Highly Electrophilic Heteroaromatics: the Hydrolysis of 7-Chloro-4,6-dinitrobenzofurazan and 7-Chloro-4,6-dinitrobenzofuroxan in Aqueous Solution

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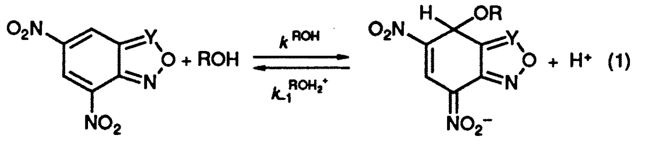
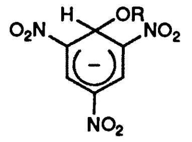
The hydrolysis of 7-chloro-4,6-dinitrobenzofurazan (**4**) and 7-chloro-4,6-dinitrobenzofuroxan (**5**) to give the related 7-hydroxy derivatives has been kinetically investigated in the pH range 1–6 in aqueous solution. The reactions occur 3500 and 10000 times more rapidly, respectively, than the hydrolysis of picryl chloride, emphasizing the much higher electrophilic character of the two heterocycles. Strong catalysis of the hydrolysis of **4** and **5** by carboxylate ions is observed, with Brønsted β values of 0.38 and 0.42, respectively, which support a concerted mechanism. Although the corresponding points ($k^{H_2O}/55.55$) show strong negative deviations from the Brønsted plots, the finding of appreciable solvent isotope effects (k^{H_2O}/k^{D_2O} *ca.* 1.75) favours a similar mechanism for the water reactions, *i.e.* water attack is assisted by a second water molecule which acts as a base catalyst. Differences in the electrostatic effects contributing to the stabilization of the transition states for the water-catalysed and carboxylate ion-catalysed reactions would account for the deviations observed for the k^{H_2O} points.

Much evidence has been accumulated that 4,6-dinitro-2,1,3-benzoxadiazole and its related 1-oxide, more commonly known as 4,6-dinitrobenzofurazan (DNBZ) and 4,6-dinitrobenzofuroxan (DNBF), respectively, are extremely electrophilic heteroaromatic substrates.[1–13] Thus, water and methanol readily react with DNBZ and DNBF according to eqn. (1) affording the hydroxide adducts (**1a**, **2a**) or the methoxide adducts (**1b**, **2b**), which are 10^{10} times thermodynamically more stable than the analogous 1,3,5-trinitrobenzene adducts **3a** and **3b**.[8] The latter are the common references in anionic σ-complex chemistry.[1b,11] More importantly, weak carbon nucleophiles like polymethoxybenzenes, anilines, pyrroles or indoles, add quantitatively to DNBZ and DNBF to give very stable carbon-bonded adducts which are formally the products of S_EAr substitution of the benzene or arene ring.[1–7] The ease of achievement of these reactions has led to the conclusion that DNBZ and DNBF may be suitable probes to assess the reactivity of weakly nucleophilic carbon centres in general.[1,2]

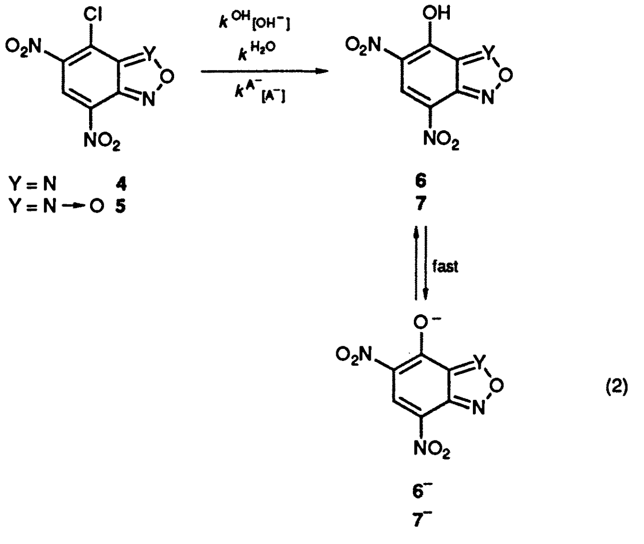


DNBZ Y = N **1** (a) R = H, (b) R = CH_3
DNBF Y = N→O **2**



3 (a) R = H
(b) R = CH_3

Contrasting with the interest devoted to the superelectrophilic behaviour of DNBZ and DNBF, so far there has been very little attention drawn to the reactivity of the related 7-chloro derivatives, *i.e.* 7-chloro-4,6-dinitrobenzofurazan **4** and 7-chloro-4,6-dinitrobenzofuroxan **5**.[14–17] Activation of the chlorine atom by the DNBF and DNBZ moieties should result, however, in a high tendency of **4** and **5** to undergo S_NAr reactions, which do not readily proceed with common electron deficient haloaromatic substrates. In this context, it was first necessary to assess the S_NAr reactivity of **4** and **5** with reference to a simple reaction. In the present paper, we report the results of a kinetic study of the hydrolysis of **4** and **5** to give the corresponding hydroxy derivatives **6** and **7** at low pH in aqueous solution [eqn. (2)].



Results

In aqueous solution, 7-chloro-4,6-dinitrobenzofurazan **4** (λ_{max} = 335 nm, ε = 8900 $dm^3\ mol^{-1}\ cm^{-1}$) and 7-chloro-4,6-dinitrobenzofuroxan **5** (λ_{max} = 421 nm, ε = 7640 $dm^3\ mol^{-1}\ cm^{-1}$) slowly decompose to give quantitatively the 7-hydroxy compounds **6** and **7**. Owing to the very strong acidity of their OH group (a $pK_a^{H_2O}$ value of −3.8 has been measured for the ionization of **6** by using the acidity function method in H_2O–

Table 1 Observed rate constants for the hydrolysis of **4** and **5** in aqueous hydrochloric acid solutions[a]

	4		**5**	
[HCl] or [DCl]/ mol dm^3	k_{obsd} $(H_2O)/10^{-4}$ s^{-1}	k_{obsd} $(D_2O)/10^{-4}$ s^{-1}	k_{obsd} $(H_2O)/10^{-4}$ s^{-1}	k_{obsd} $(D_2O)/10^{-4}$ s^{-1}
10^{-3}	—	—	6.17	3.59
2×10^{-3}	—	—	6.12[c]	3.60
5×10^{-3}	2.18	—	6.04	—
0.01	2.24	1.22	6.16	—
0.02	2.19	1.29	—	—
0.03	2.12	1.20	—	—
0.04	2.21[b]	1.17	—	—
0.05	2.24	—	—	—
0.10	2.25	—	—	—

[a] $T = 25$ °C, $I = 0.2$ mol dm^{-3}. [b] $k_{obsd} = 0.796 \times 10^{-4}$ s^{-1} at $T = 15$ °C and 6.20×10^{-4} s^{-1} at $T = 35$ °C. [c] $k_{obsd} = 1.93 \times 10^{-4}$ s^{-1} at $T = 15$ °C and 16.05×10^{-4} s^{-1} at $T = 35$ °C.

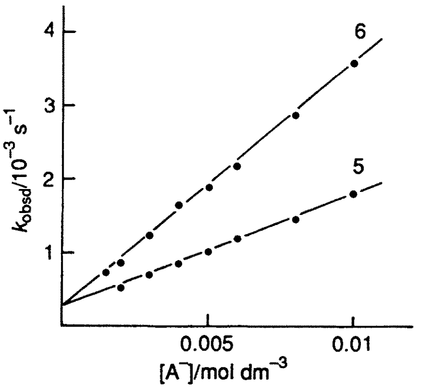


Fig. 1 Effect of buffer concentration on the observed rate (k_{obsd}) for the hydrolysis of **4** in aqueous solution: (5) Formate buffers; (6) acetate buffers.

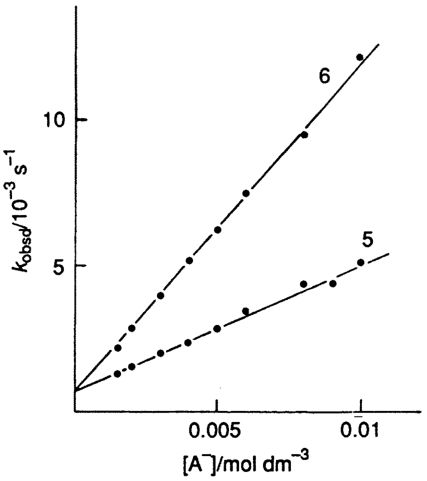


Fig. 2 Effect of buffer concentration on the observed rate (k_{obsd}) for the hydrolysis of **5** in aqueous solution: (5) Formate buffers; (6) acetate buffers.

H_2SO_4 mixtures),[18] both compounds **6** and **7** are in fact generated as the anions **6**$^-$ ($\lambda_{max} = 425$ nm, $\varepsilon = 17\,000$ dm^3 mol^{-1} cm^{-1}) and **7**$^-$ ($\lambda_{max} = 440$ nm, $\varepsilon = 19\,600$ dm^3 mol^{-1} cm^{-1}).

The kinetics of the hydrolysis of **4** and **5** have been investigated between pH 1 and 6 by monitoring spectrophotometrically the appearance of the anions **6**$^-$ and **7**$^-$ at or near λ_{max}. Experiments were carried out using dilute hydrochloric acid solutions and various buffer solutions made up from carboxylic acids. In all cases, pseudo-first-order rate constants, k_{obsd}, were measured at a constant ionic strength of 0.2 mol dm^{-3} (KCl). Investigations in a similar pH range using pyridine buffers or in more basic solutions by means of primary or secondary amine or phenol buffer solutions as well as hydroxide ion solutions have also been made. However, these buffers give rise to very complex kinetic sequences that we have not yet totally elucidated. The occurrence of competitive nucleophilic additions at C_5 and C_7 in both the starting materials, *i.e.* **4** and **5**, and some of the intermediate products formed in nucleophilic catalysis processes, appears to be responsible for this situation.

The general scheme for the hydrolysis of **4** and **5** may be written as depicted in eqn. (2) so that the expression for the observed first-order rate constant for the appearance of **6**$^-$ or **7**$^-$ is given by:

$$k_{obsd} = k^{H_2O} + k^{A^-}[A^-] + k^{OH}[OH^-] \qquad (3)$$

Values of the first-order rate constant k^{H_2O} pertaining to the non-catalysed pathway were readily obtained from measurements in HCl solutions (Table 1): $k_4^{H_2O} = 2.18 \times 10^{-4}$ s^{-1}; $k_5^{H_2O} = 6.1 \times 10^{-4}$ s^{-1}. We also determined the activation parameters and the D_2O solvent isotope effect for that process. We thus obtain at 25 °C: $\Delta H^\ddagger = 73.2$ kJ mol^{-1}; $\Delta S^\ddagger = -69$ J K^{-1} mol^{-1}; k^{H_2O}/k^{D_2O} 1.79 for **4**; $\Delta H^\ddagger = 74.6$ kJ mol^{-1}; $\Delta S^\ddagger = -56.5$ J K^{-1} mol^{-1}; $k^{H_2O}/k^{D_2O} = 1.70$ for **5**.

Figs. 1 and 2 show representative plots of k_{obsd} *vs.* buffer base concentration for the hydrolysis of **4** and **5** in the various carboxylic acid buffers studied. As can be seen, all these plots were satisfactorily linear (correction for buffer failure was taken into account in the more acidic buffers) and had an identical intercept which corresponds, within experimental error, to the value measured for k^{H_2O} in dilute HCl solutions. This indicates that the hydroxide ion catalysis is negligible in all these buffer systems. The second-order rate constants k^{A^-} determined from the slopes of the k_{obsd} *vs.* $[A^-]$ plots are given in Table 2. The isotope effect for the acetate ion catalysed reaction $k_{H_2O}^{AcO^-}/k_{D_2O}^{AcO^-}$) was measured and found to be 3.67 for **4** and 3.72 for **5**.

Discussion

Table 3 compares the kinetic parameters measured for the non-catalysed and base-catalysed hydrolysis of **4** and **5** with similar data previously reported for a number of substituted 1-X-2,4,6-trinitrobenzenes.[19–23] As can be seen, water attack results in a much faster departure of chlorine from **4** or **5** than from picryl chloride: the ratios $k_4^{H_2O}/k_{PiCl}^{H_2O}$ and $k_5^{H_2O}/k_{PiCl}^{H_2O}$ are equal to 3500 and 10000, respectively. This confirms the much greater electrophilic character of dinitrobenzofuroxan and dinitrobenzofurazan derivatives relative to the trinitrobenzene analogues.[1] The solvolysis of **4** and **5** is also much faster than that of TNB derivatives like 1-picrylimidazole, 1-picrylimidazolium cation, 2,4,6-trinitroanisole or 1-(2-acetoxyethoxy)-2,4,6-trinitrobenzene which bear 1-X substituents known to exhibit a better leaving group ability than chlorine in S_NAr reactions.[1,20,23] However, **4** and **5** hydrolyse somewhat more slowly than picryl fluoride and 1,2,4,6-tetranitrobenzene which benefit from the especially high nucleofugality of the leaving fluorine and nitro groups.[1,22]

The fact that **5** undergoes neutral hydrolysis three times faster than **4** is in agreement with previous findings that methanol reacts more rapidly with DNBF to give the σ-adduct **2b** than with DNBZ to give the σ-adduct **1b**. Also to be noted is that water attack on **5** ($k^{H_2O} = 6.1 \times 10^{-4}$ s^{-1}) occurs at a much slower rate than that on DNBF ($k^{H_2O} = 0.035$ s^{-1}) to form the

Table 2 Second-order rate constants k^{A^-} for catalysis of the hydrolysis of **4** and **5** by various buffer bases in aqueous solution [a]

	Buffer (base species)	pK_a^{BH}	$k_4^{A^-}/dm^3\ mol^{-1}\ s^{-1}$	$k_5^{A^-}/dm^3\ mol^{-1}\ s^{-1}$
1	H_2O	−1.74	4.10×10^{-6}	1.08×10^{-5}
2	$CNCH_2COO^-$	2.37	0.057	—
3	$ClCH_2COO^-$	2.71	0.085	0.196
4	$CH_3OCH_2COO^-$	3.45	0.148	0.352
5	$HCOO^-$	3.60	0.159	0.46
6	$^-OOC–COO^-$	4	0.386	1.03
7	CH_3COO^-	4.65	0.33	1.14 0.36[b]
8	$^-OOC–CH_2CH_2COO^-$	5.60	1.58	4.94

[a] $T = 25\ °C$, $I = 0.2\ mol\ dm^{-3}$. [b] In D_2O.

Table 3 Comparison of rate constants k^{H_2O} for the neutral S_NAr hydrolysis of various electron-deficient aromatic and heteroaromatic substrates[a]

Substrate	k^{H_2O}/s^{-1}	Ref.
7-Chloro-4,6-dinitrobenzofurazan	2.27×10^{-4}	*b*
7-Chloro-4,6-dinitrobenzofuroxan[c]	6.10×10^{-4}	*b*
4,6-Dinitrobenzofuroxan[c]	3.35×10^{-2}	8
Picryl fluoride	1.44×10^{-3}	22
Picryl chloride	6.44×10^{-8}	19
1,2,4,6-Tetranitrobenzene	7.57×10^{-4}	22
2,4,6-Trinitroanisole	1.99×10^{-6}	20
1-(2-Acetoxyethoxy)-2,4,6-trinitrobenzene	2×10^{-6}	23
Picrylimidazole	5.06×10^{-7}	20
Picrylimidazolium cation	4.30×10^{-6}	20
1-Picryl-3-methylimidazolium cation[d]	6.83×10^{-6}	21
2-Methyl-4-nitroisoquinolinium cation[e]	1.04	32

[a] $T = 25\ °C$. [b] This work; $\Delta S_4^\ddagger = -69\ J\ K^{-1}\ mol^{-1}$; $\Delta S_5^\ddagger = -56.5\ J\ K^{-1}\ mol^{-1}$. [c] Water addition according to eqn. (1); $\Delta S^\ddagger = -110\ J\ K^{-1}\ mol^{-1}$. [d] $\Delta S^\ddagger = -119.5\ J\ K^{-1}\ mol^{-1}$. [e] Water addition to give the pseudobase **12** (see text), $\Delta S^\ddagger = -71.05\ J\ K^{-1}\ mol^{-1}$.

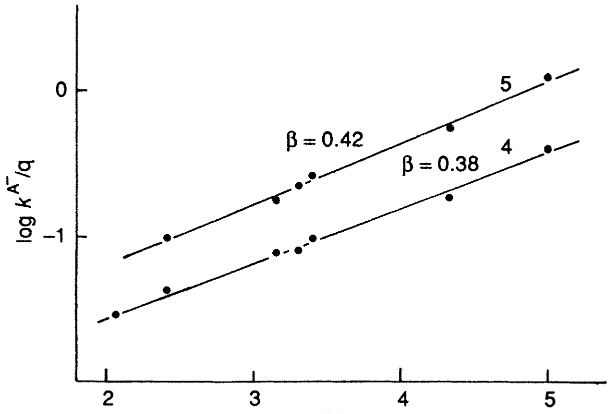
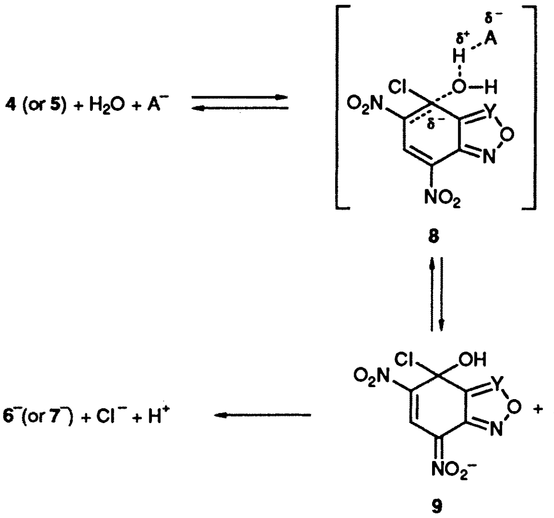


Fig. 3 Statistically corrected Brønsted plots for the catalysis of the hydrolysis of **4** and **5** by various carboxylate anions in aqueous solution, ($T = 25\ °C$; $I = 0.2\ mol\ dm^{-3}$ KCl)

σ-adduct **2a**. This result is consistent, however, with the general observation that nucleophilic attack is kinetically much more favoured at an unsubstituted aromatic or heteroaromatic carbon than at a similarly activated substituted carbon.[1,11]

The observed base catalysis of the hydrolysis of **4** and **5** by carboxylate anions appears to represent classical general base catalysis rather than nucleophilic catalysis. Thus, the rate of the reaction catalysed by acetate anion is decreased nearly four-fold in deuterium oxide solution: $k_{H_2O}^{AcO^-}/k_{D_2O}^{AcO^-} = 3.72$ for **5**. Such an isotope effect indicates that a proton transfer is involved in the rate-limiting step. This finding, together with the observation that the statistically corrected Brønsted plots pertaining to the catalysis of the hydrolysis of **4** and **5** by carboxylate bases are satisfactorily linear (Fig. 3) with slopes *β* of 0.38 and 0.42, respectively, tends to favour a concerted mechanism with transition states of type **8** [eqn. (4)].[24–26] Besides the fact that *β* values in the range of 0.35–0.65 are typical for concerted processes, the idea that the base catalysts might assist a rate-limiting deprotonation of an initially formed zwitterion **10** [eqn. (5)] can be safely rejected. A negatively charged DNBF or DNBZ moiety has been shown to be strongly electron-withdrawing, increasing the acidity of oxygen acids by about 4 p*K* units,[8,16] so that a pK_a value ≤ −5 may be estimated for the OH_2^+ group of **10**. Accordingly, proton transfer from **10** to all bases including the solvent should be diffusion controlled and no appreciable base catalysis should occur.[28]



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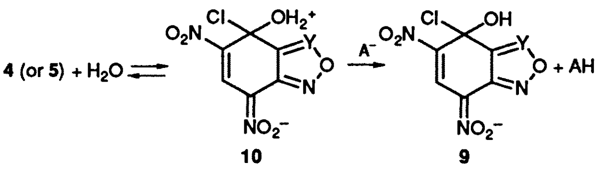
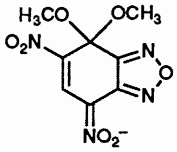


(5)

Our proposal that the hydrolysis of **4** and **5** occurs *via* a concerted process is consistent with a number of previously reported observations. Convincing evidence has thus been obtained that water or methanol addition to DNBF, DNBZ and 7-methoxy-4,6-dinitrobenzofurazan (MDNBZ) are concerted general base-catalysed reactions.[8,9] Conversely, the decomposition of the resulting σ-adducts **1**, **2** or **11**, as well as that of a number of analogous σ-adducts derived from various aromatic and heteroaromatic substrates occurs through concerted general acid catalysis.[1,11,29–33] These reactions, which correspond to the elimination of a water or an alcohol molecule are the microscopic reverse of the rate-limiting step of eqn. (4). Also, de Rossi and co-workers have established that the S_NAr

hydrolyses of picryl chloride (β = 0.50), picryl imidazole (β = 0.50) and picrylimidazolium cations (β = 0.58) involve a concerted general base-catalysed addition of water as the rate-determining step.[19–21] Transition states analogous to **8** have equally been suggested to account for the general base-catalysed addition of water to heterocyclic cations, *e.g.* 2-methyl-4-nitroisoquinolinium cation, to form pseudobases, *e.g.* **12**.[32]

Calculations based on Fig. 3 show that the points for water, based on the rate of uncatalysed hydrolysis of **4** and **5** ($k^{H_2O}/55.55$) fall well below ($\approx$ 2.45 log k unit) the Brønsted lines defined by the carboxylate catalysts. This situation is interesting because it is markedly different from that observed in previously reported examples of S_NAr hydrolysis of σ-complex formation reactions. Also, it goes along with the finding of much less negative entropies of activation for the hydrolysis of **4** and **5** than for comparable systems.[8,19–21] For example, $\Delta S^{\ddagger}$ values of -119.5 and -110 J K^{-1} mol^{-1} have been found for the S_NAr hydrolysis of 3-methyl-1-picrylimidazolium cation and the formation of the hydroxy adduct **1a** of DNBF, respectively,[8,21] as compared with $\Delta S^{\ddagger}$ values of -69 and -56.5 J K^{-1} mol^{-1} for the hydrolysis of **4** and **5**, respectively. Based on the results, one might reasonably think of a different mechanism for the water reactions of these compounds, with no proton transfer taking place in the rate-determining step, as shown in **13**.[30,32] However, this idea is very difficult to reconcile with the finding of notable solvent isotope effects for these processes: k^{H_2O}/k^{D_2O} = 1.79 and 1.70, for **4** and **5**, respectively. Such effects are in fact more consistent with a concerted transition state like **14**, which represents general base-catalysed water attack with a second water molecule acting as a base catalyst, than with transition state **13**.



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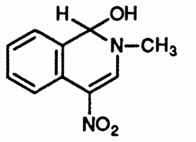

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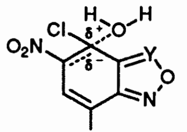

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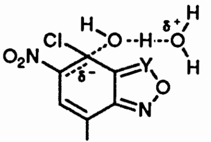

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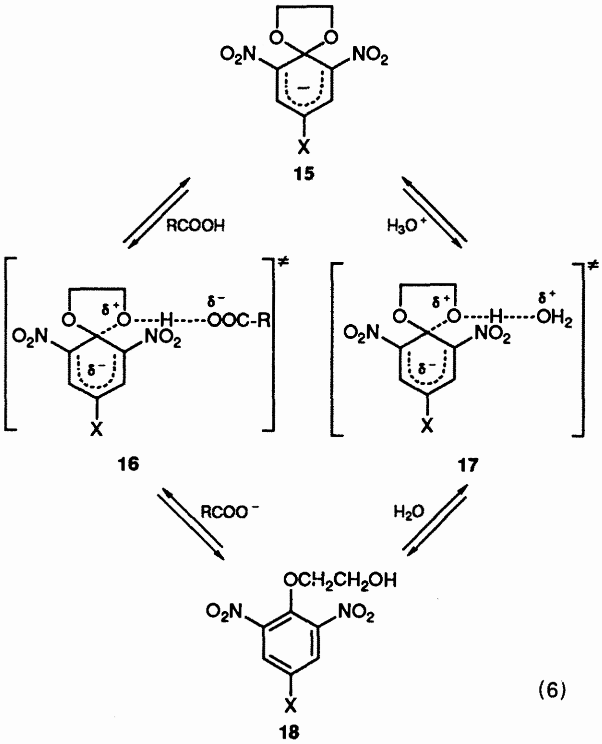
We suggest that the negative deviations of the $k^{H_2O}/55.55$ points from the Brønsted lines of Fig. 3 are in fact reminiscent of those exhibited by the $k^{H_3O^+}$ points from the Brønsted plots pertaining to the acid catalysis of the decomposition of the spiroadducts **15** by carboxylic acids [eqn. (6)]. In these systems, which closely mimic the microscopic reverse of the water attack on **4** and **5**, the deviation of the $k^{H_3O^+}$ points was shown to reflect a substantial positive charge development on the departing oxygen atom in the transition state, as shown in **17**.[30] With carboxylic acid catalysts (transition state **16**), this positive charge interacts favourably with the negative charge which develops concomitantly on the leaving carboxylate anion, thereby resulting in a stabilizing electrostatic effect which cannot operate with positively charged catalysts like H_3O^+ (transition state **17**), thus accounting for the observed deviation. Assuming, in contrast to what we suggested in writing eqn. (4), that a positive charge is similarly developed on the oxygen atom in the transition state for general base water addition to **4** and **5**, *i.e.* proton transfer lags somewhat behind C–O bond formation in the concerted process, one would expect a stabilizing electrostatic interaction in the carboxylate ion-catalysed reactions (transition state **19**) but not in the water-catalysed reactions (transition state **20**). This would therefore explain the lower catalytic efficiency of water compared to a hypothetical negatively charged carboxylate ion of the same pK_a.



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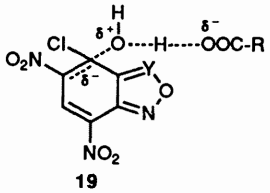

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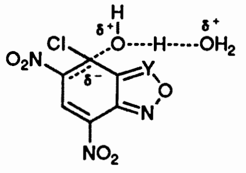

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With respect to the concerted mechanism of eqn. (4), an interesting question is whether or not it may be enforced by an impossibly short lifetime of the protonated Meisenheimer complex **10**.[27] The question can be answered by estimating the order of magnitude of k_{-1}, using the thermodynamic cycle shown below in Scheme 1. Based on this Scheme, we have $k_{-1} = K_a k^{H_2O}/K_e K_{OH}$ with K_a *ca* 10^5–10^6 (*vide supra*), k^{H_2O} = 2.18 × 10^{-4} for **4** or 6.1 × 10^{-4} for **5**, $K_e = 10^{-14}$ and an equilibrium constant K_{OH} for which a lower limit can be estimated to be *ca.* 10^{10} dm^3 mol^{-1} by using the K_{OH} value previously measured for hydroxide ion addition to the unsubstituted 7-position of DNBF.[8] One thus obtains k_{-1} *ca.* 2.3 × 10^6–2.3 × 10^7 s^{-1} or k_{-1} *ca.* 6 × 10^6–6 × 10^7 s^{-1} for **4** and **5**, respectively. Such values are several orders of magnitude below 10^{13} s^{-1} which is usually considered to be the upper limit for a viable species, indicating that the concerted base catalysis of the hydrolysis of **4** and **5** is not enforced.[27,30]

$$\begin{tikzcd}
\mathbf{4}\ (\text{or } \mathbf{5}) + H_2O + H_2O \arrow[r, shift left, "k^{H_2O}"] \arrow[d, shift left] & \mathbf{10} + H_2O \arrow[l, shift left, "k_{-1}"] \arrow[d, shift left] \\
\mathbf{4}\ (\text{or } \mathbf{5}) + H_3O^+ + OH^- \arrow[r, shift left, "K_{OH}"] \arrow[u, shift left, "K_e"] & \mathbf{9} + H_3O^+ \arrow[l, shift left] \arrow[u, shift left, "K_a"']
\end{tikzcd}$$

Scheme 1

Experimental

Materials.—7-Chloro-4,6-dinitrobenzofurazan **4** and 7-chloro-4,6-dinitrobenzofuroxan **5** were prepared according to previously reported procedures.[14-17] **4** m.p. 143 °C (lit. 143–144 °C); **5** m.p. 140 °C. Buffers were purified commercial products.

Measurements.—Kinetic measurements were carried out with a conventional UV–VIS Kontron-Uvikon spectrophotometer with a thermostatted cell compartment (T 25 ± 0.1 °C). The hydrolysis of **4** and **5** was followed at λ_{max} of the corresponding anions $\mathbf{6}^-$ and $\mathbf{7}^-$ (425 and 440 nm, respectively). First-order rate constants k_{obsd} were calculated from Ln ($D_\infty - D$) *vs.* time plots, where D_∞ is the absorbance of $\mathbf{6}^-$ or $\mathbf{7}^-$ and D is the absorbance at time t. In all cases, such plots were linear for at least 90% of the reaction. Values of k_{obsd} used to calculate the second-order rate constant k at a given pH were the average of at least three experiments with an average deviation of ±4%.

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