The Stabilities of Meisenheimer Complexes. Part 36.[1] The Reaction of 2,4,6-Trinitrobenzyl Chloride with Sodium Hydroxide in Water

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The reaction of 2,4,6-trinitrobenzyl chloride with dilute aqueous sodium hydroxide gives a σ-adduct by hydroxide ion attack at the 1-position. Kinetic and equilibrium data for this reaction are reported and are compared with those for the reaction with methoxide ions in methanol.

There have been several reports of the formation of σ-adducts [2] by hydroxide attack on ring-activated aromatic molecules. In the case of 1-X-2,4,6-trinitrobenzenes, the likely products of 1 : 1 interaction are the 3-hydroxy-adduct (1) or its 1-hydroxy-isomer (2). Adducts with structure (1) have been observed from substrates with X = H,[3,4] NO₂,[5,6] Cl,[6] OMe,[6,7] SO₃⁻,[8] O⁻,[6] CO₂Me,[9] CO₂⁻,[3] NH₂,[10] NHMe,[10] NMe₂,[10] NPr₂,[11] and CONH(Buᵗ).[12] In contrast adducts with structure (2) have been reported previously only when X = CO₂Me[9] or CONHC(Me)₃.[13] One reason for the failure to observe adducts of structure (2) is their instability with respect to nucleophilic substitution when X is a good nucleofuge.

We are interested in the reaction of 2,4,6-trinitrobenzyl chloride (TNBCl) with base since it may yield the commercially important product 2,2′,4,4′,6,6′-hexanitrostilbene (HNS).[14,15] We report here a kinetic investigation of the initial reversible reactions of TNBCl with hydroxide ions in water, leading to the formation of the 1-hydroxy adduct (2; X = CH₂Cl). These results are important in that they allow comparison of kinetic and equilibrium data for reactions of hydroxide and methoxide ions at a substituted ring position.

Experimental

2,4,6-Trinitrobenzyl chloride, m.p. 85° (lit.,[14] 85°), was prepared by the method of Shipp and Kaplan.[14] Visible spectra were measured with a Pye Unicam SP-8000 or SP-8100 instrument or with a Hi-Tech SF-3L stopped-flow spectrophotometer. All rate measurements were made on the Hi-Tech instrument at 25°.

Visible spectra of TNBCl (2 × 10⁻⁵M) in aqueous sodium hydroxide measured with a conventional spectrophotometer are shown in the Figure. In the more dilute solutions [NaOH] < 0.1M the spectrum shows a maximum at 445 nm with a shoulder at 500 nm. The reversibility of this process was proved by consecutive additions of acid and base which resulted in decolourisation of the solution and regeneration of the initial spectrum. This reversibility shows that on the time scale of our experiments inappreciable hydrolysis of the CH₂Cl group occurs. In more concentrated solutions a single broad maximum is observed at 490 nm indicating some further mode of reaction. Nevertheless use of stopped-flow spectrophotometry showed that in a solution containing 0.1M-base the initial spectrum, measured within 5 s of mixing had maxima at 445 and 500 nm and was similar to that of the time-stable species observed in more dilute solutions.

Rate and equilibrium data for the initial reaction are in Table 1. Measurements were made under first-order conditions with base in large excess over substrate. Rate data accord with equation (1) and give values for k_f of 11 ± 0.5

$$k_{obs} = k_f[OH^-] + k_r \qquad (1)$$

(1)   (2)   (3)
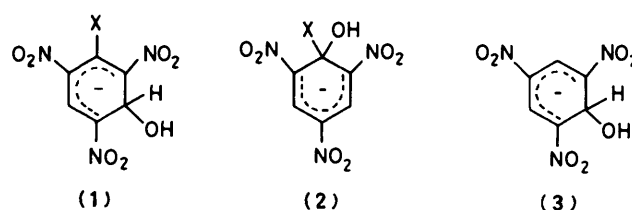
1 mol⁻¹ s⁻¹ and k_r, 0.1 ± 0.02 s⁻¹. Combination of these values gives a value for the equilibrium constant K $(=k_f/k_r)$ of 1.1×10^2 l mol⁻¹, in good agreement with that obtained from the equilibrium optical densities.

Discussion

The visible spectrum of the species initially produced from TNBCl and hydroxide ions in water shows maxima at 445 and 500 nm and is typical of 1 : 1 σ-adducts formed from trinitro-activated substrates.[2,16] It does not however distinguish the possible structures (1; X = CH₂Cl) and (2; X = CH₂Cl). However comparison of the rate and equilibrium data with those for reactions of TNB strongly suggests that our measurements relate to the formation of the 1-hydroxy adduct (2). The argument is as follows. The presence of a bulky substituent (CH₂Cl) at the 1-position of the substrate will cause the nitro-groups at the 2- and 6-positions to be rotated from the ring plane. Crystallographic data, which would give the extent of rotation, are not available for TNBCl but for 2,4,6-trinitrophenetole [17] (carrying a 1-substituent of similar size) rotations of 32 and 61° are observed for the 2- and 6-nitro-groups. Hence the electron-withdrawing power of these nitro-substituents will be reduced. Attack at the 3-position to give an adduct of structure (1) does not relieve steric congestion at the 1-position so that the thermodynamic stability of (1; X = CH₂Cl) should be lower than that of the TNB analogue (3). In agreement with this expectation it is known that the stabilities of adducts formed by attack of methoxide,[16] ethoxide,[16] or sulphite [18] nucleophiles at the 3-position of TNBCl are lower than those of the corresponding adducts from TNB. However the value of 110 l mol⁻¹ observed for hydroxide attack on TNBCl is much higher than the value of 3.7 l mol⁻¹ for reaction with TNB[4] to give (3). The value is however compatible with the formation of (2; X = CH₂Cl) since attack at the 1-position will result in rotation of the CH₂Cl substituent from the ring-plane with a consequent reduction in steric interaction with the o-nitro-groups, allowing their approach towards coplanarity with the benzene ring. The inductive withdrawal of the CH₂Cl substituent at the 1-position will also result in enhanced stability of the 1-

adduct. Since nucleophilic attack at unsubstituted ring positions is generally a faster process than attack at substituted positions [6] our failure to observe $(1; X = CH_2Cl)$ can be attributed to the relatively low thermodynamic stability expected for this adduct in water.

It is of interest to examine the effects of the CH_2Cl substituent on the relative reactivities of hydroxide and methoxide ions. Data are in Table 2. For reaction at an unsubstituted position in TNB Bernasconi [4] has shown that values of k_f for hydroxide and methoxide are in the ratio 1 : 190. The corresponding ratio for reaction with TNBCl is 1 : 70. The increase in value of the ratio for reaction at the CH_2Cl substituted position may be due to the slightly greater steric requirement of methoxide relative to hydroxide. These values contrast with the relative Brönsted basicities of hydroxide and

methoxide which are in the ratio 1 : 0.62 in water [19] and 1 : 0.3 in propan-2-ol,[20] but follow the general pattern found in other nucleophilic reactions.[2,4] The abnormal behaviour has been attributed [4] to the greater solvation of hydroxide than of methoxide. From the reactivity pattern in the forward direction it might have been expected that values of k_r for the reverse reaction would be higher for hydroxide than for methoxide. However rates of cleavage of hydroxide and methoxide from the TNB adducts are in the ratio 1 : 33. This has been interpreted [4] in terms of lowering of the value of k_r for hydroxide by intramolecular hydrogen bonding of the added hydroxy-group to an o-nitro-group. The presence of the CH_2Cl substituent at the reaction centre in $(2; X = CH_2Cl)$ might have been expected to modify this effect. Nevertheless a rather similar ratio of 1 : 22 is observed implying a similar hydrogen bonding interaction.

The presence of the CH_2Cl substituent has a rather small effect on hydroxide : methoxide rate ratios indicating the relatively small difference in steric requirements of hydroxide and methoxide ions.

We must now consider the cause of the spectral change observed in solutions where $[NaOH] \geqslant 0.1M$. It is known from measurements with related compounds [6,8] that ionisation of added hydroxy-groups may occur to give dianionic species. However the change in spectral shape associated with this type of process is usually small. Also the equilibrium between hydroxy-adduct and its dianionic form would involve a proton transfer between oxygen atoms and hence would be established very rapidly.[6,8] Our observation that in 0.1M-base the spectrum recorded by stopped-flow spectrophotometry differs from that obtained at equilibrium is not in accord with rapid deprotonation. Hence the observed change is reasonably attributed [8,21] to formation of a di-adduct by attack of hydroxide at the 1- and 3-positions and/or the 3- and 5-positions.
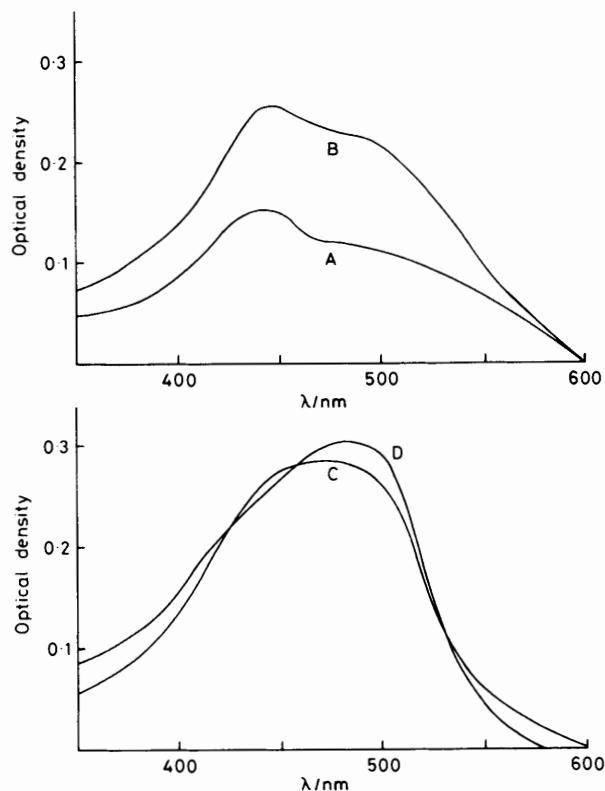

Figure. Visible spectra, recorded 1 min after mixing, with 1 cm path-length cells of TNBCl $(2 \times 10^{-5}M)$ in water containing the following concentrations of sodium hydroxide, A, 0.01M; B, 0.05M; C, 0.1M; D, 0.5M

Table 1. Kinetic and equilibrium data for the fast colour-forming reaction of TNBCl $(1 \times 10^{-5}M)$ with sodium hydroxide in water [a] at 25°

$[NaOH]$ [b]/M	k_{obs}/s^{-1}	O.D.[c] (445 nm)	K_1[d]/l mol^{-1}
0.01	0.21	0.016	110
0.02	0.33	0.022	120
0.04	0.55	0.024	90
0.06	0.74	0.027	110
0.08	1.05	0.028	
0.10	1.17	0.028	

[a] The solvent contains 1% by volume of dimethyl sulphoxide. [b] $I = 0.1M$ with sodium chloride. [c] Measured with 2 cm path-length cells. A Benesi–Hildebrand plot gives a value of 0.031 for complete conversion to adduct. [d] Calculated as O.D./(0.031 − O.D.) [NaOH].

Table 2. Comparison of rate and equilibrium data for reactions of TNB and TNBCl with hydroxide ions in water and methoxide ions in methanol

k_f/l mol^{-1} s^{-1}	37.5	7 300	11	770
k_r/s^{-1}	9.8	330	0.1	2.2
K/l mol^{-1}	3.7	20	110	350
Reference	4	4	Present work	16

Our results provide no evidence for the production in water of the conjugate base formed by transfer of a side-chain proton. This species, whose distinctive spectrum has been observed in methanol,[16] is thought to be an intermediate in the formation of HNS.[14] Hence water or media containing large proportions of water are unlikely to be suitable for HNS synthesis.

Acknowledgements

References

1 Part 35, M. R. Crampton, P. J. Routledge, and P. Golding, J. Chem. Res. 1983, 314.
2 See M. R. Crampton, Adv. Phys. Org. Chem., 1969, 7, 211; M. J. Strauss, Chem. Rev., 1970, 70, 667; F. Terrier, ibid., 1982, 82, 77; G. A. Artamkina, M. P. Egorov, and I. P. Beletskaya, ibid., p. 427.
3 V. Gold and C. H. Rochester, J. Chem. Soc., 1964, 1710; R. Gaboriaud and R. Schaal, Bull. Soc. Chim. Fr., 1969, 2683.
4 C. F. Bernasconi, J. Am. Chem. Soc., 1970, 92, 4682.
5 M. R. Crampton and M. A. El Ghariani, J. Chem. Soc. B, 1970, 391.
6 M. R. Crampton and B. Gibson, J. Chem. Soc., Perkin Trans. 2, 1979, 648.
7 C. F. Bernasconi and J. R. Gandler, J. Org. Chem., 1977, 42, 3387.
8 M. R. Crampton, J. Chem. Soc., Perkin Trans. 2, 1978, 343.
9 E. G. Kaminskaya, S. S. Gitis, A. Ya Kaminskii, and Yu. D. Grudtsyn, J. Org. Chem., USSR, 1976, 12, 917.
10 M. R. Crampton and V. Gold, J. Chem. Soc. B, 1966, 893.
11 R. H. de Rossi, O. D. Madoery, and E. B. de Vargas, J. Org. Chem., 1980, 45, 649.
12 E. J. Fendler, D. J. Koranek, and S. N. Rosenthal, ' Solution Chem. Surfactants, Proc. Sect., 52nd Colloid Surf. Chem. Sci. Symp.,' Plenum, New York, 1978, vol. 2, p. 575.
13 E. J. Fendler, D. M. Camaioni, and J. H. Fendler, J. Org. Chem., 1971, 36, 1544.
14 K. G. Shipp and L. A. Kaplan, J. Org. Chem., 1966, 31, 857.
15 G. P. Sollott, J. Org. Chem., 1982, 47, 2471.
16 D. N. Brooke, M. R. Crampton, G. C. Corfield, P. Golding, and G. F. Hayes, J. Chem. Soc., Perkin Trans. 2, 1981, 526.
17 C. M. Gramaccioli, R. Destro, and M. Simonetta, Acta Crystallogr., 1968, B24, 129.
18 D. N. Brooke and M. R. Crampton, J. Chem. Soc., Perkin Trans. 2, 1980, 1850.
19 P. Ballinger and F. A. Long, J. Am. Chem. Soc., 1960, 82, 795.
20 J. Hine and M. Hine, J. Am. Chem. Soc., 1952, 74, 5266.
21 C. F. Bernasconi and R. G. Bergstrom, J. Am. Chem. Soc., 1974, 96, 2397.