Electrophilic aromatic substitutions: reactions of hydroxy- and methoxy-substituted benzenes with 4,6-dinitrobenzo-furoxan: kinetics and mechanism

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ABSTRACT: Rate constants have been determined in aqueous Me_2SO mixtures for the reaction of super-electrophilic 4,6-dinitrobenzofuroxan (DNBF) with a series of hydroxy- and methoxy-substituted benzenes whose pK_a values range between -3 and -9. The study extends the reactivity range of weakly basic aromatics with DNBF, from the family of indoles previously studied with pK_a values ranging from -1 to -6. The overall rate constants for the reactions of DNBF as the electrophile are at least one order of magnitude greater than for the reactions of H_3O^+ with the same series of aromatics. This lends further credence to the notion that DNBF possesses super-electrophilic properties. An LFER is observed between $\log k_{50\%Me_2SO}^{DNBF}$ and $pK_a^{H_2O}$ with slope 0.54. In the case of 1,3,5-trimethoxybenzene a significant kinetic isotope effect (KIE) is observed ($k^H/k^D = 3.71$ in 50% Me_2SO). This system hence affords one of the few instances in which a KIE has been observed in S_EAr reactions. It follows from the observed KIE that the addition of DNBF to the aromatic is not rate-limiting and that reversion to reactants and proton loss from the arenonium intermediate occur at comparable rates. Structures of the products of electrophilic substitution have been confirmed by ^1H NMR. In all cases the regiochemistry of the reactions was identical to that observed in protonation studies of the starting aromatics. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: electrophilic aromatic substitutions; 4,6-dinitrobenzofuroxan; σ-complexation; superelectrophile; nitrobenzofuroxan; kinetics of S_EAr reaction

INTRODUCTION

Electrophilic aromatic substitution has remained one of the major reaction types in organic chemistry because of both its synthetic utility and mechanistic significance.[1–10] Studies of benzenoid compounds continue to provide insight, while reactions of activated π-excessive hetero-aromatic compounds such as pyrroles or indoles have afforded access into wide varieties of pharmacologically useful products.[11,12] Nitration,[3,4] nitrosation[4] and halo-genation[5,6] have provided the common reaction types, but studies with other electrophiles such as benzenediazo-nium ions[7–10,13–16] have enabled much valuable informa-tion to be derived, e.g. concerning the nature of the rate-determining step in S_EAr reactions.

In recent years a body of evidence has been accumulated showing that 4,6-dinitrobenzofuroxan (DNBF) is a neutral 10-π-electron heteroaromatic sub-strate which in many processes exhibits an extremely high electrophilic character.[17–29] In fact, recent studies have shown that DNBF is a stronger electrophile than both the *p*-nitrobenzenediazonium ion and the H^+ cation.[30,31]

In the present study we have investigated the reactions of DNBF with a series of hydroxy- and methoxy-substituted benzenes **1a–1e** (Scheme 1). The basicities of most of these derivatives are considerably lower, falling in the range from −3 to −9,[32,33] compared e.g. with indoles for which the pK_a values for protonation range between −1 and −6.[34–36] Our results further demonstrate that DNBF is a remarkable probe to assess the reactivity of extremely weak nucleophilic carbon centres[17,18,37,38] and enable comparison to be made with previous studies by Kresge and co-workers[32,33,39,40] of the protonation of these compounds. Interestingly, the 1,3,5-trimethoxybenzene (TMB)–DNBF system has pro-vided a rare instance for the observation of a kinetic isotope effect in an S_EAr reaction.
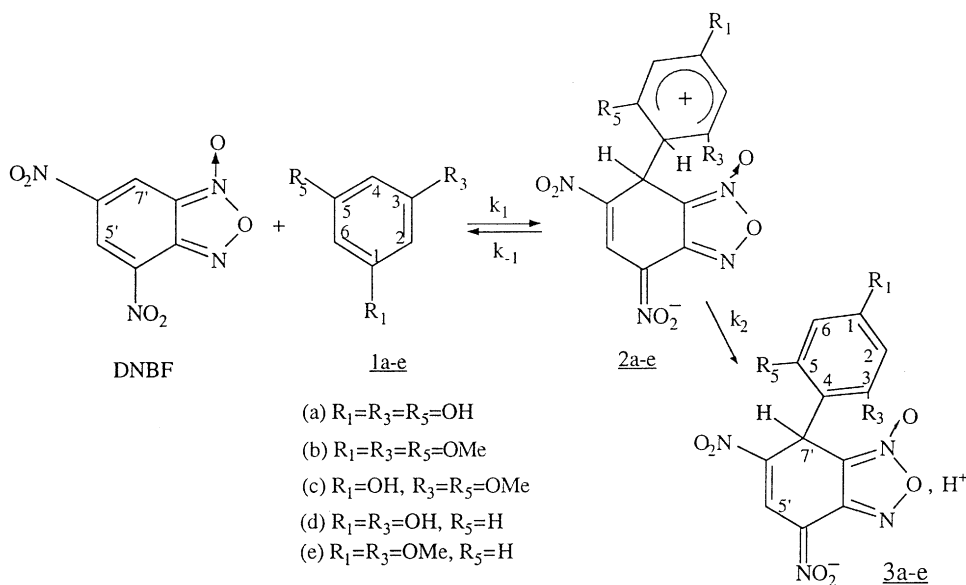
RESULTS

Structural studies

The course of the reactions of DNBF with **1a–1e**, as shown in Scheme 1, was first studied in Me_2SO, where,

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Scheme 1

Table 1. ^{1}H NMR data for hydroxy- and methoxy-substituted benzenes **1a–1e**, DNBF and related σ-adducts **3** in [[2]H$_6$]-Me$_2$SO[a,b]

R$_1$	R$_3$	R$_5$	Compound	$\delta_{H5'}$	$\delta_{H7'}$	δ_{H2}	δ_{H4}	δ_{H5}	δ_{H6}	
			DNBF	9.26	8.94	–	–	–	–	
OH	OH	OH	**1a**	–	–	5.66	5.66	–	5.66	$\delta_{OH} = 8.97$
			3a	8.58	5.69	5.66	–	–	5.66	Rapid H^{+}/H$_2$O exchange[c]
OMe	OMe	OMe	**1b**	–	–	6.09	6.09	–	6.09	$\delta_{OMe} = 3.71$
			3b	8.65	5.83	6.19	–	–	6.19	$\delta_{OMe(1)} = 3.74$; $\delta_{OMe(3,5)} = 3.68$
OH	OMe	OMe	**1c**	–	–	5.95[d]	5.95[d]	–	5.95[d]	$\delta_{OH} = 9.41$; $\delta_{OMe(3,5)} = 3.67$
			3c	8.60	5.76	6.00	–	–	6.00	$\delta_{OMe(3,5)} \approx 3.6$ (br); rapid H^{+}/H$_2$O exchange[c]
			3c'[e]	8.60	5.76	–	5.90 or 6.00	–	6.00 or 5.90	$\delta_{OMe(3)} = 3.66$; $\delta_{OMe(5)} \approx 3.6$ (br); rapid H^{+}/H$_2$O exchange[c]
OH	OH	H	**1d**	–	–	f	f	6.93	f	$\delta_{OH} = 9.15$
			3d	8.60	5.27	g	–	6.96	g	Rapid H^{+}/H$_2$O exchange[c]
OMe	OMe	H	**1e**	–	–	h	h	7.18	h	$\delta_{OMe} = 3.73$
			3e	8.64	5.42	6.49[i]	–	7.11[i]	6.46[i]	$\delta_{OMe(1)} = 3.72$; $\delta_{OMe(3)} = 3.63$; $J_{H3,5} = 2.4$; $J_{H5,6} = 8.5$

[a] δ in ppm relative to internal SiMe$_4$; J in hertz.
[b] See Scheme 1 for the numbering of ring positions.
[c] Owing to the presence of some adventitious water in the Me$_2$SO solvent, rapid exchange of the phenolic proton occurs.
[d] Apparent singlet.
[e] See text for structure **3c'**.
[f] Second-order spectrum; δ values in the range 6.16–6.19.
[g] Second-order spectrum; δ values in the range 6.11–6.16.
[h] Second-order spectrum; δ values in the range 6.47–6.53.
[i] Values deduced from a second-order analysis.

on mixing the two reagents in equimolar quantities, complete σ-complex formation resulted. Structures of the resulting σ-adducts **3** were identified by ^{1}H NMR spectroscopy in [[2]H$_6$]-Me$_2$SO. Parameters given in Table 1 are typical of C-adduct formation by DNBF. First, all H$_{7'}$ resonances are in the range 5.30–5.83, as previously observed in many couplings of this heteroaromatic with various carbon bases.[17,18,23–26,30,31] Also in accord with previous observations is the fact that the chemical shift of the H$_{5'}$ proton located between the two nitro groups of the

negatively charged DNBF moiety is essentially independent of the nature of the bonded aromatic donor.[17,18] To be noted is that the reactions of the two 1,3-disubstituted aromatics **1d** and **1e** lead regioselectively to the adducts **3d** and **3e**. In contrast, the coupling of 3,5-dimethoxyphenol. (**1c**) affords the two isomeric adducts **3c** and **3c'** in a 3:2 ratio (see Discussion).

Following a procedure previously described,[30,31] some of the adducts **3**, namely **3b**, **3d** and **3e**, could be isolated as the sodium or potassium salts. UV–visible spectra of

3c　　　　　**3c'**
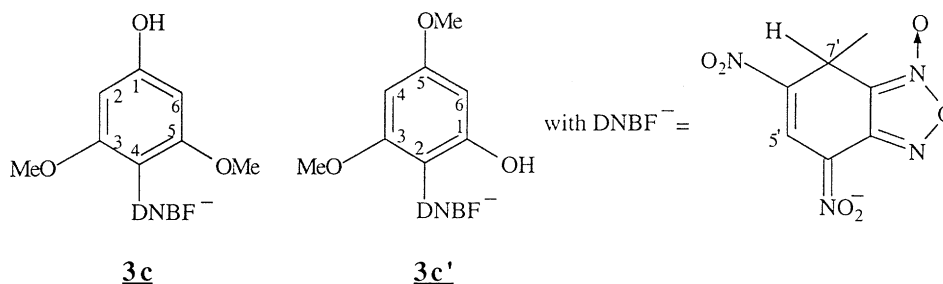
these salts dissolved in various media, e.g. in H_2O–Me_2SO mixtures of various compositions as well as in methanol, exhibited the same strong absorption maximum at $\lambda = 490$ nm, a wavelength known to be typical of all C-bonded σ-adducts of $DNBF^{23–26,30,31,41}$. Solutions of the adducts **3a** and **3c** (**3c'**) showed similarly a strong visible absorption at 490 nm. Equally consistent with the C-bonded character of **3a–3e** was their stability in dilute HCl solutions.

Kinetic studies

Kinetic studies were carried out in aqueous Me_2SO and methanolic solutions because of the very low solubility of some of the substrates in purely aqueous solution. Experiments were conducted at 25 °C under pseudo-first-order conditions with respect to the benzenoid donor as the excess component.

$$DNBF + ROH \rightleftharpoons \quad + H^+ \quad (1)$$

4a　R=H
4b　R=Me
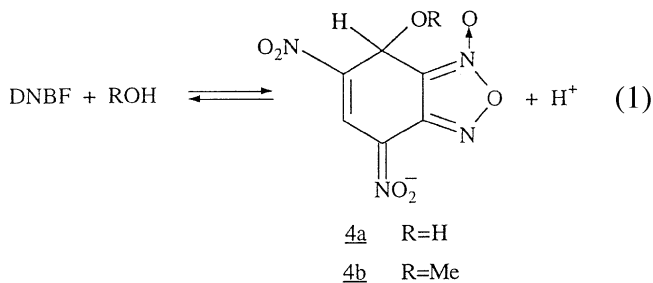
As previously reported,[20–22] DNBF has a strong tendency to react according to eqn (1) in aqueous or methanolic solution. The pK_as at 25 °C for formation of the hydroxy adduct **4a** are equal to 3, 2.7 and 1.75 in 70–30, 50–50 and 30–70 (v/v) H_2O–Me_2SO respectively, while the pK_a for formation of the methoxy adduct **4b** is equal to 6.46 at 20 °C in methanol. To avoid any interference between Scheme 1 and eqn (1), our experiments were conducted at low pH in these solvents. In 70%, 50% and 30% aqueous Me_2SO, 0.2 or 0.1 mol dm^{-3} HCl solutions of DNBF (~5×10^{-5} mol dm^{-3}) were mixed with equal volumes of **1a–1e** (10^{-3}–1.5×10^{-2} mol dm^{-3}) in a stopped-flow apparatus; the final ionic strength was maintained at 0.1 mol dm^{-3} by addition of KCl as needed. Similarly, 2×10^{-3} or 10^{-3} mol dm^{-3} methanesulphonic acid solutions of DNBF

were mixed with the appropriate solutions of **1b** (10^{-3}–10^{-2} mol dm^{-3}) in methanol, not correcting, however, for changes in the final ionic strength. Interestingly, we could detect only one relaxation time pertaining to the complexation of DNBF in all experiments conducted under the experimental conditions indicated above. This was in particular the case for the DNBF–3,5-dimethoxy-phenol (**1c**) system, suggesting that only one of the two isomeric adducts, **3c** or **3c'**, is formed in aqueous solutions. It was not possible to differentiate between these two structures, because solubility problems precluded proper NMR experiments in H_2O–Me_2SO mixtures. At this stage the important point is that this structural uncertainty is of minor importance for our discussion. Possible reasons favouring the predominant formation of **3c** rather than **3c'** will be considered at the end of this paper.

Based on Scheme 1, the general expression for the observed first-order rate constant k_{obs} for formation of the adducts **3a–3e**, as derived under the assumption that the zwitterions **2** are low-concentration ('steady state') intermediates,[30,31] is given by

$$k_{obs} = \frac{k_1 k_2}{k_{-1} + k_2}[\mathbf{1a} - \mathbf{1e}] = k[\mathbf{1a} - \mathbf{1e}] \qquad (2)$$

In accordance with eqn (2), excellent straight lines with zero intercepts were obtained in all cases when the k_{obs} values were plotted vs the aromatic donor (**1a–1e**) concentration, with no evidence of a pH dependence of the rates (Fig. 1). Determination of the second-order rate constant k from the slopes of the k_{obs} vs [**1a–1e**] plots was straightforward in the different systems studied. The results are summarized in Tables 2 and 3, the latter including rate constants obtained from experiments conducted under similar experimental conditions with 1,3,5-trimethoxybenzene-2,4,6-d_3 as the benzenoid donor. The corresponding k^H/k^D ratios are also given in Table 3.

DISCUSSION

In our previous studies it was shown that DNBF is an extremely powerful electrophile—a super-electrophile—in its reactions with various heteroaromatic com-
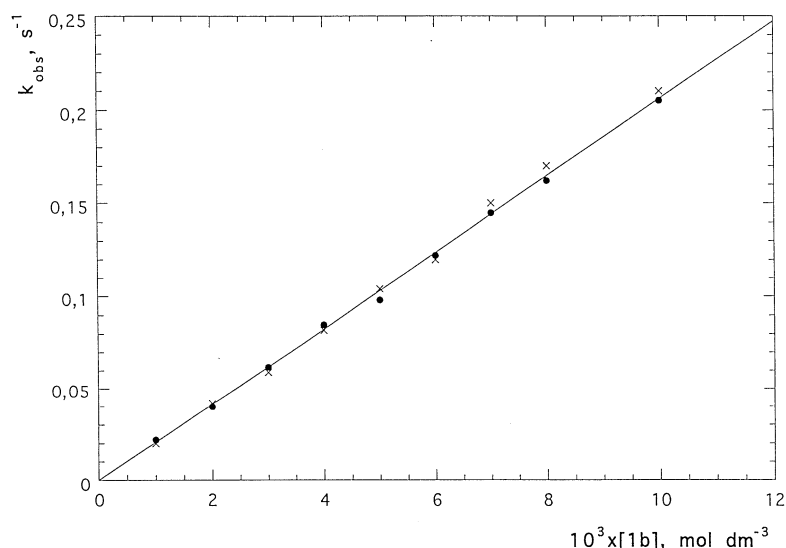
Figure 1. Effect of pH and of concentration of 1,3,5-trimethoxybenzene (**1b**) on rates of σ-complexation of DNBF in 50% H_2O–50 % Me_2SO (v/v) at 25°C: ●, $[H^+] = 0.05$ mol dm^{-3}; ×, $[H^+] = 0.1$ mol dm^{-3}

Table 2. Second-order rate constants k^{DNBF} for DNBF addition to hydroxy- and methoxy-substituted benzenes **1a–1e** in 50% H_2O–50% Me_2SO (v/v) at 25°C[a]

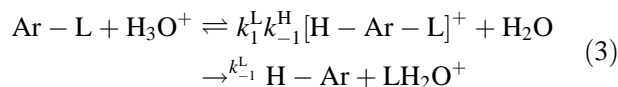| Aromatic	$pK_a^{H_2O}$	k^{DNBF} (mol^{-1} dm^3 s^{-1})
1,3,5-Trihydroxybenzene (**1a**)	−3.13	790
1,3,5-Trimethoxybenzene (**1b**)	−5.72	20.5
3,5-Dimethoxyphenol (**1c**)	−4.35	123
1,3-Dihydroxybenzene (**1d**)	−7.83	1.6
1,3-Dimethoxybenzene (**1e**)	−9	0.52

[a] $pK_a^{H_2O}$ *values taken from Refs 32 and 33.*

Table 3. Solvent effects and kinetic isotope effects on rates of coupling of DNBF with 1,3,5-trimethoxybenzene (**1b**) at 25°C

	k^{DNBF} (mol^{-1} dm^3 s^{-1})		
Solvent	**1b**	**1b**-d_3	k^H/k^D
CH_3OH	0.13	–	
70–30 H_2O–Me_2SO	30.66 (56.7)[a]	7.43	4.13
50–50 H_2O–Me_2SO	20.46 (34.2)[a]	5.45	3.75
30–70 H_2O–Me_2SO	6.11 (8.1)[a]	2.23	2.74

[a] k_1^{DNBF} values for DNBF addition to **1b** calculated as discussed in the text.

pounds.[30,31,37,38,41] In fact, DNBF was found to react readily with very weakly basic indoles with pK_a values ranging between −1 and −6.[30,31] In the present study we show that the electrophilic nature of DNBF can be further manifested via reactions with the even more weakly basic benzenoid aromatics, i.e. the hydroxy- and methoxy-substituted benzenes **1a–1e**, which have pK_a values as low as −9.[32,33]

In Fig. 2 we compare the reactivity of related families of aromatics towards the proton and towards DNBF. It is seen that the DNBF reactivity is very much greater, by at least two orders of magnitude, although the data for DNBF have not been dissected to take into account KIE results which suggest that the first step is not fully rate-determining, as is the case for protonation. In this regard one may recall that rate constants for protonation at an aromatic CH position can be safely estimated from reported protiodetritiation or protiodedeuteration exchange rate data by assuming reasonable values of 18 and 7.8 for the k_{-1}^H/k_{-1}^T and k_{-1}^H/k_{-1}^D ratios respectively (eqns (3) and (4)).[13,30,31,39,40,42–46] Using exchange rate data (k_{exch}) reported by Kresge and co-workers,[39,40,44,46] the $k_1^{H_3O^+}$ values for protonation of **1b, 1e** and related aromatics, i.e. **1f–1h** (see Fig. 2 caption), have thus been derived and used to draw the corresponding line in Fig. 2.

$$Ar - L + H_3O^+ \underset{k_{-1}^H}{\overset{k_1^L}{\rightleftharpoons}} [H - Ar - L]^+ + H_2O \\ \xrightarrow{k_{-1}^L} H - Ar + LH_2O^+ \tag{3}$$

$$k_{obs} = \frac{k_1^L[H_3O^+]}{1 + k_{-1}^H/k_{-1}^L} = k[H_3O^+] \tag{4}$$

Figure 2 further demonstrates a direct relationship (LFER) between the logarithm of the overall second-order rate constants (k) and the basicity of the aromatics. However, the meaning of the slope value (∼0.54) is not readily interpretable for at least three reasons: (i) the relationship uses rate constants measured in 50% H_2O–50% Me_2SO while the pK_a values refer to H_2O; (ii) these pK_a values are subject to some uncertainty since they have been derived from equilibrium measurements carried out in strongly acidic media;[32,33] (iii) as discussed
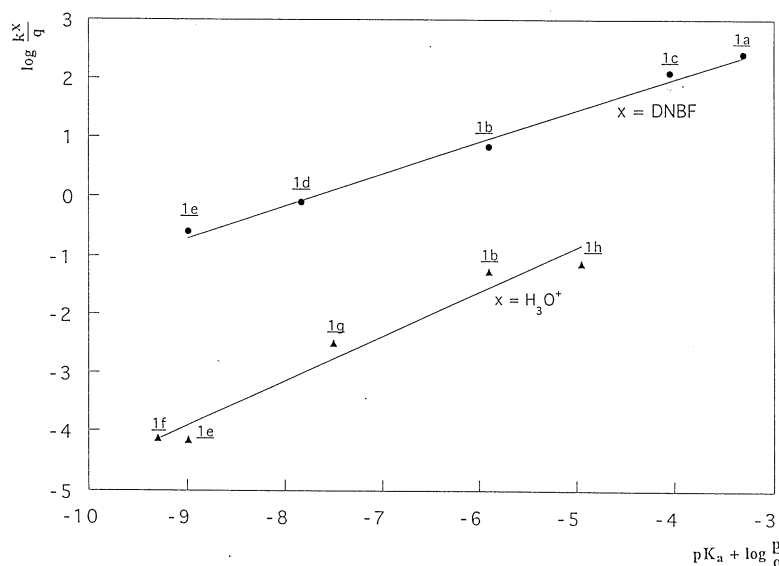
Figure 2. Effect of basicity ($pK_a^{H_2O}$) on rates of protonation and DNBF substitution of hydroxy- and methoxy-substituted benzenes in aqueous solution ($k^{H_3O^+}$) or 50% H_2O–50% Me_2SO (k^{DNBF}): **1a–1e**, as given in Scheme 1; **1f**, 1,3-dimethoxy-2-methyl benzene; **1g**, 1,3-dihydroxy-2-methyl benzene; **1h**, 1,3,5-triethoxybenzene (p and q are the classical statistical factors)

below, the rate constants k involve contributions of the individual rate constants pertaining to formation and decomposition of the arenonium ion intermediate (k_1, k_{-1}, k_2). Nevertheless, the relationship of Fig. 2 is important because it emphasizes that the rate of DNBF addition is clearly a function of the basicity of the aromatic donor.

The effect of solvent composition on the rate constants for complexation of DNBF has been studied, selecting 1,3,5-trimethoxybenzene (**1b**), whose pK_a lies in the middle range of the series examined, as representative substrate. Data pertaining to various H_2O–Me_2SO and methanol solutions are summarized in Table 3. The results show overall that the rate of complexation is favoured by increasing the polarity and hydrogen-bonding capability of the solvent, in accord with the fact that the reactions must proceed through a strongly dipolar transition state like **5**.[30,31,47] Of particular interest are the results in H_2O–Me_2SO mixtures, which reveal that the reactivity of DNBF towards **1b** increases significantly on increasing the water content. On this basis it is clear that one would have observed (Table 3) greater rates of complexation in aqueous solution, where direct measurements were precluded owing to solubility problems.

Table 3 also shows that the rate of coupling of DNBF with **1b** is subject to a significant isotope effect which is markedly dependent on the solvent. Thus the k^H/k^D ratio increases from 2.74 in 30% H_2O–70% Me_2SO to 4.13 in 70% H_2O–30% Me_2SO, indicating that the decomposition of the arenonium intermediate becomes more and more rate-limiting with increasing water concentration.

The following factors come into play on increasing the water content and concomitantly changing the solvent properties such as hydrogen bonding, polarity, etc.[47] First, one can anticipate that both the transition state **5** and the intermediate **2b** will be subject to a moderate stabilization owing to the development of (partial) positive and negative charges in the two moieties. However, dispersion of positive charge occurs on going
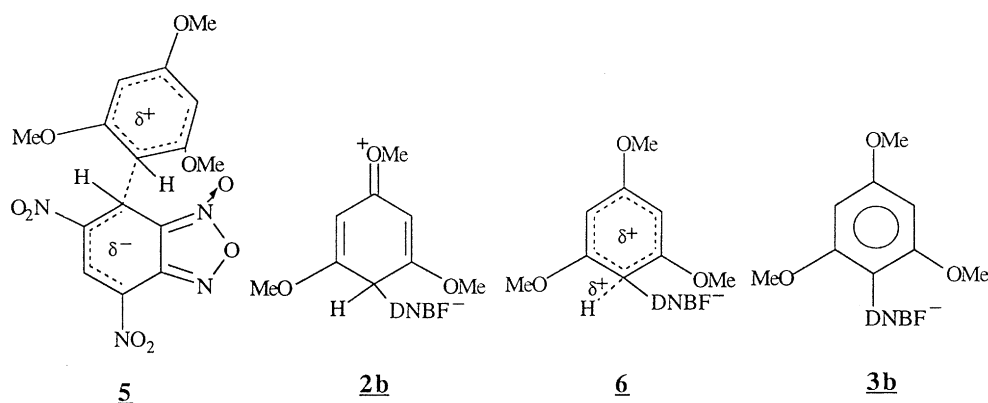
from intermediate **2b** to transition state **6**, leading to formation of product **3b**, and this can be expected to raise the energy of **6** relative to that of **5** and **2b.** Nevertheless, the overall effect of increasing solvent polarity is to increase the reaction rate, implying that the overall energy barrier for the complexation process must decrease in the more aqueous medium. Overall, the increase in KIE with increasing water content of the reaction medium follows reasonably in accord with the qualitative discussion given above.

As discussed above and indicated in Table 3, the DNBF–TMB system has provided one of the few instances in which a KIE has been observed in an S_EAr process. As to the origin of the KIE, from the first observation by Zollinger and co-workers[8,9,10] of such a finding, steric hindrance in the arenonium ion intermediate has been considered to be the primary source, although electronic effects governing the intrinsic acidity of the departing proton may also be contributing.[2,5,30,31,48] Here it is noteworthy that the situation contrasts with that previously observed in the analogous coupling of DNBF at the unsubstituted 3-carbon of various indoles, which does not exhibit a KIE.[30,31] A reasonable explanation for this was provided by Illuminati and co-workers,[49,50] who noted that addition reactions at a substituted or unsubstituted α- or β-position of a pyrrole or thiophene ring are not subject to significant steric hindrance, even when there is a substituent in the adjacent position. On the other hand, steric factors would be largely predominant in governing the feasibility of σ-complex formation at a di-*ortho*-substituted benzene ring position.[17,18] Clearly, the DNBF moiety is highly sterically demanding[48] and it is reasonable to assign this factor to the observation of the KIE in the DNBF–TMB system.

Using the observed KIE values in the DNBF–TMB system (Table 3) one can return to the possibility of dissecting the observed (composite) rate constant k into the constituent rate coefficients k_1^{DNBF}, k_{-1} and k_2 according to Scheme 1. If one neglects as a first approximation secondary isotope effects on k_1^{DNBF} and k_{-1} and assumes that the value of 7.8 for the ratio k_2^H/k_2^D is not markedly affected on going from water to our aqueous Me_2SO solvents[51] (70% Me_2SO by volume corresponds to a molar fraction of only 0.36 at 25 °C), the

following estimates of the k_{-1}/k_2^H ratio and the actual k_1^{DNBF} rate constant can be obtained from the measured k^H/k^D ratio in the three solvents: $k_{-1}/k_2^H = 0.34$, $k_1^{DNBF} = 8.1$ in 30% H_2O; $k_{-1}/k_2^H = 0.67$, $k_1^{DNBF} = 34.2$ in 50% H_2O; $k_{-1}/k_2^H = 0.85$, $k_1^{DNBF} = 56.7$ in 70% H_2O. While these k_1^{DNBF} values better reflect the actual reactivity of DNBF towards TMB, they are not profoundly changed from the composite rate constants. Hence the overall picture that emerges from our results, namely that the tendency of the present family of aromatics to electrophilic substitution by DNBF is considerably lower than that of previously studied pyrroles and indoles, is in accord with established reactivity sequences in S_EAr reactions.

The last point that remains for discussion is the regiochemistry of the coupling of DNBF with **1a–1e.** In the case of the 1,3,5-trihydroxy- and 1,3,5-trimethoxy-benzene derivatives, only one coupling mode is possible. An intriguing result, however, is the observation that the S_EAr substitution of 3,5-dimethoxyphenol (**1c**) occurs preferentially at the 4-position in pure Me_2SO, i.e. *para* to the hydroxy group, even though this position is sterically and statistically disfavoured. A similar behaviour was in fact observed by Kresge *et al.*[52] in ^{1}H NMR studies of the protonation of **1a–1e** and this is explicable in terms of the more negative σ^+ value for -OH as compared with -OCH$_3$. On the other hand, the coupling of DNBF with 1,3-dihydroxybenzene again occurs at a position *para* to OH and a corresponding result is found in the 1,3-dimethoxybenzene case. These results are also analogous to the observations of Kresge *et al.*[52] on protonation of these compounds. Interestingly, in no case have we observed the hydroxy group in these substrates acting as the nucleophilic centre towards DNBF. In contrast, previous studies in our laboratories have shown that aryloxides can act as ambident nucleophiles towards DNBF or related substrates.[23,24,53,54] However, this requires that the reactions be carried out in basic media, a situation that we have deliberately avoided in the present study.

At this stage of our work it is difficult to suggest a definitive explanation for our finding that only one of the isomeric adducts **3c** and **3c'** is apparently formed under the experimental conditions used for our kinetic experiments. A noteworthy result, however, is that Kresge *et*

7c

8c
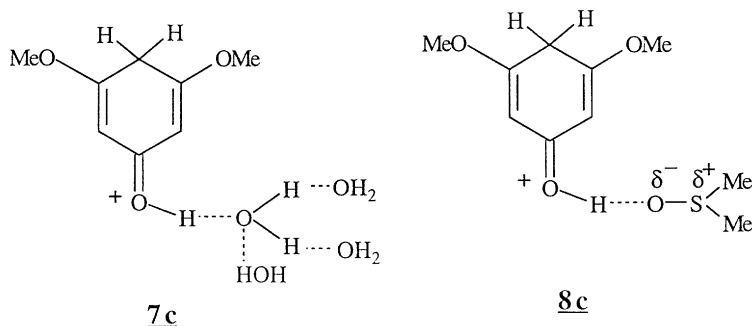
al.[32,33,52] have found that the relative stabilizing influence of *para* -OH and -OMe groups on arenonium -adducts is strongly solvent-dependent. Thus it has been suggested that the stabilizing contribution of the OH group on the adduct **7c** is markedly enhanced in aqueous solution owing to an increased dispersion of its positive charge through hydrogen-bonding solvation.[52] Should this phenomenon operate in the stabilization of the arenonium intermediates involved in the formation of our -adducts according to Scheme 1, this should enhance the stability of the intermediate **2c** as compared with that of **2c′**, supporting the idea that the only observed DNBF–3,5-dimethoxyphenol σ-adduct in H_2O–Me_2SO mixtures is **3c** and not **3c′**. However, the reason why hydrogen-bonding solvation of the type shown in **7c** would be more efficient than that which can occur in Me_2SO (structure **8c**) is not fully understood at present.[55,56]

EXPERIMENTAL

Materials

4,6-Dinitrobenzofuroxan was prepared according to the procedure of Drost,[57] m.p. 172 °C (lit. 172–174.5 °C[20–31,48,58]). All the hydroxy- and methoxy-substituted benzenes (**1a–1e**) were commercial products (Aldrich or Acros) which were purified prior to use. 1,3,5-Trimethoxy-2,4,6-trideuteriobenzene (**1b-d₃**) was prepared according to the H^+-catalysed exchange procedure previously described by Kresge and Chiang.[39]

Reactions depicted in Scheme 1 afforded the adducts **3** in their acid form, which is not very stable in air. Based on previous observations that exchanging the H^+ counterion for a K^+ or Na^+ cation often allows a facile isolation of DNBF σ-adducts as crystalline alkali salts,[30,31,41,48,58] the same procedure as that used in the pyrrole or indole series was employed here to isolate **3a–3e** as alkali salts. Using potassium fluoride or sodium acetate as the added salt, the method was actually successful in the case of the 1,3,5-trimethoxybenzene adduct **3b**, the 1,3-dihydroxybenzene adduct **3d** and the 1,3-dimethoxybenzene adduct **3e**. In contrast, we failed to salt out the 1,3,5-trihydroxy- and 3,5-dimethoxyphenol adducts **3a** and **3c**.

As with most alkali salts of DNBF σ-adducts isolated so far, the crystals obtained for **3b,d,e**,K^+ (or Na^+) were not found to melt without decomposition. Also, attempts to obtain satisfactory elemental analyses have failed. In contrast, confirmation of the structure of these complexes could be obtained from mass spectral experiments performed with the FAB technique.[37,38,48] For instance, we obtain for the parent peaks of **3b**,Na^+: $m/z = 393$ (negative ion) and $m/z = 439$ (negative ion, $2Na^+$).

Kinetic Measurements

Kinetic measurements were performed on either a Durrum-Gibson stopped-flow spectrophotometer or a conventional Kontron-Uvikon spectrophotometer whose cell compartments were maintained at 25 ± 0.2 °C. All kinetic runs were carried out in triplicate under pseudo-first-order conditions with a DNBF concentration of about 3×10^{-5} mol dm^{-3} and **1a–1e** concentrations in the range 10^{-3}–1.5×10^{-2} mol dm^{-3}. In a given experiment the rate constants were found to be nicely reproducible to $\pm$ 2%–3% and to be the same whether the process was followed by monitoring the increase in absorbance at $\lambda_{max} = 490$ nm of the resulting adduct **3** or the decrease in absorbance at $\lambda_{max} = 415$ nm of the parent DNBF substrate as a function of time.

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