Equilibrium Constants for the Formation of Sulphite Addition Compounds of Aromatic Aldehydes

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The equilibrium concentration of the sulphite Meisenheimer adduct of 1,3,5-trinitrobenzene, formed from potassium sulphite/18-crown-6 and trinitrobenzene, in dimethyl sulphoxide solution, is reduced in the presence of an aromatic aldehyde, with an accompanying decrease in the absorbance of the solution due to the intensely coloured Meisenheimer adduct. Equilibrium constants have accordingly been determined for the formation of the sulphite Meisenheimer adduct of trinitrobenzene and for the formation of a series of substituted benzaldehyde sulphite dianions in dimethyl sulphoxide solution.

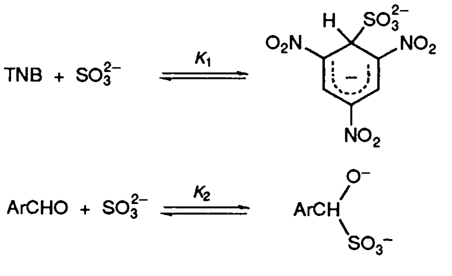
The formation of crystalline salts from carbonyl compounds and an alkali hydrogen sulphite or sulphite is well known. Although the reaction is reversible, the equilibrium often shifts towards the addition product, and the sulphite adduct may later be decomposed to yield the original carbonyl compound, hence the reaction constitutes one of the most familiar procedures for the isolation, identification, and quantitative analysis of carbonyl compounds in both organic chemistry and biochemistry.[1]

It is surprising that so little information is available with regard to equilibria of sulphite adduct formation and decomposition. We are aware of only three other reports on the equilibration of benzaldehyde and sulphite ion.[2–4] In these reports the extent of reaction has been determined in aqueous media either by titration of unchanged sulphite ion with iodine or by spectroscopic measurements of rate constants for the reactions in both the forward and the reverse direction. It was shown later[4] that the titration method yielded inaccurate equilibrium constants.

The procedure utilised in this paper is an indirect method for determination of the equilibrium constants by the monitoring of an 'indicator' equilibrium.[5] This method is a thermodynamic counterpart of the kinetic competition method applicable when the competing reactions are, for practical purposes, irreversible.[6,7]

Crampton[8] has shown that sulphite ions add reversibly to 1,3,5-trinitrobenzene (TNB) in water, with the formation of the coloured 1:1 and 2:1 Meisenheimer complexes. The formation of the 1:1 complex (I) is enhanced in water–dimethyl sulphoxide (DMSO) mixtures; thus, in contrast with the behaviour in water, it was found[8] that in solutions containing 70% dimethyl sulphoxide only the lower 1:1 complex is formed.

Spectrophotometric determination of the concentration of the adduct (I) allowed evaluation of the equilibrium constant of reaction (1).



(I) (1)

(II) (2)

When the equilibrium (1) is established in the presence of an aldehyde, the reversible reaction (2) provides an alternative destination for the sulphite anion. The concentration of adduct (I) then provides a probe for the extent of equilibrium (3). The

$$\mathrm{ArCHO} + \mathrm{(I)} \rightleftharpoons \mathrm{TNB} + \mathrm{(II)} \qquad (3)$$

equilibrium constants of the three reactions are related according to equation (4). In the absence of added aldehyde, the

$$K_3 = K_2/K_1 = \frac{[\mathrm{TNB}]_{\mathrm{eq}}}{[\mathrm{ArCHO}]_{\mathrm{eq}}} \cdot \frac{[\mathrm{(II)}]}{[\mathrm{(I)}]} \qquad (4)$$

observed concentration of adduct (I) is equal to the stoicheiometric concentration of sulphite minus the equilibrium concentration of sulphite ion [SO_3^{2-}]. When aldehyde is present, the concentration of adduct (I) is reduced by the equilibrium concentration of adduct (II) in the system. Accordingly, if $A°$ and A represent the absorbance [due to adduct (I)] in the absence and presence of added aldehyde, respectively, equation (5) applies. Combination of equations (4) and (5) give equation (6).

$$\frac{A° - A}{A} = \frac{[\mathrm{(II)}]}{[\mathrm{(I)}]} \qquad (5)$$

$$K_3 = \frac{[\mathrm{TNB}]}{[\mathrm{ArCHO}]} \cdot \frac{A° - A}{A} \qquad (6)$$

The present paper is concerned with the application of equation (6) to the reaction between the members of series of substituted benzaldehydes and potassium sulphite (with equimolar addition of 18-crown-6) in DMSO solution at 25 °C.

Experimental

Spectrophotometric observations were made with a Perkin-Elmer 555 UV spectrophotometer at 25.00 ± 0.05 °C with both graphical and digital recording of absorbance.

Potassium sulphite (anhydrous; Fisher Analar) was used without further purification. TNB was prepared from picryl chloride (1-chloro-2,4,6-trinitrobenzene) following the procedure described before.[9] Aromatic aldehydes were washed with aq. sodium hydrogen carbonate to remove carboxylic acids,

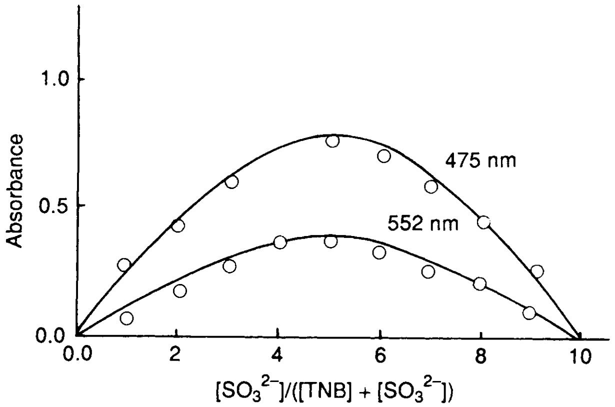


Figure 1. Continuous variation method for complex (I). Total concentration TNB plus potassium sulphite–18-crown-6 (10^{-4} mol dm^{-3}). Absorbance recorded at 475 and 552 nm.

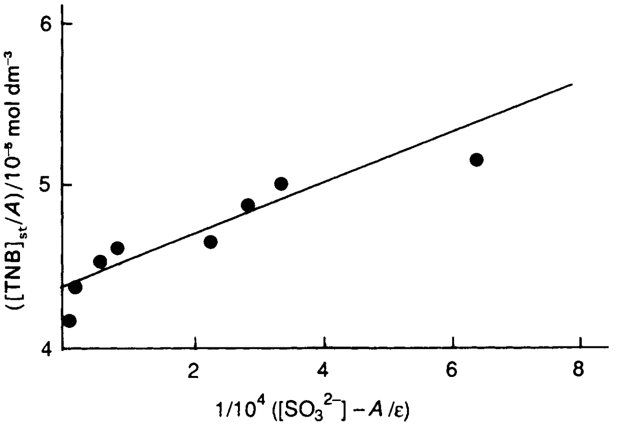


Figure 2. Test of equation (7) for evaluation of K_1, and from absorbance measurements at low concentrations of TNB.

dried ($CaSO_4$ or Na_2SO_4), and either distilled or crystallised. DMSO (Aldrich) was dried for several days over molecular sieves (4 Å), distilled under reduced pressure from calcium hydride, and kept out of the contact with the atmosphere.

Stock solutions of potassium sulphite and 18-crown-6 in equal concentrations (0.05–0.10 mol dm^{-3}) were prepared from degassed distilled water containing 50% (v/v) dimethyl sulphoxide and were stored under nitrogen at 4 °C.

For equilibrium determinations, sample and reference cuvettes (1 cm path-length) were filled with 2.5 cm^3 of a solution of either TNB or TNB–aldehyde mixture in DMSO, and allowed to reach thermal equilibrium. A small volume (5–15 mm^3) of the stock solution of sulphite ion–18-crown-6 was then injected into the sample cuvette from a Hamilton syringe, and the reactants were thoroughly mixed. To check the stability of the stock solution of sulphite–18-crown-6, measurements were repeated periodically. The rate of formation of Meisenheimer adduct (I) was too fast for rate measurements. The absorption spectrum of the product solution was closely similar to that previously reported for adduct (I) in different solvents.[8,10] The maximum value recorded (after 5–10 min) was taken to correspond to the equilibrium concentration of Meisenheimer adduct (I).

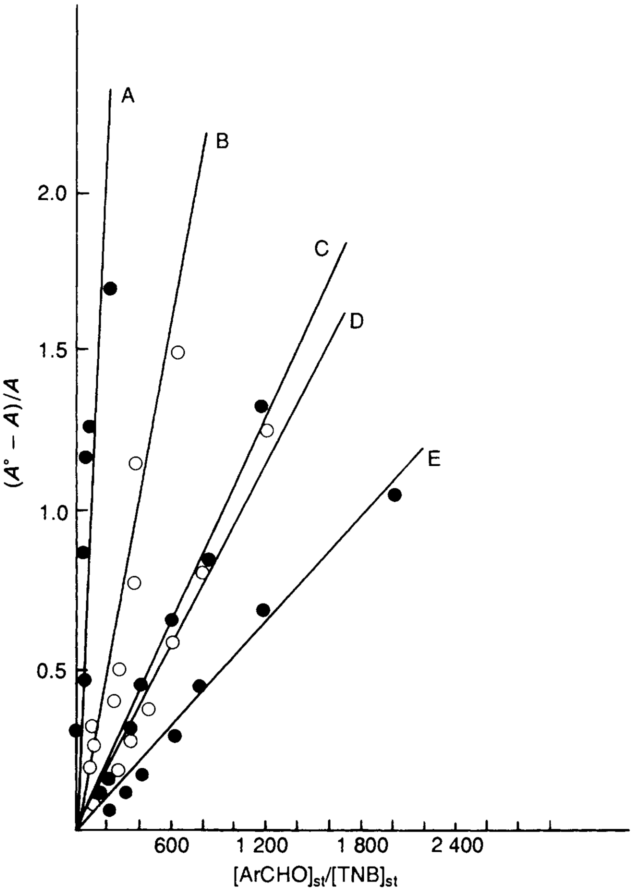


Figure 3. Specimen graphs for evaluationn of K_3 from equation (6): A, 4-NO_2; B, 3-NO_2; C, 3-Cl; D, 4-Cl; E, H.

Table 1. Equilibrium constants for formation of sulphite addition dianions from substituted benzaldehyde.

Substitution	$10^3\ K_3$	$K_2/10^2$ dm^3 mol^{-1}	σ^+
p-NO_2	10.00	40.20	0.790
m-NO_2	2.75	11.06	0.674
o,p-Cl_2	2.35	9.45	
m-Cl	1.44	5.79	0.399
p-Cl	1.00	4.02	0.114
H	0.56	2.25	0

The method of continuous variations[11] indicated that, over the range of concentrations studied, only the 1:1 complex (I) was formed (Figure 1). The equilibrium constant (K_1) for the reversible equilibrium (1) and the molar extinction coefficient (ε) at the maximum absorption were evaluated from equation (7),[5] where $[TNB]_{st}$ is the constant TNB concentration,

$$\frac{[\mathrm{TNB}]_{st}}{A} = \left[K_1\varepsilon\left([\mathrm{SO}_3^{2-}]_{st} - \frac{A}{\varepsilon}\right)\right]^{-1} + \varepsilon^{-1} \qquad (7)$$

$[SO_3^{2-}]_{st}$ is the potassium sulphite–18-crown-6 concentration, and A is the absorbance. A plot of the results (Figure 2) gave an intercept corresponding to a value of 2.23×10^4 dm^3 mol^{-1} cm^{-1} for the molar extinction coefficient (ε) of the complex at a wavelength of 475 nm, and a slope corresponding to a value of 4.02×10^5 dm^3 mol^{-1} for the equilibrium constant K_1.

Discussion

The usefulness of the procedure utilised depends on the high molar absorption coefficient of the Meisenheimer complex (I), which allows the measurements to be carried out on very dilute solutions.

Table 2. Absorbance measurements for solutions containing sulphite ion, TNB, and aromatic aldehydes (XC_6H_4CHO).

	$(A^\circ - A)/A$					
$ArCHO_{st}/TNB_{st}$	p-NO_2	m-NO_2	o,p-Cl_2	m-Cl	p-Cl	H
20	0.32	0.13	0.11			
40	0.48					
60	0.87	0.20	0.23			
80	1.16					
100	1.25	0.39	0.35	0.12	0.98	
120	1.65					
160	1.69	0.48		0.18		
200		0.68	0.62	0.23	0.21	0.07
300		0.80	0.70	0.33	0.30	0.13
400		1.15	0.80	0.46	0.39	0.19
600		1.50	1.42	0.66	0.61	0.31
800			1.70	0.86	0.81	0.45
1 200				1.33	1.28	0.69
2 000						1.06

[TNB] 4×10^{-5} mol dm^{-3}. Sulphite added as K_2SO_3/18-crown-6.

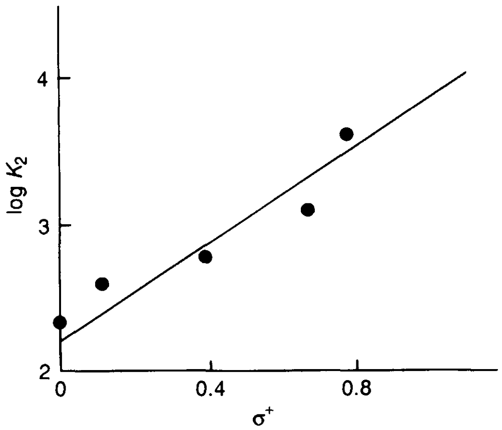


Figure 4. ρ–σ^+ Correlation for K_2-values.

Both the method of continuous variation and the linearity of the $[TNB]_{st}/A$ *versus* $[K_1\varepsilon([SO_3^{2-}]_{st} - A/\varepsilon)]^{-1}$ plot (Figure 2) suggest that TNB and sulphite ion interact to form a 1:1 complex.

We carried out the measurements in the presence of an equimolar concentration of 18-crown-6 to minimise possible effects of ion association between potassium and sulphite ions.[12]

The reported values of K_1 for the TNB–sulphite complex were obtained in aqueous solutions but the present study appears to be the first one using DMSO. Cuta and Beranek[13] have reported a K_1-value of 5.12×10^2 dm^3 mol^{-1}, while Norris[10] reported a value of 3.12×10^2 dm^3 mol^{-1}. Crampton[8] reported a value of 2.5×10^2 dm^3 mol^{-1} for the equilibrium constant in water and expected that in 70:30 DMSO-water (v/v) the constant K_1 would be in excess of 5×10^4 dm^3 mol^{-1}. Our high value of K_1 in DMSO (4.02×10^5 dm^3 mol^{-1}) is inconsistent with the increased activity of sulphite ion, which will be poorly solvated in aprotic solvent. Also, the complex (I) will be well solvated in DMSO and this will favour its production. In contrast, the value of K_2 for the addition of sulphite ion to benzaldehyde in DMSO at 25 °C (225.1 dm^3 mol^{-1}) is smaller than the previously determined values relating to aq. solution. Kokesh and Hall[4] reported a K_2-value of 354 dm^3 mol^{-1} at pH 8.14 and 21 °C. Van Tamelen *et al.*[3] reported a value of 657 dm^3 mol^{-1} at 20 °C. It might be argued that the dianionic addition compound, produced in equilibrium (2), resembles an inorganic salt so that solvation by the aprotic solvent is poor. Thus the equilibrium constants measured in DMSO are of the order expected. Plots of log K_2 against σ^+ (Figure 4) lead to a ρ^+-value of 1.57, comparable to those for equilibria involving the addition of hydroxide[14] or methoxide ion,[15] however, it is larger than that found for cyanide addition[5] to aromatic aldehydes.

Acknowledgements

Partial financial support from the Royal Society of Chemistry to W. N. W. is gratefully acknowledged.

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Paper 9/05257G
Received 11*th December* 1989
Accepted 4*th June* 1990