Interaction of nitroalkane anions with superelectrophilic 4,6-dinitrobenzofuroxan: σ-adduct formation and vicarious heteroaromatic substitution of hydrogen

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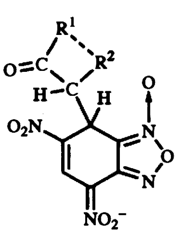
Carbanions of nitromethane, nitroethane, 1-nitropropane and 2-nitropropane readily add to 4,6-dinitrobenzofuroxan (DNBF) to form carbon-bonded σ-adducts (**5a–d**) which are very stable and isolable as crystalline alkali salts. In the case of the nitroethane and 1-nitropropane systems, the complexation results in the formation of two chiral centres, so that diastereoisomeric σ-adducts are formed. Structural features are discussed on the basis of the collected ^1H and ^{13}C NMR parameters. Contrary to expectation, addition of base (MeO^-, $CF_3CH_2O^-$, NEt_3) to dimethyl sulfoxide solutions of **5a–c** did not result in further ionization of the nitroalkane moiety and formation of dianions **7a–c**. Instead, it promotes a base-catalysed β-elimination of nitrous acid. This process also occurs and is especially clean with the 2-nitropropane adduct **5d**, an example of the rare occurrence of a nucleophilic aromatic substitution of an hydrogen atom assisted by the departure of a vicarious nitro group in the exocyclic moiety. The result is re-aromatization of the carbocyclic ring of **5a–d** with formation of carbanions (**8a–d**) which are the conjugate bases of the corresponding 7-R-4,6-dinitrobenzofuroxans (R = Me, Et, Pr^n, Pr^i). Despite their lack of stability, NMR characterization of these carbanions could be made. Rate and equilibrium data for DNBF complexation by the four nitroalkane anions studied have been obtained in aqueous solution. The results show that the thermodynamic stability of the adducts **5a–d** is 10^5–10^8 times greater than that of the analogous σ-adducts of 1,3,5-trinitrobenzene, the common reference aromatic electrophile in σ-complexation processes. Such stability differences emphasize the extremely high electrophilic character of DNBF. Analysis of the rate data reveals that nitrocarbanions exhibit especially low intrinsic reactivities in σ-adduct forming reactions.

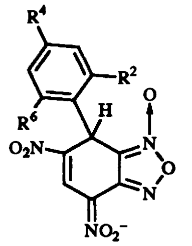
Much evidence has been recently accumulated that 4,6-dinitro-2,1,3-benzoxadiazole 1-oxide, commonly known as 4,6-dinitrobenzofuroxan (DNBF), is a neutral 10 π-electron heteroaromatic substrate which exhibits a considerably higher electrophilic character than common electron-deficient aromatics like 1,3,5-trinitrobenzene (TNB) or 1,3,6,8-tetranitronaphthalene (TNN) in σ-complex formation processes.[1–6] Weak nucleophilic carbon centres which do not directly react with TNB or TNN add quantitatively to DNBF under very smooth experimental conditions. Prototype examples of this behaviour are the coupling reactions of DNBF with enols and a number of π-excessive aromatic or heteroaromatic substrates, *e.g.* 1,3,5-trimethoxybenzene, anilines, phenols or indoles, which afford very stable carbon-bonded σ-adducts of the type **1**–**3**.[1,6,7]

Owing in part to the difficulty of generating the adducts under conditions suitable for kinetic and thermodynamic analysis of the reactions, so far little quantitative data have been obtained regarding the reactivity of DNBF towards nucleophilic carbons. However, we were recently able to carry out a detailed kinetic analysis of the coupling reactions of DNBF with a number of 5-X-substituted indoles to give the adducts **3** according to eqn. (1).[8] This study was very important in that it revealed for the first time that the neutral DNBF molecule is actually a stronger electrophile than positively charged species like benzenediazonium cations, including the 4-nitrobenzenediazonium cation, or the proton, at least in S_EAr-type reactions of eqn. (1).



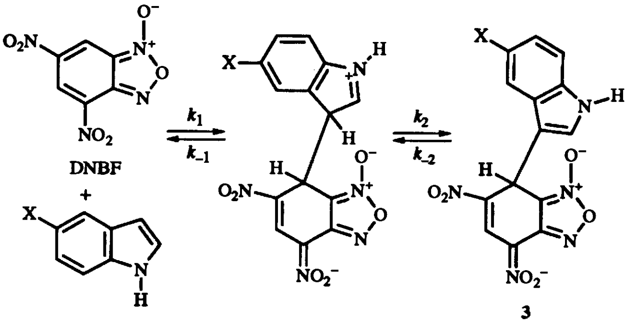
1

$R^1 = CH_3, R^2 = H$
$R^1 = CH_3, R^2 = COCH_3$
$R^1 .....R^2 = –[CH_2]_3–$
$R^1 .....R^2 = –[CH_2]_4–$



2

$R^2 = R^4 = R^6 = OCH_3$
$R^2 = R^6 = H, R^4 = NH_3^+$
$R^2 = R^4 = R^6 = OH$



3

X = CN, Br, Cl, H, Me, OMe

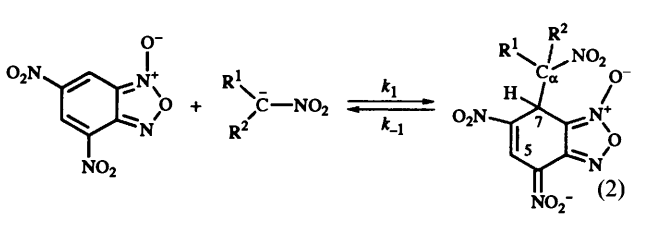
(1)

We have succeeded in obtaining new quantitative information on the electrophilic behaviour of DNBF in looking at the interaction of this compound with a series of nitroalkane anions (**4a–d**). We report here kinetic and equilibrium data for these

Table 1 ^1H NMR parameters for adducts **5a–d** and carbanions **8a–d**[a]

σ-Adduct or carbanion		5-H	7-H	α-H	CH_3	CH_2	Coupling constants
5a		8.61	5.02 (C)	5.09 (A) 5.00 (B)	—	—	$J_{HAHB} = 12.7$; $J_{HAHC} = 4.0$; $J_{HBHC} = 3.0$
8a		8.78	—	6.60 (A) 6.42 (B)	—	—	$J_{HAHB} = 0.9$; $J_{HAH_5} = 0.9$
5b	M	8.64	5.14	5.07	1.44	—	$J_{H\alpha H_7} = 2.3$; $J_{H\alpha CH_3} = 6.8$
	m	8.67	5.39	5.06	1.27	—	$J_{H\alpha H_7} = 2.5$; $J_{H\alpha CH_3} = 6.8$
8b	M	8.59	—	6.85	1.88	—	$J_{H_\alpha CH_3} = 7.8$
	m	8.46	—	6.74	1.61	—	$J_{H\alpha CH_3} = 7.8$
5c	M	8.59	5.07	4.99	0.88	2.02[b]	$J_{H\alpha H_7} = 2.8$
	m	8.64	5.24	4.82	0.85	1.84 1.68	$J_{H\alpha H_7} = 2.8$
8c	M	8.60	—	6.74	1.01	2.26	$J_{H\alpha H_7} = 7.6$; $J_{CH_2CH_3} = 7.6$
	m	8.45	—	6.59	0.98	1.91	$J_{H\alpha H_7} = 7.3$; $J_{CH_2CH_3} = 7.3$
5d		8.69	5.27	—	1.51 1.49	—	$J_{H_5H_7} = 0.7$
8d		8.60	—		2.00 1.68	—	

[a] Relative to internal $SiMe_4$; solvent $[^2H_6]Me_2SO$. [b] Complex pattern centred at 2.02.



(2)

DNBF **4a–d** **5a–d**

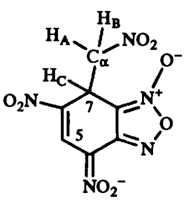
a $R_1 = R_2 = H$; **b** $R_1 = H$, $R_2 = CH_3$; **c** $R_1 = H$, $R_2 = CH_2\text{–}CH_3$; **d** $R_1 = R_2 = CH_3$

reactions which proceed according to the simple equilibrium of eqn. (2) in aqueous solution. Based on ^1H and ^{13}C NMR data obtained in dimethyl sulfoxide solution, we will also emphasize some structural features of the resulting σ-adducts **5a–d** as well as their high susceptibility to suffer base catalysed β-elimination of nitrous acid. This process provides a rare example of a vicarious nucleophilic aromatic substitution involving a NO_2 group as the leaving group.

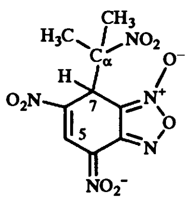
Results

NMR Studies

Formation of the adducts 5a–d. Addition of 1 equiv. of the nitroalkane anions **4a–d** to a solution of DNBF in $[^2H_6]Me_2SO$ resulted in the immediate and quantitative formation of σ-adducts **5a–d**. Owing to the chirality of the tetrahedral ring C-7 of the nitromethane adduct **5a**, the geminal protons are diastereotopic and appear as the AB part of an ABC system. A second-order analysis gave the ^1H NMR parameters reported in Table 1 while the recorded and calculated spectra are compared in Figs. S_1 and S_2 given as supplementary material.† For the same reason, the two geminal methyl groups in the 2-nitropropane adduct **5d** are seen as being slightly non-equivalent in the ^1H NMR spectra.

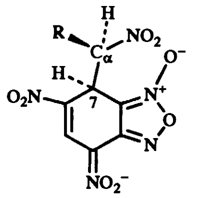


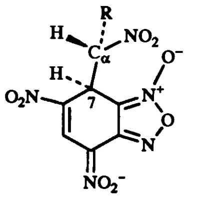
5a

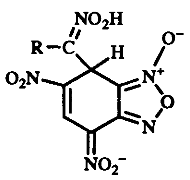


5d

Complexation of DNBF by nitroethane and 1-nitropropane results in the formation of two chiral centres at C-7 and C-α, leading to the possible observation of diastereoisomeric complexes of the type **5b₁–5b₂** (or **5c₁–5c₂**; only one enantiomer for each is shown). In agreement with this expectation, the corresponding ^1H NMR spectra exhibited two similar sets of signals with relative intensities of 3:2 in the two systems. Successive irradiation of the methyl and 7-H doublets assignable to the major (M) and minor (m) diastereoisomers were carried out to clarify the ^1H NMR spectra recorded for **5b**. In each case, collapse of the quadruplet of doublets typical for H_α of the complex at hand (M or m) occurred with concomitant appearance of the doublet or the quadruplet due to the $J_{H\alpha H_7}$ and $J_{H\alpha CH_3}$ couplings, respectively. On this basis, the δ and J values for M and m of **5b** could be determined (Table 1). Owing to the non-equivalence of the two vicinal methylene protons (H_β), the α-H resonances of the major and minor species appear as very complex multiplets in the ^1H NMR spectra pertaining to the DNBF–1-nitropropane system. Although irradiation experiments were carried out, we failed to complete a rigorous analysis of the corresponding spectra. Accordingly, the NMR parameters reported for M and m of **5c** in Table 1 are those afforded by a first-order analysis.







5b₁ $R = C_\beta H_3$ **5b₂**
5c₁ $R = C_\beta H_2C_\gamma H_3$ **5c₂**

6
a R = H; **b** $R = CH_3$; **c** $R = CH_2CH_3$

Both noise proton-decoupled and proton-coupled ^{13}C NMR spectra have been recorded for the various adducts. Based

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† Supplementary material available. Sup. No. 57097 (6 pp.). For details of the Supplementary Publications Scheme see 'Instructions for Authors (1995)', *J. Chem. Soc., Perkin Trans. 2*, 1995, issue 1.

Table 2 ^{13}C NMR parameters for adducts **5a–d** and the carbanion 8d[a,b]

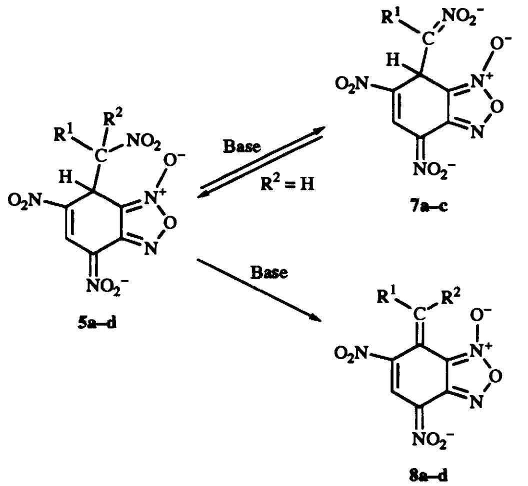
σ-Adduct or carbanion		C-4	C-5	C-6	C-7	C-8	C-9	C-α[b]	CH_3	CH_2	Coupling constants
5a		109.96	132.73	120.78	33.62	111.34	148.73	71.59	—	—	$^1J_{C\alpha H\alpha} = 153$; $^2J_{C\alpha H_7} = 4.5$; $^3J_{C_5H_7} = 1.9$; $^2J_{C_7H\alpha} = 3$; $^1J_{C_7H_7} = 142.7$; $^1J_{C_5H_5} = 162$
5b	M	110.17	132.62	121.32	38.49	110.83	149.09	81.98	15.06	—	$^1J_{C\alpha H\alpha} = 153.2$; $^2J_{C\alpha H_7} = 4.4$; $^1J_{C_5H_5} = 163.3$; $^3J_{C_5H_7} = 2.4$; $^2J_{C_7H\alpha} = 4.1$; $^1J_{C\beta H\beta} = 130.4$
	m	110.23	132.92	121.42			149.13	79.93	13.13	—	$^1J_{C\alpha H\alpha} = 154.5$; $^2J_{C\alpha H_7} = 4$; $^1J_{C_5H_5} = 163.6$; $^3J_{C_5H_7} = 2.3$; $^2J_{C\beta H\alpha} = 3.2$; $^1J_{C\beta H\beta} = 130.2$
5c	M	(110.16)[c]	132.39	121.18	37.30	(110.50)[c]	149.36	90.54	10.42	23.68	$^1J_{C\alpha H\alpha} = 153.0$; $^1J_{C_5H_5} = 163.5$; $^3J_{C_5H_7} = 2.3$; $^1J_{C_7H_7} = 142.8$; $^2J_{C_7H\alpha} = 2.8$; $^1J_{C\gamma H\gamma} = 126.6$; $^1J_{B\beta H\beta} = 136.6$
	m	(110.37)[c]	133.01	121.34	37.60		149.08	87.59	10.51	21.82	$^1J_{C\alpha H\alpha} = 153.0$; $^1J_{C_5H_5} = 163$; $^3J_{C_5H_7} = 2.7$; $^1J_{C_7H_7} = 140$; $^2J_{C_7H\alpha} = 3$; $^1J_{C\gamma H\gamma} = 126.7$; $^1J_{C\beta H\beta} = 136.7$
5d		110.61	133.33	120.99	41.32	110.11	149.76	92.06	23.30 23.23	—	$^1J_{C_5H_5} = 164.0$; $^3J_{C_5H_7} = 3.4$; $^1J_{CH_3} = 130.8$; $^1J_{CH_3} = 130.1$
8d		111.21	131.90	127.04	109.08	113.0	150.77	143.70	24.74 23.75	—	$^1J_{C_5H_5} = 165.4$; $^3J_{C_7H_5} = 5.9$; $^1J_{CH_3(A)} = 127.5$; $^1J_{CH_3(B)} = 132$

[a] Relative to internal $SiMe_4$; solvent $[^2H_6]Me_2SO$. [b] δ_{C_α} in the parent nitroalkanes:[18] 61.40 for CH_3NO_2; 70.8 for $CH_3CH_2NO_2$, 77.4 for $CH_3CH_2CH_2NO_2$, 79.10 for $(CH_3)_2CHNO_2$. [c] Values in parentheses represent tentative assignments for C-4 and C-8 (see text).

on previous reports of ^{13}C NMR data for various DNBF σ-adducts as well as J_{CH} values, irradiation experiments and J-modulation experiments, the ^{13}C chemical shifts listed in Table 2 were determined. In the case of **5c**, some ambiguities remain regarding the quaternary C-4 and C-8 carbons of both the major and minor adducts; the tentative assignments are therefore indicated in parentheses in Table 2.

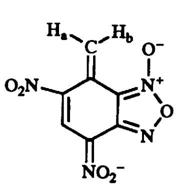
No evidence for an appreciable contribution of the *aci*-form **6** to the structure of the adducts **5a–c** could be obtained from the various ^{1}H and ^{13}C NMR spectra recorded in this work. Interestingly, we have succeeded in isolating **5a–d** as crystalline potassium salts. Dissolution of these salts in $[^2H_6]Me_2SO$ afforded NMR spectra which were identical to those recorded in the *in situ* generation of **5a–d** in this solvent. Also, these adducts exhibited a strong absorption maximum at $\lambda \approx 480$ nm, a wavelength typical for all C-bonded σ-adducts of DNBF in H_2O–Me_2SO mixtures. In addition, an X-ray analysis of the crystal structure of **5d,K**$^+$ was recently reported.[19] Structural features of adducts **5a–d** will be considered further in the discussion section.

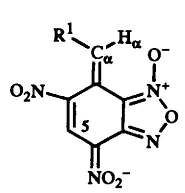
Base-catalysed decomposition of 5a–d. As outlined in eqn. (3), further ionization of the exocyclic moiety of **5a–c** might have reasonably occurred in the presence of excess base. However, no evidence for the formation of the dianions **7a–c** could be obtained upon addition of 1 equiv. of a strong base like MeO^- or a moderately strong base like $CF_3CH_2O^-$ or NEt_3 to Me_2SO solutions of **5a–c**. Instead, treatment of **5a** with MeO^- was found to produce a new set of resonances which was typical for the formation of the alkenic carbanion **8a** ($\delta_{H5} = 8.78$, $\delta_{Ha} = 6.60$, $\delta_{Hb} = 6.42$, $J_{HaHb} = 0.9$, $J_{Hb\text{-}H5} = 0.9$). Full assignment of this species was obtained from a sample prepared by direct ionization of 7-methyl-4,6-dinitrobenzofuroxan **9a**.[9] Owing to an extensive delocalization of the negative charge over the nitro groups and the furoxan ring, the exocyclic carbon of **8a** is essentially alkenic in nature, accounting for the observation of two non-equivalent methylene protons in the ^{1}H NMR spectra. As previously noted, the carbanion **8a** is not very stable, showing a strong tendency to dimerize in dimethyl sulfoxide as well as in aqueous solution.[9] Buncel and Menon have reported similar behaviour for carbanions derived from nitrotoluenes.[10]

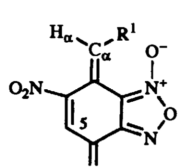


(3)

(4)


8a


(*E*)-8b, c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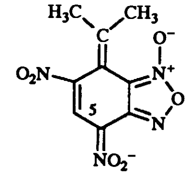
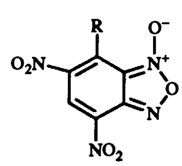

8d


9a–d

a R = Me, **b** R = Et, **c** R = Pr, **d** R = Pr^i

Table 3 Rate and equilibrium data for formation and decomposition of DNBF adducts in aqueous solution[a]

Incoming nucleophile	$pK_a^{H_2O}$	Adduct	$k_1/dm^3\ mol^{-1}\ s^{-1}$	k_{-1}/s^{-1}	$K_1/dm^3\ mol^{-1}$
$CH_2NO_2^-$	10.22[b,c]	**5a**	2.6×10^5	$\approx 4 \times 10^{-5}$	$\approx 6.5 \times 10^9$
$CH_3CH_2CHNO_2^-$	8.98[b]	**5c**	3.34×10^4	$< 10^{-6}$	$> 3.3 \times 10^{10}$
$CH_3CHNO_2^-$	8.60[b]	**5b**	2.67×10^4	$< 10^{-6}$	$> 2.6 \times 10^{10}$
$(CH_3)_2CNO_2^-$	7.74[b,c]	**5d**	2200	1.4×10^{-5}	1.57×10^8
$C_6H_5O^-$	9.95[d]	**20**[e]	1.27×10^4	≈ 1.6	≈ 7960
OH^-	15.74	**10**[f]	3.35×10^4	2.5×10^{-6}	1.78×10^{10}

[a] $T = 25$ °C, $I = 0.1$ mol dm^{-3} KCl. [b] Ref. 23. [c] Ref. 24. [d] Ref 25. [e] Unpublished results. [f] Ref. 2*a*.

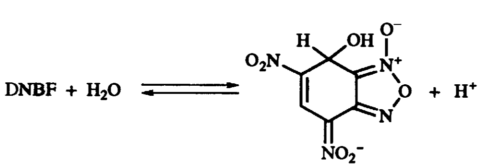
Although other extraneous and unidentified peaks were present in the initially acquired ^{1}H NMR spectra, essentially the reactions of the nitroethane and 1-nitropropane adducts **5b** and **5c** with MeO$^-$ or CF$_3$CH$_2$O$^-$ produced the signals attributable to formation of the isomeric carbanions (*E*)-**8b** and (*Z*)-**8b** or (*E*)-**8c** and (*Z*)-**8c**, respectively, in an approximately 3:2 ratio. In the 1-nitroethane system, the formation of (*E*)-**8b** and (*Z*)-**8b** was indicated by the observation of two similar sets of resonances, each of them consisting of a singlet at δ 8.59 or 8.46 (5-H), a quadruplet at δ 6.85 ($J_{H\alpha CH_3} = 7.8$) or 6.74 ($J_{H\alpha CH_3} = 7.8$) and a doublet at δ 1.88 ($J_{H\alpha CH_3} = 7.8$) or 1.61 ($J_{H\alpha CH_3} = 7.8$) whose relative intensities were in a 1:1:3 ratio. Interestingly, we observed that the α-H and 5-H resonances for the major species were slightly broadened, implying the existence of a weak long range $^5J_{HH}$ coupling. Although this coupling could not be fully resolved, its observation was very important because it is known to be highly stereospecific and typical for a situation where the intervening bonds take up a coplanar zig-zag arrangement.[11–13] On this basis, we have attributed the first set of resonances to the *E* isomer, **8b**, which formed as the major species. In the 1-nitropropane system, the formation of the carbanions (*E*)-**8c** and (*Z*)-**8c** was reflected by two sets of resonances consisting of a singlet at δ 8.60 or 8.45, a triplet at 6.74 ($J_{H\alpha CH_2} = 7.6$) or 6.59 ($J_{H\alpha CH_2} = 7.3$), a quintuplet-like multiplet at 2.26 ($J_{H\alpha CH_2} = 7.6$, $J_{CH_2CH_3} = 7.6$) or 1.92 ($J_{H\alpha CH_2} = 7.3$, $J_{CH_2CH_3} = 7.3$) and a triplet at 1.02 ($J_{CH_2CH_3} = 7.6$) or 0.98 ($J_{CH_2CH_3} = 7.3$). As expected, the triplets for the α-H and methyl protons were converted to singlets upon irradiation of the CH$_2$ signals, thus allowing a definitive assignment of the δ and *J* values for the two isomers. Again, the major species was identified as the isomer (*E*)-**8c** on the basis of the observation of an unresolved $^5J_{HH}$ coupling.

Study of the reaction of the 2-nitropropane adduct **5d**, which has no ionizable exocyclic proton, with 1 equiv. of potassium methoxide or potassium trifluoroethoxide gave support to our observation that adducts of the type **5** are very prone to base-catalysed β-elimination of nitrous acid. In this instance, clean formation of the relatively stable carbanion **8d** was initially observed, allowing us to record a ^{13}C NMR spectrum. Consistent with the alkenic structure **8d** are the strong downfield shifts suffered by C-7 and C-α on going from **5d** to **8d** as well as the non-equivalence of the two methyl carbons (Table 2).

In a direct study of the acid–base behaviour of **9a**, we found it very difficult to recover this carbon acid upon acidification of Me$_2$SO solutions of its conjugate carbanion **8a** by strong acids.[9] Attempts to isolate the 7-alkyl-4,6-dinitrobenzofuroxans **9a–d** from Me$_2$SO solutions of the corresponding carbanions **8a–d** generated from base decomposition of **5a–d** have similarly failed, complicated mixtures of unidentified products being obtained in all cases. So far, our numerous efforts to understand this behaviour remain unsuccessful, even though it is reasonable to assume that protonation occurs rapidly at the 4- or 6-NO$_2$ groups of **8a–d** to give nitronic acids. Very often such species are unstable, showing a high tendency to decompose *via* different pathways.[1,14–17]

Kinetic studies

Taking advantage of the four nitroalkanes that have $pK_a^{H_2O}$ values consistent with essentially complete ionization by the hydroxide ion (see Table 3), the reactions of DNBF with carbanions **4a–d** according to eqn. (2), were kinetically studied at 25 °C in aqueous buffer solutions made up from these carbon acid themselves. In order to avoid any interference between eqn. (2) and (5), a $pK_a^{H_2O}$ value of 3.73 has been reported for



(5)

10

formation of the hydroxide adduct **10** at 25 °C in aqueous solution,[2a] experiments were carried out using stopped-flow spectrophotometry by mixing 5×10^{-3} or 0.01 mol dm^{-3} HCl solutions of DNBF (*ca.* 3×10^{-5} mol dm^{-3}) with equal volumes of freshly prepared solutions of nitroalkanes and KOH made up so as to obtain the desired final nitroalkane ion concentration at constant pH, *i.e.* at a given [R^{1}R^{2}CNO$_2^-$]:[R^{1}R^{2}CHNO$_2$] ratio. The ionic strength of the solutions was kept constant at 0.1 mol dm^{-3} KCl. Because of the relatively low solubility of the carbon acids, only buffer solutions with final nitroalkane anion concentrations in the range (0.5–8 $\times 10^{-3}$ mol dm^{-3}) could be used. These concentrations were controlled by titration with standardized acid. In all experiments, only one relaxation time corresponding to the formation of the adducts **5a–d** ($\lambda_{max} \approx 480$ nm) was observed.

Based on eqn. (2) and the experimental conditions employed, the general expression for the observed first-order rate constant, k_{obsd}, for formation of **5a–d** is given by eqn. (6).

$$k_{obsd} = k_1[R^1R^2CNO_2^-] + k_{-1} \qquad (6)$$

Tables 4 and 5 summarize the k_{obsd} values obtained at different R^{1}R^{2}CNO$_2^-$ concentrations and different pH for the four reactions studied. In accordance with eqn. (6), excellent straight lines with essentially negligible intercepts were obtained in all systems on plotting k_{obsd} *vs.* the nitroalkane anion concentration. Moreover, no evidence for a pH dependence of the rates was observed (Figs. 1 and 2), confirming the total absence of reaction (5). Determination of the second-order rate constants, k_1, from the slopes of the k_{obsd} *vs.* [R^{1}R^{2}CNO$_2^-$] plots was therefore straightforward.

Since the k_{-1} values were too low to be obtained from the intercepts, attempts to study directly the decomposition of **5a–d** were made by taking advantage of the isolation of these adducts as potassium salts. Experiments were carried out under pseudo-first-order conditions by monitoring the decrease in absorbance of **5a–d** ($\approx 3 \times 10^{-5}$ mol dm^{-3}) at λ_{max} in various aqueous HCl

Table 4 Kinetic data for reactions of DNBF with nitromethane and nitroethane anions in aqueous solution at $T = 25$ °C[a]

$[R_1R_2CNO_2^-]$/ 10^{-4} mol dm^{-3}	$R^1 = R^2 = H$			$R^1 = H, R^2 = CH_3$		
	k_{obsd}/s^{-1}			k_{obsd}/s^{-1}		
	pH = 10.22[b]	pH = 9.74[c]	pH = 10.52[d]	pH = 8.60[b]	pH = 8.12[c]	pH = 8.90[d]
5	135	127	—	12.8	13	—
6	—	—	170	16.8	15	14.5
6.5	170	176	—	—	—	—
7.5	—	—	—	20.1	21.2	—
8	205	210	215	—	—	22.5
9	—	—	—	22.8	24	—
10	245	270	255	26.8	27.4	26.5
12	305	330	315	31.9	29.6	34
15	400	390	370	40.1	42	40

[a] $I = 0.1$ mol dm^{-3} KCl. [b] 1:1 Buffer. [c] 1:3 Buffer. [d] 2:1 Buffer.

Table 5 Kinetic data for reactions of DNBF with 1-nitropropane and 2-nitropropane anions in aqueous solution at $T = 25$ °C[a]

$[R_1R_2CNO_2^-]$/ 10^{-3} mol dm^{-3}	$R^1 = H, R^2 = CH_2CH_3$			$R^1 = R^2 = CH_3$		
	k_{obsd}/s^{-1}			k_{obsd}/s^{-1}		
	pH = 8.98[b]	pH = 8.50[c]	pH = 9.28[d]	pH = 7.74[b]	pH = 7.26[c]	pH = 8.04[d]
0.5	—	—	—	1.1	1.35	—
0.8	—	—	—	—	—	1.8
0.9	—	28	—	—	1.9	—
1	36	—	30	2.2	—	2
1.2	—	—	—	—	2.6	—
1.5	55	55	—	3.2	3.3	—
1.8	—	—	64	—	3.9	—
2	66	70	71	4.4	—	4.3
2.2	71	—	—	—	4.8	—
2.5	—	—	—	5.4	—	5.7
3	108	100	100	—	6.6	6.85
3.5	—	—	—	7.7	—	—
4	—	135	135	8.9	—	8.4
5	176	—	165			
6	—	—	204			
7	240		—			
8	276		265			

[a] $I = 0.1$ mol dm^{-3} KCl. [b] 1:1 Buffer. [c] 1:3 Buffer. [d] 2:1 Buffer.

Table 6 Observed rate constants k_{obsd} for decomposition of the adducts **5a** and **5d** in aqueous HCl solutions[a]

$[H^+]$/mol dm^{-3}	$k_{obsd}^{5a}/10^{-5}$ s^{-1}	$k_{obsd}^{5d}/10^{-5}$ s^{-1}
0.01	3.5	1.4
0.02	5	2
0.04	4	1.4
0.06	4	1.4
0.08	3.8	—
0.10	4.4	1.4

[a] $T = 25$ °C; $I = 0.1$ mol dm^{-3} KCl.

solutions (0.01–0.1 mol dm^{-3}), keeping the ionic strength constant at 0.1 mol dm^{-3} with KCl. Table 6 summarizes the rate data obtained for the recovery of DNBF from the nitromethane and 2-nitropropane adducts. As can be seen, this process was extremely slow and showed no susceptibility to H^+ catalysis, indicating that only the non-catalysed pathway corresponding to the first-order rate constant k_{-1} is operating, *i.e.* $k_{obsd} = k_{-1}$. We thus readily determine $k_{-1} = 4 \times 10^{-5}$ s^{-1} for **5a** and 1.4×10^{-5} s^{-1} for **5d**. After combination of these values with the corresponding k_1 values, the K_1 values given in Table 3 were obtained. In the case of the nitroethane and 1-nitropropane adducts, no appreciable decomposition was observed even after two days, suggesting very low k_{-1} values ($< 10^{-6}$ s^{-1}).

Discussion

Structures of the adducts

^{1}H and ^{13}C NMR chemical shifts of the DNBF–nitroalkane adducts **5a–d** (Tables 1 and 2) agree well with the proposed structures. In accord with previous observations that the bonded exocyclic moiety at C-7 has very little effect on the position located between the two nitro groups of the negatively charged DNBF structure, the chemical shifts of 5-H and C-5 compare well with analogous data reported for many DNBF adducts.[3–5,7,8] On the other hand, all the 7-H and C-7 resonances are typical for DNBF C-adducts. Regarding the exocyclic moiety, the C-α resonance appears to be typical for an sp^3 carbon bonded to an NO_2 group, thus ruling out the *aci*-structures **6a–d**.[18] However, a comparison of the data for **5a–d** with those for the parent nitroalkanes (see footnote *b* in Table 2) shows that the presence of the adjacent DNBF structure causes a notable shift of this resonance to a low field, *e.g.* $\delta_{C\alpha} = 71.59$ in **5a**; $\delta_{C\alpha} = 61.40$ in CH_3NO_2. This result is in agreement with previous evidence that a negatively charged DNBF structure still exerts a considerable −I effect.[1,2]

The NMR parameters of Table 1 also allow some specul-

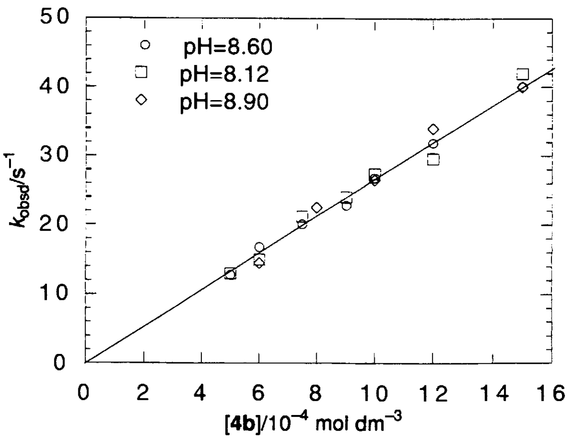


Fig. 1 Effect of the nitroethane anion concentration and pH on the observed rate constant (k_{obsd}) for formation of the adduct **5b** in aqueous solution: t = 25 °C, I = 0.1 mol dm^{-3} KCl

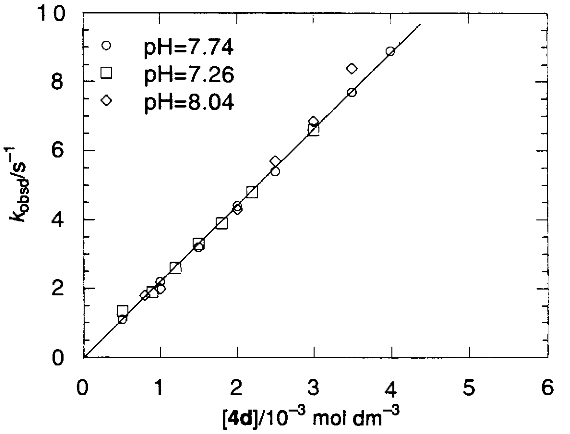
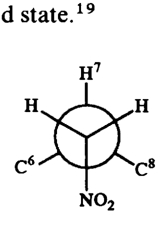


Fig. 2 Effect of the 2-nitropropane anion concentration and pH on the observed rate constant (k_{obsd}) for formation of the adduct **5d** in aqueous solution: t = 25 °C, I = 0.1 mol dm^{-3} KCl

ation about the preferred conformations of the adducts in solution. In the case of the nitromethane adduct **5a**, the two vicinal coupling constants $^3J_{AC}$ and $^3J_{BC}$ are equal to 4.0 and 3.0 Hz, respectively. In as much as there is no major difference in the neighbourhood of the C-6 and C-8 carbons (they are bonded to an NO_2 group and an annelated -N(O)O- structure, respectively) the similarity of $^3J_{AC}$ and $^3J_{BC}$ suggests that the dihedral angles H_A–C_α–C_7–H_C and H_B–C_α–C_7–H_C are close to 60° or 120°. This favours the bisected conformation **11**. Based on the nearly identical chemical shifts found for the two non-equivalent methyl groups of **5d**, this conformation would also prevail in the case of the 2-nitropropane adduct (structure **12**). Interestingly, the X-ray analysis of the structure of the potassium salt of **5d** has revealed that it is the conformation **13** with the hydrogen and nitro substituents at C-7 and C-α, respectively, in a *cis*-configuration, which is favoured in the solid state.[19]



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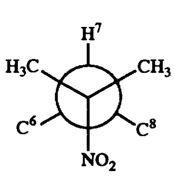

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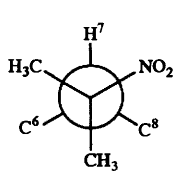

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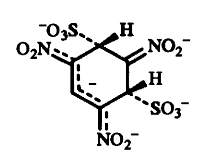

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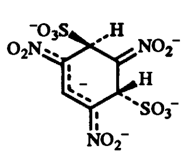

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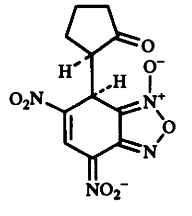

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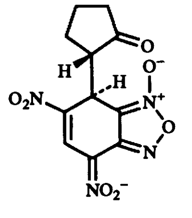

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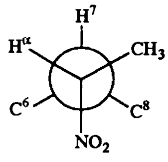
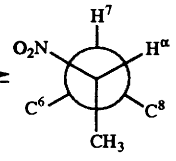
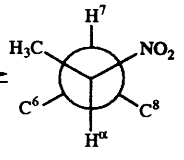
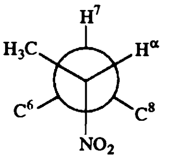
In contrast with the situation for 1 : 2 di-adducts where the formation of diastereoisomeric species, *e.g.* **14** and **15**, is well documented,[1,20,21] the observation of diastereoisomerism is not a common feature in 1 : 1 mono-adduct formation.[1,7,22] Accordingly, our finding that the nitroethane and nitropropane adducts **5b** and **5c** form as a mixture of two diastereoisomers (**5b**$_1$, **5b**$_2$, or **5c**$_2$, **5c**$_2$) is a noteworthy result. Only in the case of the DNBF–cyclopentanone system, was coupling of chirality at the tetrahedral anionic ring carbon and the sp^3 C-α of the bonded nucleophilic moiety previously found to result in the formation of diastereoisomeric adducts, *e.g.* **16** and **17**.[7]

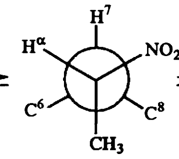


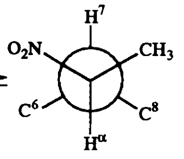




18a **18b** **18c**





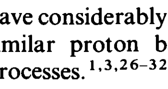


19a **19b** **19c**

The most reasonable conformations for the two diastereoisomeric species which form in a 3 : 2 ratio in the 1-nitroethane–DNBF system are shown as the staggered structures **18a–c** and **19a–c**, respectively (only one enantiomer for each is considered). In this system, the $^3J_{H_\alpha H_7}$ coupling constants found for the major (M) and minor (m) species are equal to 2.3 and 2.5 Hz, respectively. Such values imply H_α–C_α–C_7–H_7 dihedral angles of the order of < 60°, indicating that structures **18a**, **18b** or **19a**, **19b** must be largely favoured compared with **18c** or **19c**. The observation that the α-H chemical shifts of M and m are comparable ($\delta^{M}_{H_\alpha}$ = 5.07, $\delta^{m}_{H_\alpha}$ = 5.06) and close to those found for the α-H of the nitromethane adduct supports this proposal. On the other hand, the methyl resonance of M (δ_{Me} = 1.44), but not that of m (δ_{Me} = 1.26), compares well with that for the 2-nitropropane adduct (δ_{Me_1} = 1.49, δ_{Me_2} = 1.51). This leads to either **18a** or **19a** as the preferred conformation for M and therefore **18b** or **19b** as the preferred conformation for m. Interestingly, structures **18a** and **19a** seem also consistent with the finding that the chemical shift of 7-H of M (δ_{H_7} = 5.14) is intermediate between those found for the analogous protons of **5a** (δ_{H_7} = 5.03) and **5d** (δ_{H_7} = 5.27).

Similarly, the closer proximity of the 7-H and NO_2 groups in structures **18b** or **19b** may account for the observed downfield shift of the 7-H resonance for m (δ_{H_7} = 5.39). At this stage, it is difficult to definitively assign the preferred conformations for M and m, but examination of molecular models suggests **19a** and **18b**, respectively. In as much as twisting out of the plane of the rings is possible for the NO_2 group at C-6, but not for the annelated-N(O)O-functionality at C-8, less steric compression is expected in **19a** and **18b** where the exocyclic methyl and nitro groups are located in the vicinity of C-6.

Stability and rates of formation of 5a–d. Rate and equilibrium data for formation of the nitroalkane adducts **5a–d** are collected in Table 3 where they are compared with analogous data for formation of the related phenoxide and hydroxide adducts, **20** and **10**. Although their basicity is close to or lower than that of $C_6H_5O^-$,[23–25] the four nitroalkane anions **4a–d** add to DNBF in forming σ-adducts which are considerably more stable than the oxygen-bonded aryloxide adduct **20**. In fact, the stability of **5a–d** is of the same order as that of the hydroxide adduct **10**. However, OH^- is 3 × 10^5–10^8 times more basic than the carbanions **4a–d**. These results are consistent with other observations showing that carbon bases have considerably higher carbon basicities than oxygen bases of similar proton basicities, especially in σ-adduct formation processes.[1,3,26–32] In this respect, it is noteworthy that Crampton and co-workers have recently reported on the reactions of 1,3,5-trinitrobenzene (TNB) (the common reference aromatic electrophile) with carbanions **4a**, **4b** and **4d** in methanol.[26] In these instances, the resulting σ-adducts **21a**, **21b** and **21d** have stabilities comparable to or higher by one to three orders of magnitude than that of the methoxide complex **22** in methanol. Interestingly, values of K_1 for formation of **21a**, **b**, **d** are 10^5–10^8 times smaller than the corresponding K_1 values for the DNBF adducts **5a**, **b**, **d**. Such differences are too large to be accounted for on the simple basis of changing the solvent from water to methanol. Then, there is no doubt that they reflect the exceptional ability of DNBF to undergo σ-complexation with relatively weak nucleophiles.



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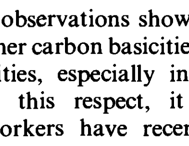

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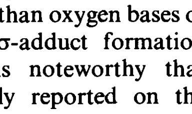

22

a $R^1 = R^2 = H$

b $R^1 = H, R^1 = CH_3$

d $R^1 = R^2 = CH_3$

In view of the similarity of the $pK_a^{H_2O}$'s of the two incoming nucleophiles, a comparison of the rate parameters for formation and decomposition of the nitromethane and phenoxide adducts **5a** and **20** is of interest for understanding the thermodynamic affinity of DNBF for carbon bases **4a–d**. Table 3 shows clearly that the higher stability of **5a** derives for the most part from the low rate for its uncatalysed decomposition: the ratio k **20**/-1:k **5a**/-1 is equal to *ca.* 4 × 10^4, compared with a k **5a**/1:k **20**/1 ratio of 20. As it is well known, nitroalkane anions exist essentially as strongly solvated nitronate anions (structures **4′a–d**) in polar solvents like water or methanol.[33,34] Accordingly, decomposition of the adducts **5a–d** requires both C–C bond cleavage and concomitant carbon rehybridization from sp^3 to sp^2 as well as substantial solvent reorganization. Such phenomena are energetically very costly, accounting for the low k_{-1} values measured for the spontaneous decomposition of **5a–d**. Such a considerable structure–electronic reorganization is not required for departure of an oxyanion, in agreement with the finding of a much higher nucleofugality of the aryloxide group.

$$\underset{\textbf{4a–d}}{R^1R^2C^{-}\text{–}NO_2} \longleftrightarrow \underset{\textbf{4′a–d}}{R^1R^2C{=}NO_2^{-}}$$

Interestingly, the phenomena responsible for the low departing ability of $CR_1R_2NO_2^-$ anions are the same as those commonly invoked to explain the low rates of nitroalkane deprotonation and nitronate anion reprotonation.[33–36] The low k_{-1} values for decomposition of **5a–d** may therefore be taken as evidence that nitroalkane anions exhibit low intrinsic reactivities in σ-adduct forming reactions as they do in proton transfer reactions. This conclusion agrees with recent reports by Crampton and co-workers who were able to determine the intrinsic reactivities of nitromethane and nitroethane anions as well as of a number of cyanocarbanions in σ-complexation reactions at an unsubstituted carbon of various 1-X-2,4,6-trinitrobenzenes in methanol.[26,28a] The reported log k_0 values are equal to −0.65 and −0.72 for $CH_2NO_2^-$ and $CH_3CHNO_2^-$ anions, respectively, but of +4.4 for the malonitrile $CH(CN)_2^-$ ion.[26,28a] The latter has the same Brønsted basicity as the $CH_2NO_2^-$ ion, but due to the low resonance capability of a CN group[34,37,38] it has more of the character of a true carbanion requiring less reorganization during reaction and higher reactivity. The observed trend in C–C coupling reactions is therefore the same as in proton transfer reactions.

Based on the finding of essentially similar log k_0 values for nitromethane and nitroethane addition to TNB derivatives, it seems reasonable to assume that the energetics of the structural and solvational reorganization will affect similarly the reactivity of all simple nitroalkane anions in a given σ-complexation process. Interestingly, our k_1 values for formation of the adducts **5a–d** increase regularly with increasing basicity of the nitrocarbanion. An approximate Brønsted line (not shown) with a slope, $\beta_{Nu} \approx 0.75$, can actually be drawn using the four available points, thus supporting the above assumption.

However, it has to be noted that the intrinsic reactivity arguments developed above in the light of the comparison of the k_{-1} values for decomposition of the adducts **5a** and **20** normally imply that the rate constant for DNBF complexation by phenoxide ion will be somewhat greater than that by the nitromethane ion, which is not borne out by the experimental results: k **5a**/1:k **20**/1 = 20.‡ We believe that a reasonable explanation for this conflicting result is that the decomposition pathway for the phenoxide adduct **20** does not represent the microscopic reverse of the complexation step. Thus, there is presently ample evidence that strongly basic and therefore strongly hydrogen bond solvated oxyanions like OH^-, phenoxide or oximate ions, must suffer desolvation prior to bond formation in many nucleophilic addition, substitution or ionization processes.[34,39,40] This desolvation requirement is commonly reflected in important decreases in intrinsic reactivity[26,28,34–36] and there is little doubt that this factor may be responsible for the lower k_1 values found for formation of the phenoxide and hydroxide adducts **20** and **10**, respectively, compared with that for formation of the nitromethane adduct **5a**. Hence, the transition state for the rate-limiting addition of the desolvated $C_6H_5O^-$ ion may be visualized as **23** (R = C_6H_5). On the other hand, it has been found that the non-catalysed decomposition of many oxygen-bonded σ-adducts in aqueous solution is not a unimolecular process proceeding

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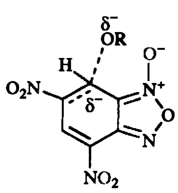
‡ We are grateful to a referee for this comment.



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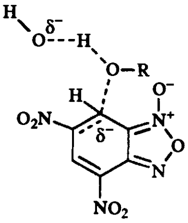

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through a transition state of type **23** ($R = H$), but a bimolecular reaction involving the transition state **24**, in which a water molecule acts as a general acid catalyst.[1,41] If one assumes that the decomposition of the phenoxide adduct **20** is better described by **24** ($R = C_6H_5$) than by **23** ($R = C_6H_5$), the anomalies observed in the respective magnitudes of the k **5a**/-1:k **20**/-1 and k **5a**/1:k **20**/1 ratios may then be rationalized.

Elimination of nitrous acid from 5a–d

Even though the failure to reprotonate the resulting carbanion makes it presently of little synthetic interest, the high susceptibility of **5a–d** to suffer loss of nitrous acid in basic solutions is a significant result. In general, the NO_2 group is not a good leaving group in base-induced β-eliminations, being only capable of departing when there is a strong electron-withdrawing group in the β-position.[42–50] On this basis, the facile elimination of HNO_2 from **5a–d** provides strong evidence that a negatively charged DNBF moiety still acts as a powerful electron-withdrawing ($-I$) functionality. This conclusion is consistent with our previous observation that the OH group of the hydroxy adduct **10** undergoes ionization in dilute aqueous hydroxide solutions ($pK_a^{H_2O} = 11.30$).[2a]

In as much as it results in sp^2-rehybridization of the C-7 carbon of the carbocyclic ring, the formation of the alkenic carbanions **8a–d** also constitutes a rare example of a nucleophilic heteroaromatic substitution of a hydrogen atom which is assisted by the departure of a vicarious nitro group. Following the initial discovery of the process by Makosza and Winiarski,[51] many vicarious nucleophilic aromatic substitutions of hydrogen have been reported, but they involve in general more efficient leaving groups (Cl, Br, RO, RS) than an NO_2 group.[52–54]

Considering the strong acidifying $-I$ effect exerted by the $DNBF^-$ moiety, one can reasonably postulate that the elimination of HNO_2 occurs either *via* a carbanionic E1cB mechanism involving initial breaking of the C-7–H bond or *via* a concerted E_2 mechanism involving a transition state of considerable anionic character.[55–60] In contrast, the results obtained did not allow us to draw reliable conclusions regarding the *anti* and/or *syn* stereochemistry of the elimination reaction, even in the case of the formation of the carbanions **8a** and **8d** which are not subject to Z and E isomerism.[61–64]

Experimental

Materials

4,6-Dinitrobenzofuroxan was prepared according to the procedure of Drost:[65] mp 172 °C (lit., 172–174.5 °C).[3,4b,6] Nitromethane, nitroethane, 1-nitropropane and 2-nitropropane were purified according to standard procedures.

Adducts **5a–d** were prepared as crystalline potassium salts as follows. To 0.226 g (1 mmol dm^{-3}) of DNBF dissolved in the parent nitroalkane (*ca.* 2 cm^3) was added whilst stirring 1 equiv. of the corresponding potassium nitroalkenide salt suspended in the same solvent (5 cm^3). After 5 min, the resulting red–orange precipitates were filtered, washed with diethyl ether and dried under reduced pressure to give the salts **5a–d,K**$^+$ in good yields (*ca.* 80%). With the exception of **5a,K**$^+$, these salts were very stable in air, but they all decompose upon heating (*ca.* 155–175 °C). As it is the case for most σ-adducts of DNBF isolated as crystalline alkali salts, attempts to obtain satisfactory elemental analysis for **5a–d,K**$^+$ have failed. In contrast, an X-ray structure of **5d,K**$^+$ could be made[19] and ^1H and ^{13}C NMR spectra consistent with the structure of the adducts were obtained (*vide supra*). Satisfactory mass spectra were also obtained (ESI), base peaks corresponding to the loss of K^+ being observed (*e.g.* $m/z = 314$ for **5d,K**$^+$) with no detection of the pseudo-molecular ions.

NMR and UV–VIS measurements

^1H and ^{13}C NMR spectra were recorded on a Bruker AC 300 spectrometer. Chemical shifts were measured relative to the solvent $[^2H_6]Me_2SO$ and converted into the TMS scale ($\delta_H = 2.50$, $\delta_C = 3.95$). They were generated *in situ* by adding an equimolar amount of nitroalkenide ion to $[^2H_6]Me_2SO$ solutions of DNBF (*ca.* 0.2 mol dm^{-3}) or introduced directly in the form of potassium salts in this solvent. The adducts **5a–d** show a high stability, making it possible to obtain well resolved ^1H and noise proton-decoupled, as well as proton-coupled ^{13}C NMR spectra. In the case of the carbanions **8a–d** which have a notable tendency to decompose in basic media, satisfactory ^1H NMR spectra were also obtained. In contrast, proton-coupled ^{13}C NMR spectra, which require longer acquisition times, could only be recorded for **8d**.

All visible spectra of **5a–d** exhibited a strong absorption maximum at $\lambda = 480$–490 nm in H_2O–Me_2SO mixtures. These wavelengths are typical for C-bonded σ-adducts in these media.

Kinetic measurements

Stopped-flow determination of the rates of reaction (2) in aqueous solution were performed on a Durrum stopped-flow spectrophotometer the cell compartment of which was maintained at 25 ± 0.2 °C. A conventional Kontron-Uvikon spectrophotometer was also used to follow the slow decomposition process of the adducts **5a–d**. All kinetic runs were carried out in triplicate under pseudo-first-order conditions with a large excess of the nitroalkenide, H^+ or water reagents over the DNBF or adduct concentration (*ca.* 3×10^{-5} mol dm^{-3}). The ionic strength was kept constant at $I = 0.1$ mol dm^{-3} with KCl. In a given stopped-flow experiment at constant pH, excellent reproducibility of the rates (±2%) was generally obtained. When studying the formation of **5a–d**, the visible absorption spectra of the final solutions were in all cases identical to those recorded by dissolving samples of the isolated potassium salts of these adducts (*vide supra*) in aqueous solution.

Acknowledgements

We are grateful to Chantal Robert-Labarre for assistance in NMR spectroscopy and to Dr. Jean-Michel Cense for the simulation of some NMR spectra.

References

1 (*a*) F. Terrier, in *Nucleophilic Aromatic Displacement*, ed. H. Feuer, VCH, New York, 1991, pp. 18 and 138; (*b*) E. Buncel, M. R. Crampton, M. J. Strauss and F. Terrier in *Electron-Deficient Aromatic and Heteroaromatic Base Interactions*, Elsevier, Amsterdam, 1984, pp. 166 and 296; (*c*) F. Terrier, *Chem. Rev.*, 1982, **82**, 77.

2 (*a*) F. Terrier, F. Millot and W. P. Norris, *J. Am. Chem. Soc.*, 1976, **98**, 5883; (*b*) F. Terrier, A. P. Chatrousse, Y. Soudais and M. Hlaibi, *J. Org. Chem.*, 1984, **49**, 4176.

3 (*a*) M. J. Strauss, R. A. Renfrow and E. Buncel, *J. Am. Chem. Soc.*, 1983, **105**, 1555; (*b*) E. Buncel, R. A. Renfrow and M. J. Strauss, *J. Org. Chem.*, 1987, **52**, 488.

4 (*a*) R. J. Spear, W. P. Norris and R. W. Read, *Tetrahedron Lett.*, 1983, **24**, 1555; (*b*) W. P. Norris, R. J. Spear and R. W. Read, *Aust. J. Chem.*, 1983, **36**, 297.

5 (*a*) J. C. Hallé, M. P. Simonnin, M. J. Pouet and F. Terrier, *Tetrahedron Lett.*, 1985, **26**, 1307; (*b*) F. Terrier, J. C. Hallé, M. P. Simonnin and M. J. Pouet, *J. Org. Chem.*, 1984, **49**, 4363; (*c*) J. C. Hallé, M. P. Simonnin, M. J. Pouet and F. Terrier, *Tetrahedron Lett.*, 1983, **24**, 2255.

6 (*a*) J. Kind and H. J. Niclas, *Synth. Commun.*, 1993, **23**, 1569; (*b*) H. J. Niclas, B. Göhrmann and E. Gründemann, *Synth. Commun.*, 1991, **333**, 909; (*c*) B. Göhrmann and H. J. Niclas, *J. Prakt. Chem.*, 1989, **331**, 819; (*d*) H. J. Niclas, J. Kind and M. Ramm, *J. Prakt. Chem.*, 1991, **333**, 909.

7 F. Terrier, M. P. Simonnin, M. J. Pouet and M. J. Strauss, *J. Org. Chem.*, 1981, **46**, 3537.

8 (*a*) F. Terrier, E. Kizilian, J. C. Hallé and E. Buncel, *J. Am. Chem. Soc.*, 1992, **114**, 1740; (*b*) F. Terrier, M. J. Pouet, J. C. Hallé, S. Hunt, J. R. Jones and E. Buncel, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1665.

9 F. Terrier, D. Croisat, A. P. Chatrousse, M. J. Pouet, J. C. Hallé and G. Jacobs, *J. Org. Chem.*, 1992, **57**, 3684.

10 E. Buncel and B. C. Menon, *J. Am. Chem. Soc.*, 1980, **102**, 3499.

11 R. Wasylishen and T. Schaefer, *Can. J. Chem.*, 1971, **49**, 3216.

12 (*a*) W. Danchura, T. Schaefer, J. B. Rowbotham and D. J. Wood, *Can. J. Chem.*, 1974, **52**, 3986; (*b*) J. B. Rowbotham, A. F. Janzen, J. Peeling and T. Schaefer, *Can. J. Chem.*, 1974, **52**, 481.

13 M. P. Simonnin, H. Q. Xie, F. Terrier, J. Lelièvre and P. G. Farrell, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1553.

14 (*a*) C. Möberg and O. Wennerstrom, *Acta Chem. Scand.*, 1971, **25**, 2355; (*b*) O. Wennerström, *Acta Chem. Scand.*, 1971, **25**, 2341.

15 (*a*) C. Bjorklund, M. Nilsson and O. Wennerström, *Acta Chem. Scand.*, 1970, **24**, 3599; (*b*) C. Möberg and O. Wennerström, *Acta Chem. Scand.*, 1971, **25**, 2871.

16 In Ref. 1*b*, pp. 433–438.

17 R. A. Manderville and E. Buncel, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1887.

18 A. Ejchardt, *Org. Magn. Res.*, 1977, **10**, 263.

19 F. Terrier, J. Lelièvre, A. P. Chatrousse, T. Boubaker, B. Bachet and A. Cousson, *J. Chem. Soc., Perkin Trans. 2*, 1992, 361.

20 (*a*) C. F. Bernasconi and R. G. Bergström, *J. Am. Chem. Soc.*, 1973, **95**, 3603; (*b*) M. J. Strauss and S. B. Taylor, *J. Am. Chem. Soc.*, 1973, **95**, 3813.

21 (*a*) J. A. Chudek and R. A. Foster, *J. Chem. Soc., Perkin Trans. 2*, 1979, 628; (*b*) J. A. Chudek, R. A. Ellingham and R. Foster, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1477.

22 M. J. Strauss, A. de Fusco and F. Terrier, *Tetrahedron Lett.*, 1981, **22**, 1845.

23 (*a*) D. Turnbull and S. Maron, *J. Am. Chem. Soc.*, 1943, **65**, 212; (*b*) G. W. Wheland and J. Farr, *J. Am. Chem. Soc.*, 1943, **65**, 1433.

24 J. R. Jones, in *The Ionization of Carbon Acids*, Academic Press, London and New York, 1973.

25 A. Albert and E. P. Serjeant in *Ionization Constants of Acids and Bases*, Wiley, New York, 1962.

26 J. P. L. Cox, M. R. Crampton and P. Wight, *J. Chem. Soc., Perkin Trans. 2*, 1988, 25.

27 C. F. Bernasconi, *J. Am. Chem. Soc.*, 1970, **92**, 4682.

28 (*a*) M. R. Crampton and J. A. Stevens, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1715; (*b*) J. H. Atherton, M. R. Crampton, G. L. Duffield and J. A. Stevens, *J. Chem. Soc., Perkin Trans. 2*, in the press.

29 J. Hine and R. D. Weimer, *J. Am. Chem. Soc.*, 1965, **87**, 3387.

30 I. Kolb, V. Machacek and V. Sterba, *Collect. Czech. Chem. Commun.*, 1976, **41**, 1914.

31 F. Terrier, E. Kizilian, M. J. Pouet, J. C. Hallé, F. Outurquin and C. Paulmier, *J. Org. Chem.*, 1993, **58**, 4696.

32 C. F. Bernasconi, K. A. Howard and A. Kanavarioti, *J. Am. Chem. Soc.*, 1984, **106**, 6827.

33 (*a*) F. G. Bordwell and W. J. Boyle, *J. Am. Chem. Soc.*, 1972, **94**, 3907; (*b*) 1975, **97**, 3447.

34 C. F. Bernasconi, *Adv. Phys. Org. Chem.*, 1992, **27**, 119.

35 F. G. Bordwell, J. E. Bartmess and J. A. Hautala, *J. Org. Chem.*, 1978, **43**, 3107.

36 C. F. Bernasconi, D. A. V. Kliner, A. S. Mullin and J. X. Ni, *J. Org. Chem.*, 1988, **53**, 3342.

37 S. Bradamante and G. A. Pagani, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1036.

38 (*a*) F. Aiken, B. G. Cox and P. E. Sorensen, *J. Chem. Soc., Perkin Trans. 2*, 1993, 783; (*b*) W. H. Saunders and J. E. Van Verth, 12th IUPAC Conference on Physical Organic Chemistry, Padova, 1994.

39 (*a*) F. Terrier, G. Moutiers, L. Xiao, E. LeGuevel and F. Guir, *J. Org. Chem.*, 1995, **60**, 1748; (*b*) F. Terrier, P. MacCormack, E. Kizilian, J. C. Hallé, P. Demerseman, F. Guir and C. Lion, *J. Chem. Soc., Perkin Trans. 2*, 1991, 153.

40 W. P. Jencks, S. R. Brant, J. R. Gandler, G. Friedrich and C. Nakamura, *J. Am. Chem. Soc.*, 1982, **104**, 7045 and references therein.

41 G. Ah-Kow, F. Terrier and F. Lessard, *J. Org. Chem.*, 1978, **43**, 3578.

42 N. Ono, in *Nitro Compounds. Recent Advances in Synthesis and Chemistry*, eds. H. Feuer and A. T. Nielsen, VCH, 1990, ch. 1, pp. 86–110.

43 J. W. Patterson and J. E. McMurry, *J. Chem. Soc., Chem. Commun.*, 1971, 488.

44 D. Seebach, M. S. Hoekstra and G. Protschuk, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 321.

45 G. Bartoli, *Acc. Chem. Res.*, 1984, **17**, 109.

46 (*a*) N. Ono, H. Miyake, R. Tanikaga and A. Kaji, *J. Org. Chem.*, 1982, **45**, 5017; (*b*) N. Ono, R. Tamura, H. Eto, I. Hamamoto, T. Nakatsuka, J. Hayami and A. Kaji, *J. Org. Chem.*, 1983, **48**, 3678; (*c*) N. Ono, A. Kanimmura, S. Kawai and A. Kaji, *Nippon Kagaku Kaishi*, 1987, 1338.

47 D. Seebach, R. Hemming and T. Makhopadkyay, *Chem. Ber.*, 1982, **115**, 1705.

48 C. D. Weis and G. R. Newkome, *J. Org. Chem.*, 1990, **55**, 5801.

49 A. P. Marchand, B. C. Suri, A. D. Earlywine, D. R. Powell and D. Van der Helm, *J. Org. Chem.*, 1984, **49**, 670.

50 R. Beugelmans, A. Lechevallier and H. Rousseau, *Tetrahedron Lett.*, 1983, **24**, 1787.

51 M. Makosza and J. Winiarski, *Acc. Chem. Res.*, 1987, **20**, 282.

52 M. Makosza, in *Current Trends in Organic Chemistry*, ed. H. Nozaki, Pergamon, New York, 1983, p. 401.

53 (*a*) M. Makosza, *Synthesis*, 1991, 103; (*b*) M. Makosza, *Chimia*, 1994, **48**, 499.

54 In Ref. 1*a*, pp. 284–299.

55 R. A. Bartsch and J. Zavada, *Chem. Rev.*, 1980, **80**, 453.

56 G. Petrillo, M. Novi, G. Garbarino, C. Dell'Erba and A. Mugnoli, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1291.

57 J. R. Gandler, J. W. Storer and D. A. A. Ohlberg, *J. Am. Chem. Soc.*, 1990, **112**, 7756.

58 A. Thibblin, *J. Am. Chem. Soc.*, 1988, **110**, 4582.

59 (*a*) R. A. More O'Ferrall and S. J. Slae, *J. Chem. Soc. B*, 1970, 260; (*b*) R. P. Kelly, R. A. More O'Ferrall and M. O'Brien, *J. Chem. Soc., Perkin Trans. 2*, 1982, 211.

60 (*a*) R. A. More O'Ferrall, F. Larkin and P. Walsh, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1573; (*b*) F. Larkin and R. A. More O'Ferrall, *Aust. J. Chem.*, 1983, **36**, 1831.

61 R. D. Bach, R. C. Radger and T. J. Lang, *J. Am. Chem. Soc.*, 1979, **101**, 2845.

62 E. Bacciocchi, R. Ruzziconi and G. V. Sebastiani, *J. Am. Chem. Soc.*, 1983, **105**, 6114.

63 J. R. Mohrig, S. C. Schultz and G. Morin, *J. Am. Chem. Soc.*, 1983, **105**, 5150.

64 M. J. S. Dewar and Y. C. Yuan, *J. Am. Chem. Soc.*, 1990, **112**, 2088.

65 D. Prost, *Justus Liebigs Ann. Chem.*, 1899, **307**, 49.

Paper 5/01097G
Received 23*rd February* 1995
Accepted 18*th April* 1995