Carbanion reactivity — σ -adduct formation and elimination in the reactions of the carbanion from bis(phenylsulfonyl)methane with 4-nitrobenzofurazan derivatives

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Abstract: ¹H NMR studies in [²H₆]-DMSO show that the carbanion **4** from bis(phenylsulfonyl)methane reacts with 4,6dinitrobenzofuroxan to yield a σ -adduct that undergoes base-catalysed elimination to yield an alkene derivative. Rate constants, measured spectrophotometrically, are reported for the corresponding reactions in methanol of **4** with 4nitrobenzofurazan and some derivatives that give adducts at the 5-position. The intrinsic rate constant, k_0 , for this process has a value of 1.5 ± 0.5 . The 5-adducts undergo methoxide-catalysed elimination of phenylsulfinic acid to yield alkene derivatives and rate constants for this process are reported.

Key words: carbanions, 4-nitrobenzofurazan, σ-adducts, elimination reactions.

Résumé : Des études de RMN du ¹H dans du [²H₆]-DMSO montrent que le carbanion **4** obtenu à partir du bis(phénylsulfonyl)méthane réagit avec le 4,6-dinitrobenzofuroxane pour donner un adduit σ qui subit une élimination catalysée par les bases pour conduire à la formation d'un alcène. On rapporte les constantes de vitesses, mesurées d'une façon spectroscopique, pour les réactions correspondantes du composé **4** avec le 4-nitrobenzofurazane et quelques dérivés qui conduisent à la formation d'adduits en position 5. La valeur de la constante intrinsèque de vitesse pour ce processus, $k_0 = 1,5 \pm 0,5$. Les adduits en position 5 subissent une élimination d'acide phénylsulfinique catalysée par l'ion méthylate pour conduire à des alcènes et on rapporte les constantes de vitesse de ce processus.

Mots-clés : carbanions, 4-nitrobenzofurazane, adduits σ , réactions d'élimination.

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Introduction

There is much current interest in quantitatively assessing both nucleophilic and electrophilic reactivities. The nucleophilicities of many carbanions have been measured (1–4) using their reactions with benzhydrylium cations and quinone methides, while the electrophilicities of compounds ranging in reactivity from 1,3,5-trinitrobenzene to 4,6-dinitrotetrazolopyridine have been compared by measuring rate constants for their σ -adduct forming reactions with some standard nucleophiles, such as *N*-methylpyrrole and indole derivatives (5–7).

We have recently used the reactions with 4nitrobenzofurazan and some derivatives to compare the nucleophilicities in methanol of some nitroalkane anions (8)(1) and benzyltriflone anions (9) (2). These reactions result

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initially in the formation of anionic adducts at the 5-position of the nitrobenzofurazans, as shown in the general scheme 1. These results indicate that factors that affect the reactivities include the extent of charge delocalization, high in the case of 1 and low in the case of 2, in the nucleophiles and steric hindrance to bond formation, which is significant for the reaction of 2.

 $R^{1}_{R^{2}} = NO_{2}^{-}$ $R^{3}_{R^{3}}$ $R^{1}_{R^{2}} = H, Me$ $R^{3} = H, CF_{3}, CN$

It is also of interest that the initially formed adducts may undergo a base-catalysed elimination reaction to produce alkene derivatives.

Following many earlier studies (10–12), there has recently been renewed interest (13) in measuring nucleofugalities of leaving groups. The elimination process shown in Scheme 1 is likely (8, 9) to involve the bimolecular E2 mechanism so that values of the rate constants do not give nucleofugalities directly. Nevertheless, it is useful to examine how the structure of the leaving group Z^- affects the rate of the elimination process. Scheme 1.



In the present work, we extend our studies to include reactions of the carbanion (4) from bis(phenylsulfonyl)methane (3). Rate constants in methanol as solvent are reported for the formation of the initial σ -adducts with some 4nitrobenzofurazan derivatives (5), with 4-nitrobenzofuroxan (6), and also for the methoxide catalysed elimination of phenylsulfinic acid.



¹H NMR measurements in $[{}^{2}H_{6}]$ -DMSO show that reaction of **4** with 4,6-dinitrobenzofuroxan (**7**) results in the initial formation of a σ -adduct at the 7-position followed by elimination of phenylsulfinic acid.

Results and discussion

pK_a Value of bis(phenylsulfonyl)methane 3 in methanol

Since kinetic measurements were made in methanol it was necessary to determine the pK_a value of **3** in this solvent. Reaction of **3** with sodium methoxide in methanol resulted in a strong absorbance band at 280 nm ($\varepsilon 1.6 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) attributed to formation of the carbanion **4** as indicated in eq. [1]. Absorbance measurements gave a value for *K* of 40 ± 5 dm³ mol⁻¹, and the use of eq. [2] leads to a value for pK_a of 15.3 for **3**.

$$[1] \quad \mathbf{3} + \mathrm{MeO^{-}} \xleftarrow{\kappa} \mathbf{4} + \mathrm{MeOH}$$

$$[2] \quad pK_a = pK_{MeOH} - \log K$$

¹H NMR spectra

4,6-Dinitrobenzofuroxan 7 is classed as a super-electrophile (14) and will form σ -adducts at the 7-position by reaction with many weakly acidic carbon acids (15–16). ¹H NMR spectra in [²H₆]-DMSO of a mixture of 7 (0.1 mol dm⁻³), **3** (0.1 mol dm⁻³), and triethylamine (0.1 mol dm⁻³) provide

evidence for the formation of the σ -adduct **8**. Chemical shifts are given in Table 1. Interestingly, the spectrum of **8** shows that the two phenyl rings are not exactly equivalent so that two sets of bands, with equal intensities, are observed for their ring hydrogens. In the presence of excess triethylamine, new bands are observed that are consistent with the formation of the product **9** of the elimination of phenylsulfinic acid. Notably, two singlets due to **9** are observed at δ 8.62 (H5) and δ 7.17 (CH). These results are summarized in Scheme 2. It is known (17) that **7** will react with methanol to give a very stable 7-methoxy adduct, and this precluded kinetic studies of reactions of **7** with **3** in this solvent.

Spectra of 1,3,5-trinitrobenzene in $[{}^{2}H_{6}]$ -DMSO containing **3** and triethylamine gave no evidence of strong interaction. After several hours only bands due to the parent molecules were present.

Kinetic measurements

Reactions of the carbanion 4, generated from 3 and sodium methoxide, with 5a-5c and 6 were investigated spectrophotometrically in methanol. It is known that methoxide ions themselves will react with 5a-5c and 6 to give σ adducts (18, 19), and in the case of 5b a substitution product (19). To minimize these reactions, the equilibrium methoxide concentrations were reduced to low levels by working with [3] >> [NaOMe] and (or) by using phenolic buffers. Under these conditions the UV-vis spectra of 5a revealed two processes well separated in time. The first process resulted in a shift in the absorption maximum from 325 nm ($\varepsilon 8 \times 10^3$ dm³ mol⁻¹ cm⁻¹) in the parent to 335 nm ($\varepsilon 1.2 \times 10^4$ dm³ mol⁻¹ cm⁻¹) and is attributed to σ -adduct formation. The second slower process gave rise to a strong band at 430 nm ($\varepsilon 2.0 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and is attributed to the formation of the alkene derivative 11a by elimination of phenylsulfinic acid from the σ -adduct. The UV-vis spectra of **5b**, **5c**, and **6** similarly showed a fast process, giving a band in the region 330-340 nm. In the case of 5b and 6, this was followed by a slower reaction giving an absorption band in the region 430-450 nm. However, with 5c this process was too slow for measurement. These reactions are shown in Scheme 3.

Our justification for assigning structure 10, resulting from attack at the 5-position, to the product of the fast reaction is that previous studies with carbanions derived from benzylcyanides (20), nitroalkanes (8), and benzyltriflones (9), have shown that formation of 5-adducts is kinetically favoured relative to the formation of the isomeric 7-adducts. Also in the case of **5b** and of **5c**, reaction at the 7-position is unlikely because of the presence of the 7-substituent (8, 21). That the slower process involves elimination follows by analogy with the behaviour of the nitroalkane adducts (8), which eliminate nitrous acid, and the benzyltriflone adducts (9), which eliminate trifluoromethylsulfinic acid. In these cases, as in the present case, the elimination process involves a shift to longer wavelength in the absorption maximum, consistent with the increased electron delocalization possible in the elimination products. A further analogy is with the behaviour of 8, which will eliminate phenylsulfinic acid.

Kinetic measurements of the fast reaction were made either with [3] and [NaOMe] >> [5] or [6], or with methoxide

Table 1. ¹H NMR data for **3**, **7**, and **8** in $[{}^{2}H_{6}]$ -DMSO.

	δ						
Compound	H7	H5	CHn	Ph	J_{57}		
3	_	_	5.93(s, CH ₂)	7.88(d), 7.63(t), 7.76(t)	_		
7	9.26	8.95			2		
8	5.56	8.37	5.91(CH)	7.62(d), 7.46(t), 7.27(t)	<1		
				7.64(d), 7.47(t) 7.29(t)			

Note: J values in Hz. Coupling J = 7.4 Hz is observed between adjacent hydrogens in the phenyl rings.

Scheme 2.



concentration (hence the concentration of 4) buffered at constant values. Under these conditions, the fast reaction k_{fast} was observed as a first-order process, and eq. [3] will apply. Values of rate constants are given in Table 2. Linear plots of k_{fast} versus the carbanion concentration allowed the evaluation of k_5 and k_{-5} . Since the intercepts of the plots had low values, there are relatively high errors associated with the values of k_{-5} determined in this way. Therefore, measurements were also made, shown in the final three rows of Table 2, using buffered solutions where the concentrations of carbanion were reduced to low levels. Here the k_{-5} term made a large contribution to the overall value of k_{fast} . Using the known values of k_5 , values of the term k_5 [carbanion] were subtracted from k_{fast} to allow the evaluation of k_{-5} . The good correspondence between experimental and calculated values of k_{fast} (Table 2) gives confidence in the results obtained. Values for k_5 , k_{-5} , and K_5 , calculated as k_5/k_{-5} , are collected in Table 4.

[3]
$$k_{\text{fast}} = k_5 [(\text{SO}_2\text{Ph})_2\text{CH}^-] + k_{-5}$$

Kinetic measurements for the slower reaction were made with concentrations of the carbanion **3** that were high enough to ensure that the initial conversion of parent nitrocompounds to adducts **10** was largely complete. In the cases of **5a**, **5b**, and **6**, a first-order process k_{slow} measured at 430– 450 nm was observed and is attributed to the elimination of phenylsulfinic acid to give the alkene derivatives **11**. The results in Table 3 show that values of k_{slow} increase linearly Scheme 3.



with the equilibrium concentrations of methoxide ions, so that eq. [4] is applicable, and there is no dependence on the carbanion concentration. Values obtained for k_{el} were 2.6, 12, and 8 dm³ mol⁻¹ s⁻¹ for **5a**, **5b**, and **6**, respectively. In the case of **5c**, this reaction was too slow for convenient measurement.

$$[4] k_{slow} = k_{el} [MeO^{-}]$$

Comparisons

Results are collected in Table 4. Variations in values among the compounds **5a–5c** and **6** are largely in line with data obtained with other nucleophiles (8, 19, 22, 23). Thus the higher value of k_5 found for **5b** compared with **5a** reflects the inductive effect of the chlorine meta to the position of attack. The reduced electrophilicity of **5c** is attributed to resonance stabilization in the parent between the NO₂ and OMe ring-substituents. The N \rightarrow O functionality (18) in **6** results in increases in values of k_5 and K_5 compared with **5a**.

Although the data is limited, we thought it worthwhile to estimate a value for the intrinsic rate constant k_0 , in the Marcus (24–26) sense, for reactions of the carbanion **3** with the nitrobenzofurazan derivatives. A plot, not shown, of the values of log k_5 and log k_{-5} vs. log K_5 gave a value for k_0 of 1.5 ± 0.5. The values of intrinsic rate coefficients are thought (26–29) to reflect the amount of electronic– structural reorganisation and solvent reorganisation accompanying a reaction; the more reorganisation required, the lower the reactivity. The value obtained here is significantly higher than that ($k_0 = 0.05$) found (8) for the reaction of nitroalkane anions **1** with nitrobenzofurazans. This suggests that in the carbanions **4**, as with the benzyltriflone anions (4,

	[NaOMe]	$[MeO^{-}]_{aa}^{a}$		$k_{\text{fast}}^{b,c}$ (s ⁻¹)			
[3] (mol dm ⁻³)	$(10^{-3} \text{ mol } \text{dm}^{-3})$	$(10^{-4} \text{ mol } \text{dm}^{-3})$	$[4]_{eq}^{a}$ (10 ⁻⁴ mol dm ⁻³)	5a	5b	5c	6
0.03	1.0	4.5	5.5	0.30 (0.31)	7.9	0.26 (0.27)	1.0 (0.93)
0.05	1.0	3.3	6.7	0.35 (0.37)	9.8	0.29 (0.31)	1.1 (1.1)
0.05	1.5	5.0	10.0	0.52 (0.54)	12	0.42 (0.43)	1.8 (1.7)
0.05	2.0	6.7	13.3	0.67 (0.70)	21	0.58 (0.55)	2.6 (2.2)
0.022		0.54^{d}	0.48	0.057 (0.064)	_		0.13 (0.13)
0.034	_	0.54^{d}	0.73	0.090 (0.080)			0.18 (0.17)
0.044	—	0.54^{d}	0.95	0.098 (0.090)	1.3	0.13 (0.11)	0.21 (0.20)

Table 2. Kinetic data for the fast reactions of the carbanion 4 with 5a-5c and 6 in methanol at 25 °C.

Note: The concentration of the nitro compounds **5a–5c and 6** is 5×10^{-5} mol dm⁻³.

^{*a*}Calculated using the value for K of 40 dm³ mol⁻¹ (eq. [1]).

^{*b*}For **5a** and **5b** measured as a forming reaction at 330-340 nm, for **5c** as a forming reaction at 330 nm or fading reaction at 370 nm, and for **6** as a forming reaction at 340 nm or fading reaction at 410 nm.

'Values in parentheses were calculated using eq. [3] using the values given in Table 4.

^dMaintained using bromophenol buffers.

[3]	[NaOMe]	$[MeO^{-}]_{eo}^{a}$	$[4]_{ea}^{a}$	k _{slow} (10	$k_{slow} (10^{-3} s^{-1})$		
$(\text{mol } \text{dm}^{-3})$	$(10^{-3} \text{ mol } \text{dm}^{-3})$	$(10^{-4} \text{ mol } \text{dm}^{-3})$	$(10^{-4} \text{ mol } \text{dm}^{-3})$	5a	5b	6	
0.10	0.5	1.0	4.0	0.28	1.3	1.0	
0.05	1.0	3.3	6.7	0.91	3.9	2.6	
0.08	1.5	3.6	11.4	—	4.4	2.8	
0.10	2.0	4.0	16	0.95	4.8	3.0	
0.10	3.0	6.0	24	1.33	7.8	4.6	

Table 3. Kinetic data for the slow reactions of 5a, 5b, and 6 in methanol at 25 °C.

Note: The concentration of 5a, 5b, and 6 is 5×10^{-5} mol dm⁻³.

^aCalculated using the value for K of 40 dm³ mol⁻¹ (eq. [1]).

Compound	$k_5 \ (dm^3 \ mol^{-1} \ s^{-1})$	$k_{-5} (s^{-1})$	$K_5 (\mathrm{dm}^3 \mathrm{mol}^{-1})$	$k_{\rm el} \ ({\rm dm}^3 \ {\rm mol}^{-1} \ {\rm s}^{-1})$
5a	500±100	0.04 ± 0.01	$(1.25\pm0.4) \times 10^4$	2.6
5b	$(1.4\pm0.2) \times 10^4$	_	_	12
5c	350±50	0.08 ± 0.02	$(4.4\pm1) \times 10^3$	_
6	$(1.6\pm0.2) \times 10^3$	0.05 ± 0.02	$(3.2\pm1) \times 10^4$	8

Table 4. Summary of kinetic and equilibrium data for the reactions in Scheme 3.

9) **2**, the negative charge is more localized on the carbon atom than in the nitroalkane anions. In agreement with this, it should be noted that Hibbert (30, 31) found that little structural reorganisation was involved in ionization of disulfonyl carbon acids in water.

The previous study (9) with carbanions 2 derived from benzyltriflones found evidence for some steric hindrance to the reaction with 4-nitrobenzofurazan derivatives, and the reaction with the more sterically demanding 1,3,5-trinitrobenzene was not observed. The present results suggest that the nucleophilicity of the carbanion 4 from bis(phenylsulfonyl)methane may similarly be reduced by its high steric requirements. Thus again, no reaction is observed with 1,3,5-trinitrobenzene and the values of k_5 for the reaction with 4-nitrobenzofurazan are similar for carbanions 4 and 2 (R3=CN) derived from carbon acids with similar pK_a values. Thus for 4, $k_5 = 500 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and pK_a for 3 is 15.3, and for 2 (R3 = CN) $k_5 = 1500 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and pK_a for 4-cyanobenzyltriflone (9) is 16.0.

Elimination reactions have now been observed from 5adducts produced from 4-nitrobenzofurazan derivatives and

three types of carbanion, i.e., nitroalkane anions (8), benzyltriflone anions (9), and the bis(phenylsulfonyl)methane anion, and it is useful to compare kinetic data in methanol. Values of the rate constant k_{el} for the methoxidecatalysed elimination of nitrous acid from the nitromethane and nitroethane adducts of 4-nitrobenzofurazan 5a are 3.0 and 1.4 dm³ mol⁻¹ s⁻¹, respectively (8), and are similar to the value of 2.6 dm³ mol⁻¹ s⁻¹ found here for the elimination of phenylsulfinic acid from 10, R = H. In both types of reaction, the presence of the electron-withdrawing 7-chloro substituent in **5c** increases values of k_{el} . Interestingly, in the reactions with the benzyltriflone anion the elimination of trifluoromethylsulfinic acid from the initially formed 5adducts is faster than their reversal to parent, $k_{el}[MeO^-] >$ k_{-5} , so that values of k_{el} are not measurable (9). It might be inferred that the value of k_{el} for the elimination of trifluoromethylsulfinic acid is higher than the corresponding values for the elimination of nitrous acid and phenylsulfinic acid. Indeed, the high nucleofugal character of the SO₂CF₃ group and the possible use of SO₂CF₃ activated carbon acids in vicarious nucleophilic substitutions has been noted previously (32, 33). Nevertheless, our results (9) do not yield a value for k_{el} for trifluoromethyl sulfinic acid so that a direct comparison is not possible.

In fact, the elimination process is likely (34) to involve the E2 mechanism so that factors other than the nucleofugality of the leaving group are involved. These include steric factors involving the accessibility to the catalysing base of the acidic hydrogen to be removed from the reaction centre in the adducts, such as 10, and possible steric interaction with the ring nitro-group in the alkene products, such as 11. For example, the adduct 10, carrying two phenylsulfonyl groups, is likely to be more sterically demanding than the corresponding adduct produced from the nitromethane carbanion. It should also be noted that in the elimination process in methanol, catalysis has been observed only by the methoxide ion and not by unreacted carbanions, present in excess, which will be more sterically inhibited.

Experimental

Nitro-compounds 5a-5c, 6, and 7 were available from previous work [9]. Bis(phenylsulfonyl)methane was a commercial sample. Solutions of sodium methoxide were prepared by dissolving clean sodium in AnalaR methanol under nitrogen. Solutions containing very low equilibrium concentrations of methoxide ions were prepared using buffers prepared from 4-bromophenol, whose pKa value (35) in methanol is 13.61. All other materials and solvents were the purest available commercial samples.

¹H NMR spectra in [²H₆]-DMSO were recorded with a Bruker Avance 400 MHz instrument, UV-vis spectra and kinetic measurements were made at 25 °C with a Shimadzu UV-2101 PC spectrophotometer or an Applied Photophysics SX-17 MV stopped-flow instrument. First-order rate constants, precise to \pm 5%, were evaluated using standard methods.

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