[m]	1.23×10^{-2}
5.66[e]	0.295	10.73[i]	5.25×10^{-4}	14.98[m],[n]	1.33×10^{-2}
5.96[e]	0.143	10.70[j]	4.50×10^{-4}	15.28[m],[n]	1.23×10^{-2}
6.26[e]	6.43×10^{-2}	10.88[j]	6.54×10^{-4}	15.46[m],[n]	1.31×10^{-2}
6.78[f]	3.70×10^{-2}	11.18[j]	7.70×10^{-4}	15.68[m],[n]	1.18×10^{-2}
6.96[f]	2.24×10^{-2}	11.48[j]	1.42×10^{-3}		

[a] T = 20 °C, I = 0.01 mol dm^{-3} except for the last four measurements at MeO^- concentrations > 10^{-2} mol dm^{-3} (pH 14.98–15.68) where the levelling off of k_{obsd} is not found to depend on the ionic strength. [b] pH = –log[H$^+$] – log $\gamma\pm$ = –log[H$^+$] + 0.18. [c] Methanesulfonic acid solutions. [d] Trichloroacetate buffers. [e] Dichloroacetate buffers. [f] 3,5-Dinitrobenzoate buffers. [g] 3-Chlorobenzoate buffers. [h] Benzoate buffers. [i] 2,4,6-Trichlorophenoxide buffers. [j] 2,6-Dichlorophenoxide buffers. [k] 4-Cyanophenoxide buffers. [l] 2-Bromophenoxide buffers. [m] Sodium methoxide solutions; pH = pK_s + log[MeO^-] + log $\gamma\pm$ = 16.68 + log[MeO^-] with pK_s = 16.86 at 20° C;[33,36] [n] pH Values calculated by assuming no notable variation in $\gamma\pm$ at [MeO^-]concentration in the range 0.01–0.10 mol dm^{-3}.

the sum of the individual rate constants for formation (k_f) and decomposition (k_d) of **4a-Me** [eqn (8)]. Thus, values of k_f and k_d can be readily derived from k_{obsd} through eqn (9) and (10).



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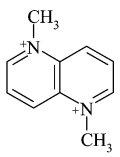

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$$k_{obsd} = k_f + k_d \tag{8}$$

$$k_f = \frac{k_{obsd}}{1 + \dfrac{10^{-pH}}{10^{-pH_{1/2}}}} \tag{9}$$

$$k_d = \frac{k_{obsd}}{1 + \dfrac{10^{-pH_{1/2}}}{10^{-pH}}} \tag{10}$$

Fig. 4 shows the corresponding k_f and k_d pH-rate profiles for the pH range of 2–10.7 where the formation of **4b-Me** does not interfere with that of **4a-Me**. These are consistent with eqn (11) and (12), respectively, in which the rate constants $k^{MeOH}{}_2$, $k^{H^+}{}_{-2}$, $k^{MeO}{}_1$, k_{-1} refer to the various individual pathways depicted in eqn (4) and (5). From the line of slope –1 and the plateau observed, respectively, in the low and high pH regions of the k_d profile, the rate constants $k^{H^+}{}_{-2}$ and k_{-1} pertaining to the H$^+$-catalyzed and spontaneous decomposition of **4a-Me** were derived: $k^{H^+}{}_{-2} = 1.41 \times 10^5$ dm^3 mol^{-1} s^{-1}, $k_{-1} = 2.04 \times 10^{-4}$ s^{-1}.

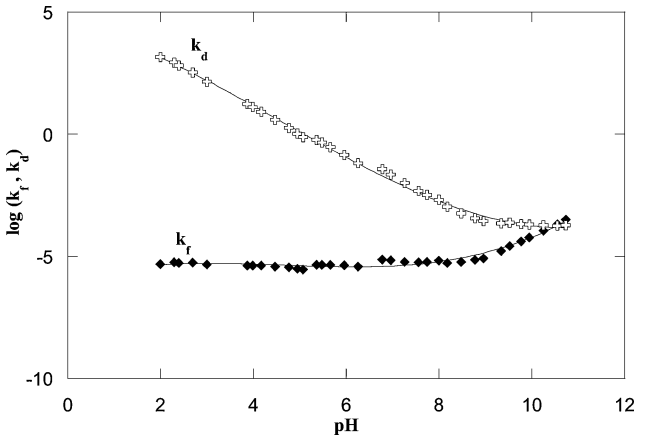


Fig. 4 The pH dependence of the first-order rate constants k_f and k_d for formation and decomposition of the 1,1-dimethoxy adduct **4a-Me** at T = 20 °C in methanol, as derived from eqn (9) and (10) in the pH range 2–10.7 where the formation of the 1,3-complex **4b-Me** does not interfere with that of **4a-Me**.

$$k_f = k_2^{MeOH} + k_1^{MeO}[MeO^-] = k_2^{MeOH} + \frac{k_1^{MeO} K_s}{10^{-pH}\gamma\pm} \tag{11}$$

$$k_d = k_{-2}^{H^+}[H^+] + k_{--} = \frac{k_{-2}^{H^+} 10^{-pH}}{\gamma\pm} + k_{-1} \tag{12}$$

Similarly, the rate constant $k^{MeOH}{}_2$ for the methanol addition pathway could be accurately determined from the plateau observed in the low pH region of the k_f profile: $k^{MeOH}{}_2 = 4.47 \times 10^{-6}$ s^{-1}. Interestingly, it appears that the contribution of the methanol pathway to k_f is not negligible relative to that of the $k^{MeO}{}_1$[MeO^-] term in the pH range of 9–10.7. This accounts for the drawing of a line of slope less than unity in the high pH region of the k_f profile in Fig. 4, making it possible to get only an estimate of the rate constant $k^{MeO}{}_1 \sim 480$ dm^3 mol^{-1} s^{-1}. However, Fig. 4 shows that the k_d plateau, *i.e.* k_{-1}, intersects with the $k^{MeO}{}_1$[MeO^-] line of k_f at a pH value which corresponds to the previously determined $pH_{1/2}$ = pK_a value for formation of **4a-Me**. This implies that the methanol pathway does not in fact contribute to an appreciable extent to the observed rate constant k_{obsd}, *i.e.* the minimum values of k_{obsd} correspond to the rate constant k_{-1} for spontaneous decomposition of **4a-Me** in the pH range 9–10.

As illustrated by the right part of the k_{obsd} profile of Fig. 3, the formation of **4a-Me** has also been studied in the pH range 10.7–15.68 where the adduct **4b-Me** is initially formed. Eqn (5) describes the interaction where the approach to equilibrium for the 1,3-complex is sufficiently fast to be considered as instantaneous relative to that for the 1,1-complex. As previously shown,[4c,33,40] the observed first-order rate constant, k_{obsd}, associated with the formation of **4a-Me** should then depend curvilinearly on the base concentration according to eqn (13), approaching a plateau at base concentrations where the initial formation of **4b-Me** is essentially complete, *i.e.* K_3[MeO^-] >> 1, pH > 13.3.

$$k_{obsd} = k_{-1} + \frac{k_1^{MeO}[MeO^-]}{1 + K_3[MeO^-]} \tag{13}$$

$$\frac{1}{k_{obsd} - k_{-1}} = \frac{1}{k_1^{MeO}[MeO^-]} + \frac{K_3}{k_1^{MeO}} \tag{14}$$

In as much as the rate constant k_{-1} is known (*vide supra*), eqn (13) can be rewritten in the form of eqn (14), allowing the determination of $k^{MeO}{}_1$ and K_3 by combining the slope and the intercept of a plot of $1/(k_{obsd} - k_{-1})$ *vs.* $1/[MeO^-]$ which was linear (Fig. 5). We thus obtain: $k^{MeO}{}_1 = 468$ dm^3 mol^{-1} s^{-1}; $K_3 = 4.12 \times 10^4$ dm^3 mol^{-1}, the former value being in good agreement with our previous estimate of $k^{MeO}{}_1$. From these two parameters, the maximum value taken by k_{obsd} at high pH can be calculated as the ratio $k^{MeO}{}_1/K_3$, *i.e.* $k^{max}{}_{obsd} = 1.14 \times 10^{-2}$ s^{-1}, in good agreement with the value directly deduced from the experimental plateau in Fig. 3; *i.e.* 1.21×10^{-2} s^{-1}.

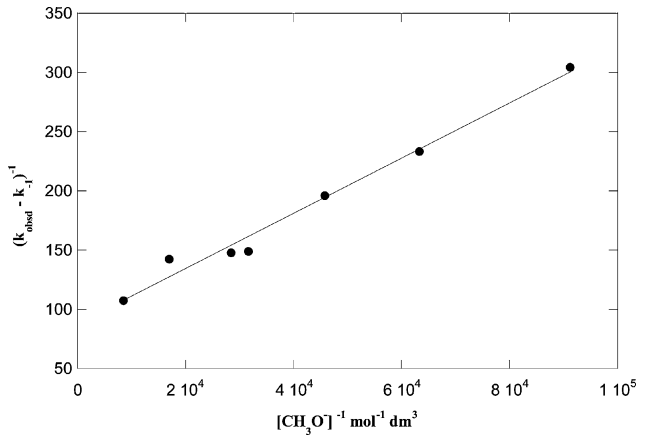


Fig. 5 Inversion plot according to eqn (14) for the appearance of the adduct **4a-Me** at high MeO^- concentrations (pH > 10.7) at $T = 20$ °C in methanol.

Formation of 4b-Me

The kinetics of the fast equilibrium between the 1,3-adduct **4b-Me** and the parent anisole **4** according to the left equilibrium of eqn (5) was investigated at MeO^- concentrations ≥ 10^{-5} mol dm^{-3} (pH > 11.7) by using 4-cyanophenol, 2-bromophenol and 4-chlorophenol buffer solutions as well as dilute sodium methoxide solutions. As observed for the formation of the 1,1-complex **4a-Me**, variation of buffer concentration at constant pH did not appreciably change the value of the observed first-order rate constant, k'_{obsd}, for the approach to equilibrium. From the straight line shown in Figure S$_3$, which describes the variations of k'_{obsd} with the MeO^- concentration [eqn (15)], the following values of the second order rate constant $k^{MeO}{}_3$ for formation and the first-order rate constant k_{-3} for decomposition of **4b-Me** were readily obtained: $k^{MeO}{}_3 = 2.63 \times 10^5$ dm^{3}mol^{-1} s^{-1}, $k_{-3} = 6.30$ s^{-1}. Combining these two values leads to an equilibrium constant K_3 of 4.17×10^4 dm^3 mol^{-1}, and therefore to a $pK^{MeOH}{}_a$ value of 12.24 for formation of **4b-Me** at 20 °C. Measured k'_{obsd} values are given in Table S1.

$$k'_{obsd} = k^{MeO}{}_3[MeO^-] + k_{-3} \quad (15)$$

Discussion

Our study of the σ-complexation of 2,6-bis(trifluoromethanesulfonyl)-4-nitroanisole **4** has revealed a number of interesting features, especially when compared to related anisoles and some recognized powerful Meisenheimer electrophiles. For a pertinent discussion, the rate and equilibrium constants for formation and decomposition of the 1,1-dimethoxy complex **4a-Me** are compared in Table 2 with the corresponding data for the adducts **5a-Me** and **6a-Me** of 2,6-dinitro-4-trifluoromethanesulfonylanisole (**5**) and TNA (**6**), respectively, as well as those for the *gem*-dimethoxy analogues of 2,4-dinitro-5-methoxythiophene and selenophene (**9-Me**, **10-Me**), and of 4,6-dinitro-7-methoxy- and 4-nitro-7-methoxy-benzofurazans (**11-Me**, **12-Me**). Similarly, Table 3 compares the rate and equilibrium data for the 1,3-dimethoxy complex **4b-Me** with those for related adducts arising from MeO^- addition to an activated unsubstituted position, namely the adducts **5b-Me** and **6b-Me**, the TNB and 1,3,5-tris(trifluoromethanesulfonyl)benzene adducts **1-Me** and **13-Me**, the 2,4-dinitrofuran, 2,4-dinitrothiophene and 2,4-dinitroselenophene adducts (**14-Me**, **15-Me** and **16-Me**), the 4,6-dinitro- and 4-nitro-benzofurazan and -benzofuroxan adducts (**17-Me**, **18-Me**, **2-Me** and **19-Me**) and the 4,6-dinitrotetrazolopyridine adduct **3-Me**. The structures and numbering of all afore-quoted adducts are given, together with those of the parent electrophiles, in Chart 1.

Also to be noted is that the following discussion is based on measured rate and equilibrium constants for the various systems. Statistical corrections pertaining to the presence of two (**4**–**6**) or even three (**1**, **13**) equivalent unsubstituted positions have not been made since they do not affect our conclusions.

Adduct stability. The role of the SO_2CF_3 group

As can be seen in Tables 1 and 2, substituting the two *ortho*-nitro groups of TNA (**6**) for two SO_2CF_3 groups increases markedly, though to a different extent, the stability of the 1,1- and 1,3-dimethoxy adducts : the ratios $K^{4a\text{-}Me}/K^{6a\text{-}Me}$ and $K^{4b\text{-}Me}/K^{6b\text{-}Me}$ are equal to 138 and 1.53×10^4, respectively. At the same time, the replacement of the 4-NO_2 group of TNA by a SO_2CF_3

Table 2 Rate and equilibrium constants for formation and decomposition of the adduct **4a-Me** in methanol. Comparison with related *gem*-dimethoxy adducts[a]

Adduct	pK_a[b]	$k^{MeOH}{}_2$/s^{-1}	$k^{H^+}{}_{-2}$/dm^3 mol^{-1} s^{-1}	$k^{MeO}{}_1$/dm^3 mol^{-1} s^{-1}	k_{-1}/s^{-1}	K_1/dm^3 mol^{-1}
4a-Me[c]	10.48	4.47×10^{-6}	1.41×10^5	480	2.04×10^{-4}	2.35×10^6
5a-Me[d]	10.68	5×10^{-5}	1.66×10^6	141	1.17×10^{-4}	1.20×10^6
6a-Me[e]	12.56	1.80×10^{-6}	2.9×10^6	11.8	6.05×10^{-4}	1.95×10^4
9-Me[f]	11.16	10^{-7}	1.05×10^4	28.2	7.8×10^{-5}	3.6×10^5
10-Me[f]	9.86	5.75×10^{-7}	2.65×10^3	69	1.04×10^{-5}	6.63×10^6
11-Me[g]	5.93	4.46×10^{-3}	1.78×10^3	2.52×10^5	4.9×10^{-6}	5.14×10^{10}
12-Me[h]	13.54			7.56	3.55×10^{-3}	2135

[a] $T = 20$ °C. [b] $pK_a = pH_{1/2}$ at I = 0.01 mol dm^{-3}. [c] This work. [d] Ref. 33*a*. [e] Calculated at 20 °C from data in ref. 38*d*. [f] Ref. 33*b*. [g] Ref. 36*a*. [h] Ref. 40*a*.

Table 3 Rate and equilibrium constants for formation and decomposition of the adduct **4b-Me** in methanol. Comparison with related monomethoxy adducts[a]

Adduct	pK_a	$k^{MeOH}{}_2$/s^{-1}[b]	$k^{H^+}{}_{-2}$/dm^3 mol^{-1} s^{-1}[b]	$k^{MeO}{}_3$/dm^3 mol^{-1} s^{-1}	k_{-3}/s^{-1}	K_3/dm^3 mol^{-1}
4b-Me[c]	12.23[m]			2.63×10^5	6.30	4.17×10^4
5b-Me[d]	15.38[m]			750	25	30
6b-Me[e]	16.46[m]			690	290	2.56
1-Me[f]	15.51[m]			5150	231	22.3
13-Me[g]	9.12[n]	3.02×10^{-2}	2.88×10^7	3.9×10^5	0.011	3.54×10^7
14-Me[h]	$\leq$ 11.16[m]			4500	$\leq 9 \times 10^{-3}$	$\geq 5 \times 10^5$
15-Me[i]	13.94[m]			10.3	1.25×10^{-2}	825
16-Me[i]	12.05[m]			18.2	2.85×10^{-4}	6.4×10^4
17-Me[j]	6.05[n]	0.028	2.09×10^4	9.30×10^5	2×10^{-6}	4.65×10^{10}
18-Me[k]	13.40[m]			3.8	1.3×10^{-3}	2920
2-Me[j]	6.46[n]	0.03	4.68×10^4	1.87×10^6	8.9×10^{-6}	2.1×10^{10}
19-Me[k]	12.96[m]			17.6	2.2×10^{-3}	8000
3-Me[l]	2.64[n]	3.50	1520	6.3×10^7	5.5×10^{-7}	1.14×10^{14}

[a] T = 20 °C. [b] $k^{MeOH}{}_2$ and $k^{H^+}{}_{-2}$ are rate constants for formation and decomposition of the methoxy adducts through methanol addition and H^+ catalysis, respectively, as defined in Scheme 1. [c] This work. [d] Ref. 33*a*. [e] Calculated at 20 °C from data in ref. 38*c*. [f] Calculated at 20 °C from data in ref. 12. [g] Ref. 32. [h] Ref. 33*c*. [i] Ref. 49. [j] Ref. 36*a*. [k] Ref. 40*a*. [l] Ref. 11. [m] Calculated from pK_a = pK_s – log K_3. [n] pK_a = p$H_{1/2}$ at I = 0.01 mol dm^{-3}.

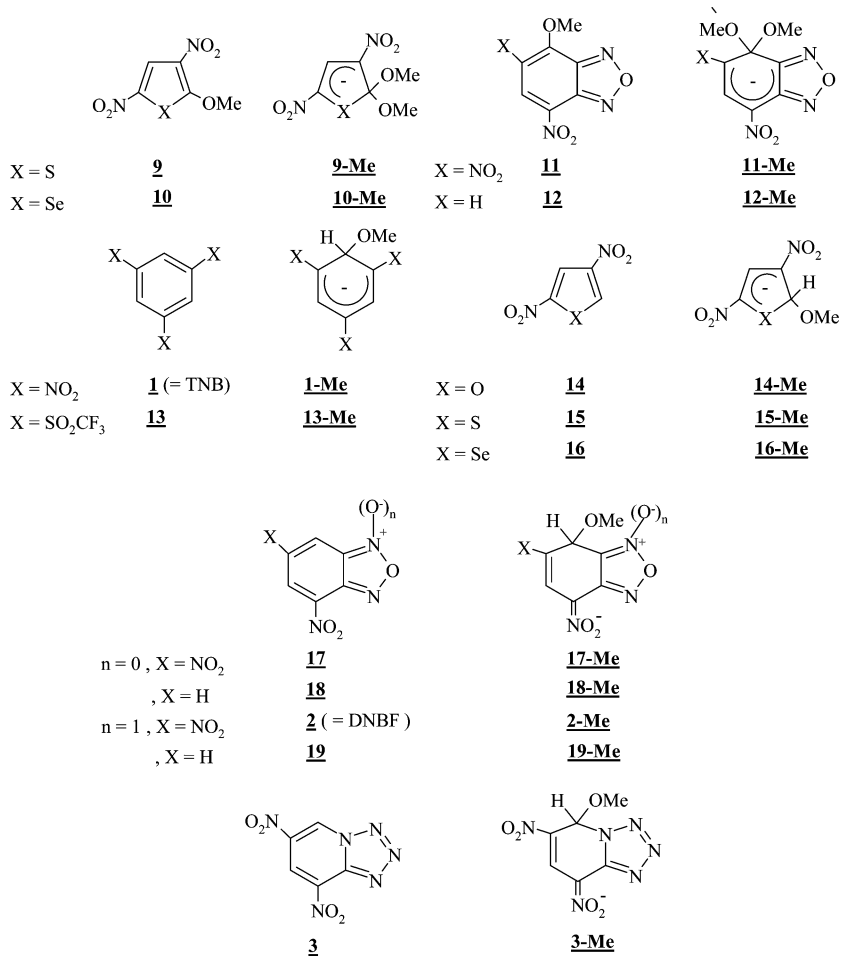
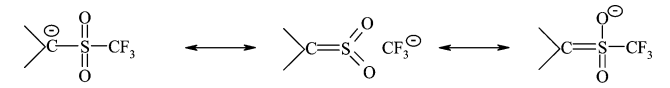


Chart 1 Structures and numbering of Meisenheimer electrophiles and related σ-adducts

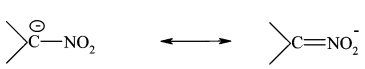
group to give **5** causes a large increase in the stability of the 1,1-dimethoxy adduct—the ratio $K^{5a\text{-}Me}/K^{6a\text{-}Me}$ is equal to 70—but only a moderate increase in stability of the 1,3-isomer—the ratio $K^{5b\text{-}Me}/K^{6b\text{-}Me}$ is equal to 11. These results emphasize two important conclusions: (1) a 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; (2) the SO_2CF_3 group exerts, as does the NO_2 group, a much greater effect on the stability of a σ-adduct when it is located in the *para* rather than the *ortho* position to the sp^3 carbon. This implies an especially high capacity of resonance stabilization of the negative charge of a σ-adduct by a *para*-SO_2CF_3 group, in

accord with previous conclusions that this group exerts a large conjugative effect in addition to a large inductive effect.[27–30] This behaviour is consistent with the Hammett substituent constants derived for SO_2CF_3 from studies of the ionization of various AH-type acids, namely benzoic acids, anilinium ions and phenols, by Sheppard and Yagupolskii.[21,22,24]: $\sigma_m = 0.76$, $\sigma_p = 0.96$, $\sigma_{p^-} = 1.65$. These values compare with the following for NO_2: $\sigma_m = 0.71$, $\sigma_p = 0.78$, $\sigma_{p^-} = 1.27$.[28] Obviously, these substituent constants fit well the finding that the SO_2CF_3 group is markedly more activating than a NO_2 group in σ-complex formation and therefore in related nucleophilic aromatic displacement processes. So far, maximum enhancement in complex stability promoted by the SO_2CF_3 group has been observed on going from the TNB methoxy adduct **1-Me** to the tris(trifluoromethanesulfonyl) analogue **13-Me**: $K^{13\text{-Me}}/K^{1\text{-Me}} = 1.36 \times 10^6$.[32]

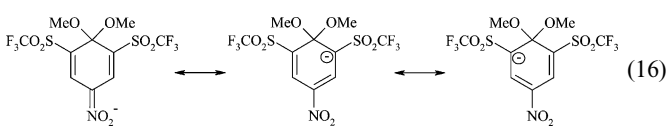
How the SO_2CF_3 group exerts its stabilizing conjugative effect in anionic σ-complexes is worthy of comment. Pertinent information on the mode of charge transmission of SO_2CF_3 has come from recent studies of the ionization of a number of α-SO_2CF_3 activated carbon acids, including aliphatic and benzylic triflones.[29–31] Mainly through a combination of results of thermodynamic and kinetic investigations with the structural information provided by NMR studies, it has been convincingly demonstrated that the exceptional electron-withdrawing capability of the SO_2CF_3 group to stabilize carbanion negative charge is essentially the result of polarizability effects (resonance structure R_1) with no significant contribution of other factors such as negative hyperconjugation (R_2)[41–43], a reasonable issue according to some theoretical studies, or d–p π-bonding (R_3), a long-rejected mode of stabilization.[44–46] The situation is obviously in contrast with the NO_2 group which acts largely through resonance stabilization (R_5) but it fits nicely the finding of a totally different solvent dependence of the acidity of α-NO_2 and α-SO_2CF_3 carbon acids in H_2O-Me_2SO mixtures.[29,30] Other things being equal, the activation by a NO_2 group is favored in aqueous solution when hydrogen bonding solvation contributes to the stabilization of nitronate structures (R_5). In contrast Me_2SO is more prone to stabilize a polarizable negative charge, thereby favoring the activation by a SO_2CF_3 group (R_1).[30] On these grounds, the main resonance structures contributing to the stability of SO_2CF_3-substituted σ-adducts may be viewed as drawn in eqn (16)–(18) for three representative systems where the conjugative influence of the SO_2CF_3 group is operating through a Fπ type effect while that of a NO_2 group derives from a $-M$ effect.[47]



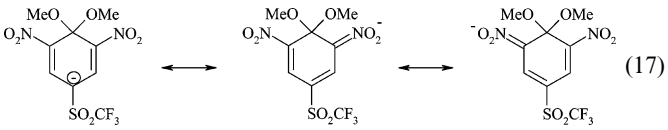
(R_1) (R_2) (R_3)



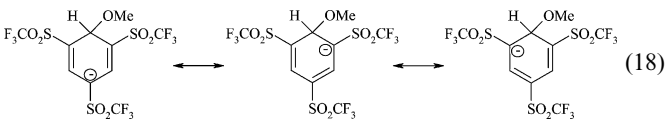
(R_4) (R_5)



(16)



(17)



(18)

Regarding the electron-withdrawing influence of the SO_2CF_3 group, it is noteworthy that the higher stability of the 1,1-adducts **4a-Me** and **5a-Me** relative to that of the trinitro analogue **6a-Me** derives both from an increase in the rate of formation and a decrease in the rate of decomposition. For methoxide ion attack on the methoxy-bearing carbon of the parent ethers **4–6**, the rate constant k^{MeO}_1 is 141 $dm^3\ mol^{-1}s^{-1}$ and 480 $dm^3\ mol^{-1}s^{-1}$ for **5a-Me** and **4a-Me**, respectively, as compared with 11.8 $dm^3\ mol^{-1}s^{-1}$ for **6a-Me** ($T = 20$ °C). For adduct decomposition, the rate constant k_{-1} is 2.04×10^{-4} s^{-1} and 1.17×10^{-4} s^{-1} for **4a-Me** and **5a-Me**, respectively, as compared with 6.05×10^{-4} s^{-1} for **6a-Me**. This is consistent with previous observations in σ-complex chemistry that changes in the equilibrium constant for adduct formation, brought about by variations in the substitution pattern of an aromatic or heteroaromatic ring, are the result of concomitant and opposite changes in the rate constants for formation and decomposition.[1,33] Interestingly, Table 3 shows that similar trends govern the formation of the 1,3-adducts. A remarkable feature, however, is that the rate constants k_3 and k_{-3} suffer especially strong variations on going from the adducts **5b-Me** and **6b-Me**, which have a NO_2 group in the *para* position to the sp^3 carbon, to the adduct **4b-Me** which has a SO_2CF_3 group in this position. The ratios $k^{4b\text{-Me}}_3/k^{6b\text{-Me}}_3$ and $k^{6b\text{-Me}}_{-3}/k^{4b\text{-Me}}_{-3}$ are equal to 380 and 46, respectively, contributing to the large change observed in the related equilibrium constant ($K^{4b\text{-Me}}_3/K^{6b\text{-Me}}_3 = 1.6 \times 10^4$) and adding to the evidence that a *para*-SO_2CF_3 group exerts an especially strong stabilizing effect on σ-adducts.

Reactivity of triflones

It has been shown in aqueous solution that, besides the pK_a value, an important parameter measuring the electrophilicity of an electron-deficient aromatic or heteroaromatic substrate is its susceptibility to undergo σ-complexation through an effective water pathway.[2c,9,13] As elaborated on in detail in previous kinetic and thermodynamic investigations of covalent hydration,[2c,48] a primary requirement for having H_2O compete effectively as a nucleophile with OH^- in the formation of an hydroxy σ-adduct is in fact that the first-order rate constant $k^{H_2O}_2$ be appreciably greater than the first-order rate constant k_{-1} for spontaneous decomposition of this species, *i.e.* $k^{H_2O}_2 > k_{-1}$. From the numerous systems studied,[48] it appears that the water pathway contributes to some extent to the formation of hydroxy σ complexes of all Meisenheimer electrophiles with $pK^{H_2O}_a < 8$.[20,48] This pK_a value has been proposed as a key index to demarcate the superelectrophilic reactivity from a normal electrophilic reactivity of electron-deficient aromatic or heteroaromatic substrates.[2c,48]

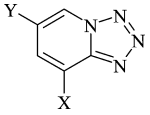
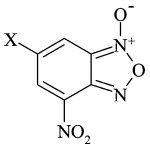
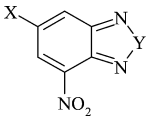
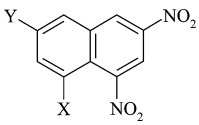
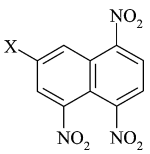
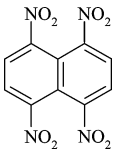
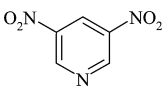
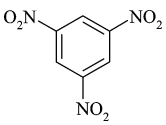
The very poor solubility of aromatic triflones in aqueous solution precluded the use of the $k^{H_2O}_2$ approach to assess their electrophilic character. With a similar reasoning, it was reasonable

to envision that reaction of the weak nucleophile, MeOH, with an electron-deficient substrate to give a methoxy σ-adduct might also be a sensitive measure of the electrophilicity of the substrate. Focusing first on 1,1-dimethoxy complex formation (Table 2), the $k^{MeOH}{}_2/k_{-1}$ ratio is equal to 0.46, 0.022 and 1.73×10^{-3}, respectively, for the triflones **5** and **4** and TNA **6**. Thus, the methanol pathway is negligible in the case of TNA, rather weak for **4** and moderate for **5**. Calculation of each term of eqn (11) and (12) shows in fact that methanol attack contributes only for 10–15% to the rate of appearance of the adduct **5a-Me** in the most favorable pH range of 10–11 in methanol. Table 2 shows that the solvent pathway plays equally a negligible role in the formation of the *gem*-dimethoxy adducts **9-Me** and **10-Me** of 2,4-dinitro-5-methoxythiophene ($pK_a = 11.16$, $k^{MeOH}{}_2/k_{-1} = 1.28 \times 10^{-3}$) and 2,4-dinitro-5-methoxyselenophene ($pK_a = 9.86$, $k^{MeOH}{}_2/k_{-1} = 0.055$) whose thermodynamic stability is of the same order of magnitude as that of **4** and **5**.[49] Similarly, methanol addition was not detected in the formation of the adduct **12-Me** of 4-nitro-7-methoxybenzofurazan ($pK_a = 13.54$). On going to the very stable *gem*-dimethoxy adduct **11-Me** of 7-methoxy-4,6-dinitrobenzofurazan ($pK_a = 5.93$), methanol addition becomes a predominant pathway over a large pH range (6–9), in agreement with a very high $k^{MeOH}{}_2/k_{-1}$ ratio of 910.[36a]

The fact that there is a small but definite contribution of the methanol pathway to the formation of the similarly stable adducts **5a-Me** and **4a-Me** suggests that the region defining the boundary between super- and normal- electrophilicity must be centered around $pK_a \sim 10$ in methanol. This view is supported by the data pertaining to the formation of the monomethoxy adducts listed in Table 3. In this instance, methanol attack is negligible in the formation of all adducts with $pK_a \geq 11$. In contrast, the solvent pathway is very effective in the formation of the tris(trifluoromethanesulfonyl)benzene adduct **13-Me** ($pK_a = 9.12$; $k^{MeOH}{}_2/k_{-1} = 2.75$) and it becomes largely predominant in the case of the 4,6-dinitrobenzofuroxan and 4,6-dinitrobenzofurazan adducts **2-Me** ($pK_a = 6.46$; $k^{MeOH}{}_2/k_{-1} = 340$) and **17-Me** ($pK_a = 6.05$; $k^{MeOH}{}_2/k_{-1} = 1400$).[32,36a] The efficiency of the methanol attack is even more spectacular in the case of the 4,6-dinitrotetrazolopyridine adduct **3-Me** ($pK_a = 2.64$; $k^{MeOH}{}_2/k_{-1} = 6.3 \times 10^6$).[11] Combining all the information provided by Tables 2 and 3, it follows that $pK^{MeOH}{}_a \sim 9.5$–10.5 can be used as a key index to define the frontier between superelectrophilicity and normal-electrophilicity in σ-complexation processes in MeOH. Focusing on triflones, the reactivity of 1,3,5-tris(trifluoromethanesulfonyl)benzene **13** appears to be clearly situated in the superelectrophilic region (*vide infra*).

There have been many reports allowing one to compare the thermodynamics of σ-complexation of electron-deficient aromatic and heteroaromatic substrates by OH^- and MeO^- ions in water and methanol, respectively.[50] All available couples of $pK^{H_2O}{}_a$ and $pK^{MeOH}{}_a$ values, together with the identification of the structures at hand, including a few structures already given in Chart 1, are collected in Table 4. Plotting $pK^{H_2O}{}_a$ *vs.* $pK^{MeOH}{}_a$ actually affords a nice straight line with slope close to unity and intercept equal to 2.52 fitting eqn (19) (Fig. 6). Applying this relationship to the above demarcation $pK^{MeOH}{}_a$ value allows an estimate of what should be the $pK^{H_2O}{}_a$ index, namely $pK^{H_2O}{}_a \sim 7$–8, defining the superelectrophilic dimension for σ-complexation processes in aqueous solution. Interestingly, this estimate is identical to the borderline $pK^{H_2O}{}_a$ value experimentally derived from direct studies of σ-complexation in aqueous solution.[2c,48] Among other substrates, TNB **1**, 2,4-dinitrothiophene **15** as well as the four nitrobenzoxadiazoles **2**,**17, 18** and **19** and the dinitrotetrazolopyridine (DNTP, **3**) were part of the studies conducted in aqueous solution.[2,13,48]

Table 4 $pK^{H_2O}{}_a$ and $pK^{MeOH}{}_a$ values for formation of hydroxy- and methoxy- σ-adducts of various nitro-aromatic and -heteroaromatic substrates at $T = 25$ °C in water and methanol, respectively

Parent substrate	Numbering	X	Y	$pK^{H_2O}{}_a$	$pK^{MeOH}{}_a$	Ref.
	**3**	NO_2	NO_2	0.40	2.64	11
	20	H	NO_2	7.55	10.65	2*c*
	21	NO_2	CH_3	8.33	10.40[a]	54
	**2**	NO_2		3.75	6.46[b]	36*a*
	19	H		10.37	12.77	40*a*
	**17**	NO_2	O	3.92	6.05[b]	36*a*
	22	NO_2	Se	6.34	10.09[a]	2*c*
	23	NO_2	S	7.86	10.90[a]	2*c*
	18	H	O	10.07	12.77	40*a*
	**24a**	NO_2	NO_2	9.96	12.82	55
	24b	NO_2	H	12.37	15.94	55
	24c	H	H	14.58	17.70	55
	**25a**	NO_2		11.20	14.00	55
	25b	H		13.16	16.53	55
	**26**			11.53	14.40	55
	**27**			12.92	14.86	56
	**1**			13.43	15.51	12

[a] $pK^{MeOH}{}_a$ values determined in this work. [b] $T = 20$ °C.

$$pK^{MeOH}{}_a = pK^{H_2O}{}_a + 2.52 \quad (19)$$

Ranking the electrophilicity of triflones on Mayr's scale

Mayr and coworkers have shown that it is possible to describe the rates of a large variety of electrophile–nucleophile combinations

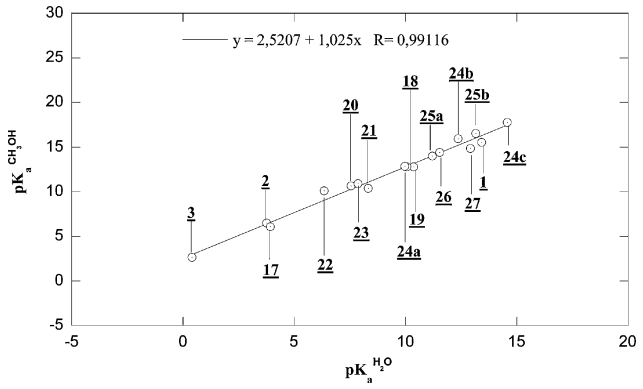


Fig. 6 The $pK^{H_2O}{}_a$ *vs.* $pK^{MeOH}{}_a$ relationship.

by the three parameter eqn (20).[34,35] In this equation, the E parameter measures the strength of the electrophile while the N and s parameters characterize the sensitivity to the nucleophile. Based on eqn (20), general electrophilicity (E) and nucleophilicity (N) scales have been defined. These scales have proved to be very useful for predicting reactivity.[34,35]

$$\log k_{(20\,^\circ C)} = s(N + E) \quad (20)$$

For the most part, the relationship of eqn (20) has been developed by modulating the strength of the electrophilic partner through structural variations of carbocationic structures but recent kinetic studies have focused on the description of uncharged electrophiles. Thus, a number of quinone methides as well as of Michael acceptors, such as benzylidenemalonitriles, benzylideneindandiones and benzylidenebarbituric and -thiobarbituric acids, have been successfully ranked on the electrophilicity scale, with all E values falling in the domain of weak electrophilicities (E from –9.42 to –17.29).[52,53] Interestingly, it has been shown that the electrophilicity of an extended series of neutral electron-deficient nitroaromatics and heteroaromatics of widely differing reactivity and structure is also appropriately described by eqn (20). Within the E scale developed by Mayr, covering a range of +6 to –18, this series embraced a domain of reactivity of more than 8 orders of magnitude, going from the least electrophilic TNB (E = –13.19) to the most electrophilic compound DNTP (E = –4.67). A most relevant feature, however, was the finding that the measured E values are linearly related to the $pK^{H_2O}{}_a$ values for covalent hydration of these Meisenheimer structures, defining a correlation, eqn (21), which in fact coincides with the comparable correlation, E *vs* pK_{R+}, reported by the Mayr group for addition of H_2O to carbocations.[2,34b,53]

$$E = -0.662\ pK^{H_2O}{}_a\ (\text{or } pK_{R+}) - 3.20 \quad (21)$$

$$E = -0.662\ pK^{MeOH}{}_a - 1.53 \quad (22)$$

Hence, if the correlation holds more generally for Meisenheimer electrophiles, the quantification of the electrophilicity of these important reaction partners can be usefully approximated on the basis of their tendency to form σ-adducts with water, or combining eqn (19) and (21) to obtain eqn (22), with methanol.

Referring to methoxylation at an unsubstituted carbon to minimize steric effects, the following estimates of the E values (~ ±0.5 unit) for our triflones are obtained from eqn (22), E = –7.56 for **13**; $E \approx -9.62$ for **4**, $E \approx -11.70$ for **5**. While the latter value falls, as do the E values for the two reference trinitro compounds (E = –12.41 for TNA and E = –13.19 for TNB), in the domain of weak electrophilicities (Fig. 7), the reactivity of the bis(SO_2CF_3) compound **4** is comparable to that of the most reactive neutral substrate studied by Mayr, namely benzylidenemalonitrile (E = –9.42). Most importantly, the electrophilicity of the tris-SO_2CF_3 benzene **13** is found to approach that of 4-nitro-6-cyanobenzofuroxan (E = –7.01), a compound the general behaviour of which is representative of a superelectrophilic ranking.[2a] Anchoring to carbocationic reactivity, the electrophilicity of **13** is of the same order as that of a benzhydrylium cation such as Michler's hydrol blue (E = –7.02),[34,35] that is the bis(4-dimethylaminophenyl)carbenium ion, but higher than that of other positively charged species such as triallyl cations or arylallylpalladium complexes, (see Fig. 7). This suggests that more of the rich chemistry established for the above cations could find analogy with this triflone whose electrophilicity remains, however, considerably lower than that of DNTP (E = –4.67), and DNBF (E = –5.06), the two most reactive Meisenheimer electrophiles known to date.

Experimental section

Materials

2,6-Bis(trifluoromethanesulfonyl)-4-nitroanisole (**4**) was prepared as previously described by Yagupolskii *et al.*: mp. 124 °C (lit.,[37] 125–126 °C). Methanol and methanolic sodium methoxide solutions were prepared as previously described.[33a,b,36 40] The various buffers used for the rate and equilibrium measurements were purified according to classical methods. Buffers used were trichloroacetate (pH = 3.87–5.07), dichloroacetate (pH = 5.36–6.26), 3,5-dinitrobenzoate (pH = 6.78–7.74), 3-chlorobenzoate (pH = 8.00–8.96), benzoate (pH = 9.34–9.52), 2,4,6-trichlorophenoxide (9.77–10.73), 2,6-dichlorophenoxide (10.70–11.66), 4-cyanophenoxide (11.72–12.18), 2-bromophenoxide (12.45–13.22).[33a,b,36,40]

The sodium salt of the 1,1-dimethoxy complex **4a-Me** was prepared as described by Yagupolskii *et al.*[37] The formation of the transient 1,3-complex **4b-Me** was studied at –30 °C by ^{1}H NMR. Adding an equivalent amount of MeONa to a solution of **4** in CD_3CN resulted in the immediate and quantitative formation of **4b-Me**, as evidenced by the disappearance of the signals ascribable to the parent molecule and the exclusive appearance of the AX system typical of the two non-equivalent protons H_3 and H_5 of **4b-Me**. Also consistent with this structure was the presence in the ^{19}F spectra of two fluorine resonances corresponding to the two non-equivalent SO_2CF_3 groups. The results are summarized in Table 5. Altogether, the changes in chemical shifts observed upon complexation of **4** to form the isomeric adducts **4a-Me** and **4b-Me** are fully consistent with previous reports dealing with the interaction of MeO^- with many 4-X-2,6-dinitrosubstituted anisoles. They do not call therefore for particular comments since they agree well with the proposed structures.[33a,38,50]

Rate measurements

Kinetic determinations were performed on an Applied-Photophysics SX-18MV stopped-flow apparatus or a conventional

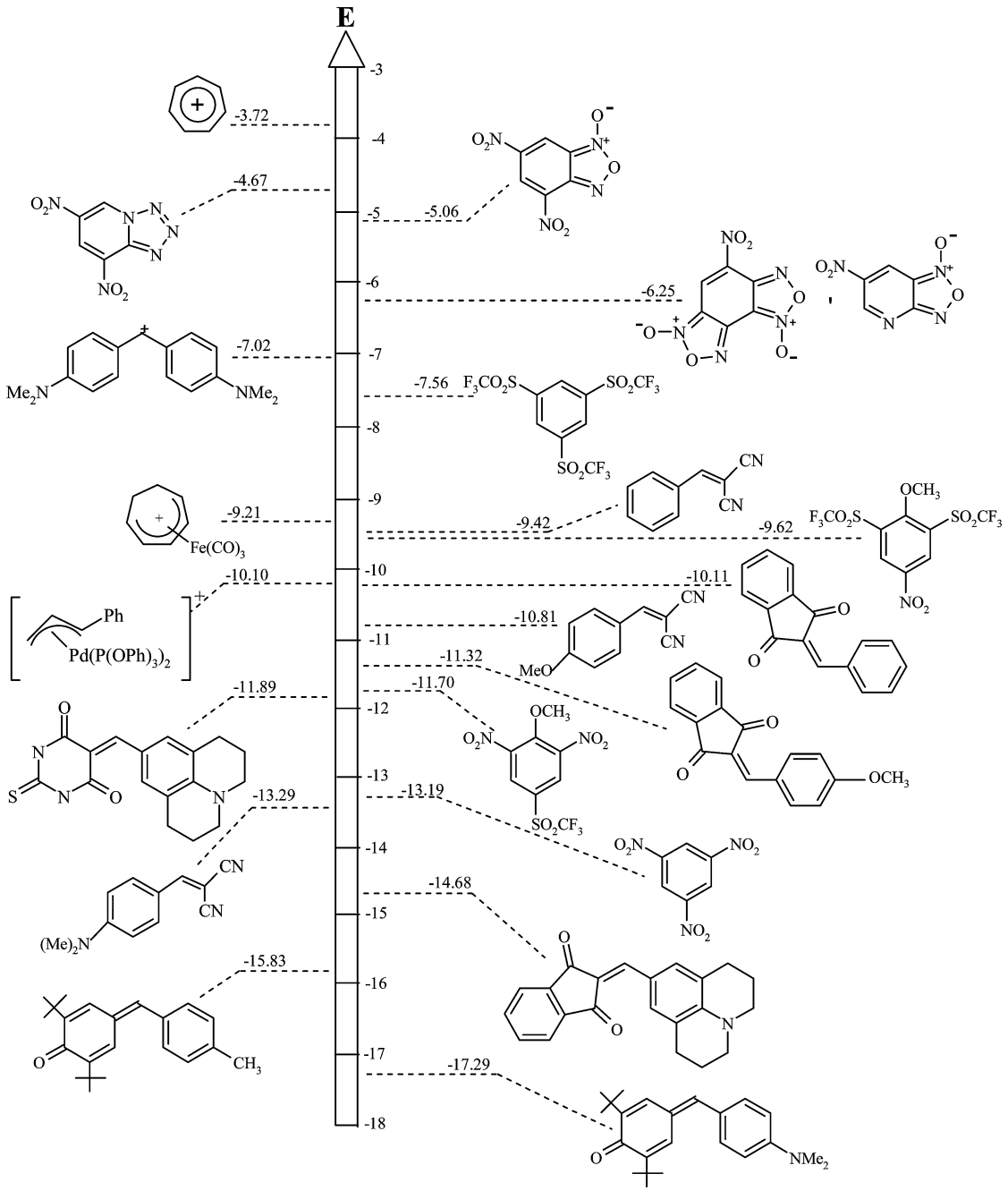


Fig. 7 The ranking of triflones on the *E* scale, as defined by Mayr *et al*.[34,51,52]

Table 5 ^{1}H, ^{13}C and ^{19}F NMR chemical shifts of the anisole **4** and the related 1,1- and 1,3-dimethoxy compounds in CD_3CN[a,b]

Compound	H-3	H-5	OCH_3	CF_3
4[c]	9.11 (9.16)	9.11 (9.16)	4.30 (4.33)	−75.60
4a-Me[d]	8.41 (8.33)	8.41 (8.33)	3.15	−78.03
4b-Me	5.97	8.09	–[e]	−78.79, −78.81

[a] δ in ppm relative to internal TMS (^{1}H, ^{13}C) and internal $CFCl_3$ (^{19}F); *J* in Hz. [b] δ values in brackets refer to Me_2SO-d_6; from ref. 37. [c] ^{13}C data for **4** : 166.7 (C_1); 139 (C_4); 136.6 ($C_{3,5}$); 131.8 ($C_{2,6}$; $^{3}J_{CF} = 2$); 124.9 (CF_3; $^{1}J_{CF} = 325$); 69.9 (OCH_3). [d] ^{13}C data for **4a-Me** : 139.3 ($C_{3,5}$); 121.7 (C_4); 119.9 (CF_3; $^{1}J_{CF} = 327$); 105.9 ($C_{2,6}$); 101.36 (C_1); 52.1 (OCH_3). [e] Too much overlap with the solvent.

HP8453 UV-Visible spectrophotometer, the cell compartments of which were maintained at 20 ± 0.1 °C. All kinetic runs were carried out in triplicate under pseudo-first-order conditions with a triflone (**4**) concentration of approximately 5×10^{-5} mol dm^{-3} and an acid, base or buffer concentration in the range of 10^{-3}–0.1 mol dm^{-3}. In a given experiment, the rates were found to be reproducible to ±2–3%.

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