PERKIN 2 COMMUNICATION

The reactions of 4,6-dinitrobenzofuroxan with sulfite ions in water; *cis–trans* isomerism in the 1:2 adducts

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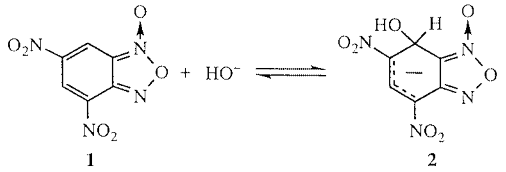
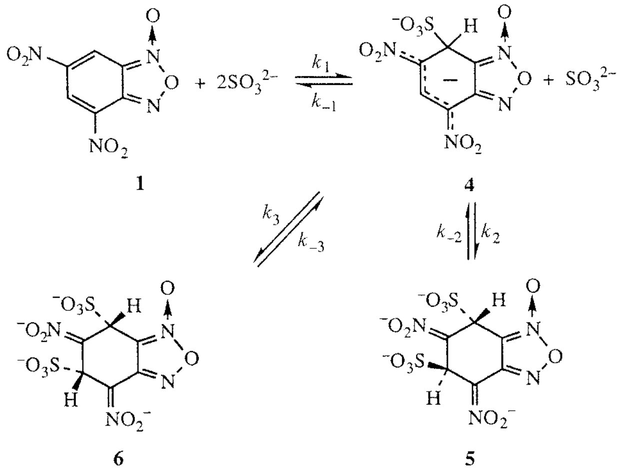
The reaction of 4,6-dinitrobenzofuroxan with sulfite ions in water results in the formation of a 1:1 adduct with high thermodynamic stability, K_1 1.3 × 10^{13} dm^3 mol^{-1}, and in a 1:2 adduct which may exist in *trans*- and *cis*-isomeric forms.

The high electrophilic reactivity of 4,6-dinitrobenzofuroxan, **1**, is well known,[1] and exceeds that of both the 4-nitrobenzenediazonium ion[2] and the proton.[3] The equilibrium constant for its reaction with hydroxide ions in water to give **2** has a value *ca.* ten orders of magnitude higher than that for the corresponding reaction of 1,3,5-trinitrobenzene, **3**, with hydroxide ions.[4] Consequently **1** exists in neutral solution in water very largely in the form of **2**. There is current interest in **1** due to biological and analytical applications,[5–8] and since its Diels–Alder reactions with dienes offer synthetic possibilities.[9–11]



Despite the extensive studies of **1** there has been no previous report of the formation of adducts with 1:2 stoichiometry[1,3,4,6,12,13] with simple oxygen, nitrogen and carbon nucleophiles. This is surprising in view of the ready formation of 1:2 adducts from **3** and related trinitro-substituted benzenes.[1,14–16] Our present studies provide evidence that reaction of **1** with sulfite ions in water yields a 1:1 adduct **4** with high thermodynamic stability and isomeric 1:2 adducts **5** and **6** (Scheme 1).



Scheme 1

Kinetic measurements were made in water using the stopped-flow technique. Mixing **1** in acid solution, to prevent formation of the hydroxy-adduct **2**, with buffered sulfite solutions resulted in a rapid increase in absorbance at 476 nm attributed to the formation of **4**. Measurements, under first-order conditions, showed that the rate constant k^1_{obs} increased linearly with sulfite concentration, and use of eqn. (1) yielded a value for k_1 2.3 × 10^7 dm^3 mol^{-1} s^{-1}. However the value of k_{-1} was too low for evaluation by this method.

Table 1 Comparison of kinetic and equilibrium data for reactions of **1**, and **3**, with sulfite in water at 25 °C

	1[a]	**3**[a,b]
k_1/dm^3 mol^{-1} s^{-1}	2.3 × 10^7	3.5 × 10^4
k_{-1}/s^{-1}	1.8 × 10^{-6}	125
K_1/dm^3 mol^{-1}	1.3 × 10^{13}	280
k_2/dm^3 mol^{-1} s^{-1}	170	195
k_{-2}/s^{-1}	16	21
K_2/dm^3 mol^{-1}	11	9.3
k_3/dm^3 mol^{-1} s^{-1}	0.44	1.2
k_{-3}/s^{-1}	0.06	0.13
K_3/dm^3 mol^{-1}	7	9.2

[a] Data for formation of 1:2 adducts are at $I = 0.3$ mol dm^{-3}. [b] Data from ref. 15.

$$k^1_{\text{obs}} = k_1[\text{SO}_3^{2-}] + k_{-1} \qquad (1)$$

$$k^2_{\text{obs}} = k_2[\text{SO}_3^{2-}] + k_{-2} \qquad (2)$$

$$k^3_{\text{obs}} = \frac{k_3[\text{SO}_3^{2-}]}{1 + K_2[\text{SO}_3^{2-}]} + k_{-3} \qquad (3)$$

At relatively high (> 0.01 mol dm^{-3}) concentrations of sulfite rapid formation of the band at 476 nm was followed by reversible fading processes which were accompanied by increased absorbance at 340 nm. Kinetic analysis indicated two distinct processes well separated in time. There is NMR evidence that these are due to the formation of the isomeric adducts **5** and **6**. Since, at these sulfite concentrations, formation of the 1:1 adduct, **4**, is virtually complete the appropriate rate expressions for these processes are eqns. (2) and (3). Values obtained for the rate constants are collected in Table 1. They lead to values for K_2 (= k_2/k_{-2}) 11 dm^3 mol^{-1} and K_3 (= k_3/k_{-3}) 7 dm^3 mol^{-1} which are similar in magnitude, showing that the isomeric adducts **5** and **6** have similar thermodynamic stabilities. Nevertheless the values of the rate constants for the formation and decomposition of **6** are both more than one hundred times lower than the corresponding values for **5**. A similar situation has been observed in the formation of *cis*- and *trans*-isomers in the 1:2 adducts of **3** and sulfite.[15] It is likely to result from electrostatic repulsion between the bound and entering sulfite groups in the transition state for formation of the *cis*-adduct which is partly relieved by ring distortion in the fully-formed adduct.

The ^{1}H NMR spectrum of **1** in the presence of one equivalent of sodium sulfite in 80:20 (v/v) D$_2$O–[^{2}H$_6$]DMSO shows bands at δ 5.96 and 8.83 attributed to the 1:1 adduct **4**. In the presence

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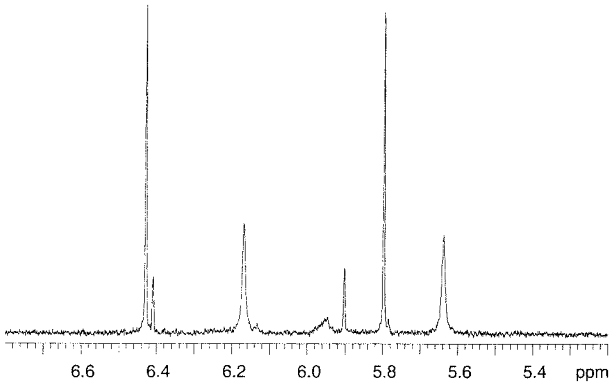
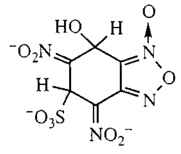


Fig. 1 ^1H NMR spectrum, 400 MHz, of **1** in the presence of excess sulfite showing bands due to **5**, **6** and **7**.

of excess sulfite all bands are observed in the region δ 5.6–6.5 indicating that nucleophilic attack has occurred at both the 5- and 7-ring positions. The spectrum shown in Fig. 1 shows two pairs of bands at δ 5.65 and 6.18 and at δ 5.81 and 6.44 which are attributed to the isomeric di-adducts **6** and **5** respectively. The latter bands have slightly higher intensity than the former corresponding to the higher equilibrium constant for formation of the *trans* di-adduct. Also present are two small singlets at δ 5.91 and 6.42 attributed to the mixed di-adduct **7**, where one isomeric form predominates. The exclusive formation of **7** was observed when the preformed adduct **2** was mixed with sulfite.



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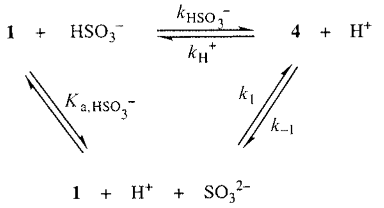
It is known that the electrophilicity of **1** is sufficiently high that reaction with water will generate **2** with the liberation of a proton.[4] Similarly we find that in strongly acidic solutions reaction with the hydrogen sulfite ion, HSO_3^-, leads to the formation of **4** together with H^+. Kinetic measurements in aqueous hydrochloric acid, 0.5–2.0 mol dm^{-3}, allowed the determination of the value for $k_{HSO_3^-}$, 130 $dm^3\ mol^{-1}\ s^{-1}$. The value for k_{H^+} for the back reaction with protons is 1.1×10^{-4} $dm^3\ mol^{-1}\ s^{-1}$. These processes are shown in Scheme 2. The other two sides of the triangle in this scheme represent dissociation of hydrogen sulfite,[17] with K_{a,HSO_3^-} 9×10^{-8} mol dm^{-3}, and the direct reaction of **1** with sulfite. Hence using eqn. (4) a

$$K_1 = \frac{k_{HSO_3^-}}{k_{H^+}} \frac{1}{K_{a,\ HSO_3^-}} \qquad (4)$$



Scheme 2

value for K_1 of 1.3×10^{13} $dm^3\ mol^{-1}$ can be determined. It follows that the value of k_{-1} (= k_1/K_1) is 1.8×10^{-6} s^{-1}.

Results are summarised in Table 1, where they are compared with corresponding values for formation of 1:1 and 1:2 adducts from **3**, 1,3,5-trinitrobenzene. They show that the stability of the 1:1 adduct from **1** is *ca.* 10^{11} higher than that of the TNB–SO_3^{2-} adduct giving further evidence of the high electrophilicity of **1**.

Nevertheless the values of the equilibrium constants for formation of 1:2 adducts from **1** and **3** have similar values. This may reflect the fact that addition of the second sulfite ion to **3** allows charge to be spread over two nitro-groups while in addition to **1** only one nitro-group remains to accommodate the added negative charge.

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