Bromopicrin Reaction. Part III.[1] Kinetics of the Ionisation of α-Nitrotoluene in Alkaline Solution

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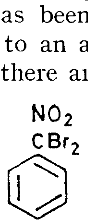
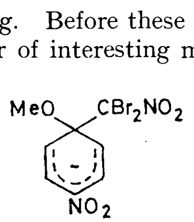
The rates of ionisation of a number of *p*-substituted α-nitrotoluenes in water have been studied. The rates correlate with σ rather than σ^-. Replacement of one of the methylene protons by bromine increases the rate of ionisation by a factor of 149. The CBr_2NO_2 group is not readily displaced from the benzene ring by a base, in spite of its stability.

ONE step in the reaction of 2-nitroethanol with sodium hypobromite to give bromopicrin was shown in Part II[1] to be the fission of 2,2-dibromo-2-nitroethanol by the action of an alkali to give the anion $^-CBr_2NO_2$. This is the reverse of the normal aldol condensation, such as that occurring between formaldehyde and nitromethane to give nitroethanol, and suggests that $^-CBr_2NO_2$ has good leaving properties. On the other hand, an hydroxy-group in the molecule appears to be essential for reaction to occur and the good leaving tendency of $^-CBr_2NO_2$ may not show up in other systems.

This has been examined for the case of CBr_2NO_2 attached to an aromatic ring. Before these results are reported there are a number of interesting mechanistic problems concerning the formation of dibromo(nitro)phenylmethane and related compounds.



(I)



(II)

Dibromo(nitro)phenylmethane (I) is made by the action of sodium hypobromite on α-nitrotoluene.[2] The base-catalysed bromination of numerous nitro-compounds has been studied in detail[3] and the slow step in the reaction is removal of a proton by the base to give an anion. Reaction between the anion and bromine is rapid. This mechanism will certainly apply to the bromination of α-nitrotoluene. The rate of bromination,

$$\mathrm{PhCH_2NO_2} \xrightarrow[\text{slow}]{\mathrm{OH^-}} \mathrm{Ph\bar{C}HNO_2} \xrightarrow[\text{fast}]{\mathrm{Br_2}} \mathrm{PhCHBrNO_2} \qquad (1)$$

therefore, is controlled by the rate of ionisation and, because of the accompanying spectral changes, this reaction is conveniently studied as a measure of the rate of bromination. The effect of a number of substituents in the phenyl ring has been examined as part of an elegant study of isotope effects by Bordwell and Boyle,[4] but it is of interest to extend the range of substituents. Ionisation is a fairly rapid reaction but the rates may be conveniently measured in borax buffers in the pH range 8·0—9·5. Serial dilution of the buffer (at a constant ionic strength of 0·1M) permits

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[1] Part II, R. I. Aylott, A. R. Butler, D. S. B. Grace, and H. McNab, preceding paper.

[2] G. Ponzio, *Gazzetta*, 1906, **38II**, 417.

[3] R. P. Bell and D. M. Goodall, *Proc. Roy. Soc.*, 1966, *A*, **294**, 273; D. J. Barnes and R. P. Bell, *ibid.*, 1970, *A*, **318**, 421.

[4] F. G. Bordwell and W. J. Boyle, *J. Amer. Chem. Soc.*, 1971, **93**, 511.

the rate constant at zero buffer concentration to be determined by extrapolation. The results for *p*-cyano-α-nitrotoluene are shown in Figure 1.

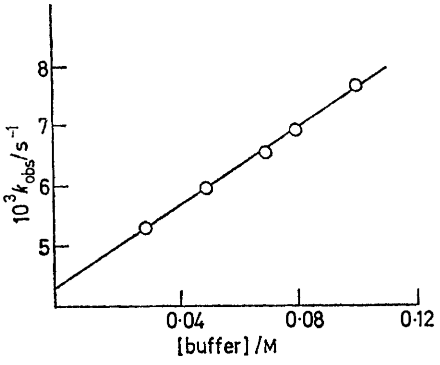

FIGURE 1 Variation of k_{obs} with buffer concentration for the ionisation of *p*-cyano-α-nitrotoluene at pH 8·21 and 25°

The second-order rate constant (k_2) for transfer of a proton from the methylene group to a hydroxide ion was obtained by dividing the rate constant at zero buffer concentration by the hydroxide ion concentration of the buffer. The results for the substituted phenylnitromethanes studied are collected in the Table.

Ionisation of substituted α-nitrotoluenes

Substituent	pH	Intercept $10^3k/s^{-1}$	$10^{-3}k_2/l\ mol^{-1}\ s^{-1}$
p-Me	9·01	2·33	0·229
H	9·01	3·60	0·355
p-Br	8·10	0·990	0·785
p-CN	8·21	4·25	2·62
p-NO_2	8·10	5·75	4·68

For the compounds examined by us and by Bordwell and Boyle[5] (α-nitrotoluene and the *p*-nitro-compound) the agreement is not good. Our values are bigger by a factor of 2 and the reason for this is not clear. Bordwell and Boyle used higher pH values and a stopped-flow technique and this may be a factor. However, there is good agreement about the accelerating effect of the *p*-nitro-group and a plot of log k_2 against σ for the substituent is linear (Figure 2) and the slope (ρ) is 1·31, in close agreement with the value of 1·28 obtained by Bordwell and Boyle,[4] using only *meta*-substituents.

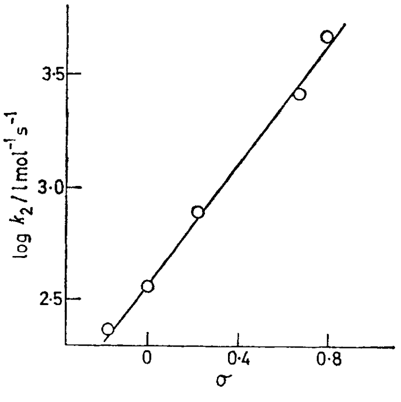

FIGURE 2 Plot of log k_2 against σ for the ionisation of substituted α-nitrotoluenes

The linearity of this plot confirms the surprising observation reported by Bordwell *et al.*[6] for a similar system that, although the α-nitrotoluenes are carbon analogues of the phenols, the exalted values of σ (*i.e.* σ^- values) do not apply to the ionisation of these compounds. There should be extensive direct resonance interaction between the anionic site and a substituent at the *para*-position, unlike the ionisation of substituted benzoic acids, but this does not appear to be the case. One possible explanation for this is that the negative charge is so extensively delocalised over the nitro-group that it is no longer located in a position favourable for resonance interaction with a substituent at the *para*-position of the phenyl ring. The effect of the substituent is then mainly inductive.

Reaction of bromine with the anion produces the monobromo-compound and a second ionisation is necessary before the dibromo-compound can form. Because of the inductive effect of the bromine atom the second ionisation is certain to be faster than the first, but there does not appear to be any measurement of this effect. We have prepared a sample of bromo-(nitro)phenylmethane and measured the rate of ionisation in a buffer of pH 8·07 at varying buffer concentration. The second-order rate constant is $5·30 \times 10^4$ l mol^{-1} s^{-1} and can be compared with a value of $3·55 \times 10^2$ l mol^{-1} s^{-1} for ionisation of α-nitrotoluene itself. Thus, replacing one hydrogen atom by bromine increases the rate of ionisation by a factor of 149.

Having discussed some factors relevant to the formation of dibromo(nitro)phenylmethane we can now consider CBr_2NO_2 as a leaving group. No reaction between 4M-sodium hydroxide solution and the dibromo-compound could be detected, even on warming. Also, no bromopicrin was formed by the reaction of dibromo(nitro)phenylmethane with sodium hypobromite, and it was concluded that, if the CBr_2NO_2 group is to be displaced by a base, the molecule must be activated in some manner but this does not produce the required effect. Even refluxing dibromo(nitro)-*p*-nitrophenylmethane with 1M-sodium hydoxide for 3 h caused no reaction and the starting material was recovered unchanged. Also, recording the spectrum of a methanolic solution of dibromo(nitro)-*p*-nitrophenylmethane ($1·07 \times 10^{-4}$M) and sodium methoxide (0·054M) at timed intervals over several hours gave no indication of reaction.

Although the CBr_2NO_2 group is not easily displaced, it is possible that a Meisenheimer complex might result by the addition of methoxide ion (II). Such a complex would have a distinctive n.m.r. spectrum.[7] However, no change in the n.m.r. spectrum of dibromo-(nitro)-*p*-nitrophenylmethane in methanol was observed on addition of sodium methoxide. Therefore,

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[5] F. G. Bordwell and W. J. Boyle, *J. Amer. Chem. Soc.*, 1972, **94**, 3907.

[6] F. G. Bordwell, W. J. Boyle, and K. C. Yee, *J. Amer. Chem. Soc.*, 1970, **92**, 5926.

[7] M. R. Crampton and M. El-Ghariani, *J. Chem. Soc.* (*B*), 1969, 330.

a Meisenhiemer complex is not formed in detectable amounts. The ready loss of the $^{-}CBr_2NO_2$ anion from 2,2-dibromo-2-nitroethanol, discussed in Part II, is not reflected in its easy replacement in nucleophilic aromatic substitution. This result confirms the important role of the hydroxy-group in the reaction of 2-nitroethanol. Steric factors may also reduce the ease of replacement of CBr_2NO_2 in aromatic systems.

EXPERIMENTAL

Materials.—α-Nitrotoluene was reagent grade and distilled before use. Literature methods were used for the preparation of *p*-methyl- and *p*-nitro-α-nitrotoluene.[8] The *p*-bromo-compound was prepared by refluxing *p*-bromobenzyl bromide (12·5 g) and silver nitrite (9·0 g) in dry ether for 2 h. Silver bromide was filtered off and the ether removed from the filtrate. Recrystallisation from ethanol gave *crystals*, m.p. 46° (50%) (Found: C, 38·8; H, 2·85; N, 6·15. $C_7H_6BrNO_2$ requires C, 38·9; H, 2·8; N, 6·5%). p-*Cyano-α-nitrotoluene* was prepared in a similar manner, m.p. 84° (67%) (Found: C, 58·8; H, 3·65; N, 17·5. $C_8H_6N_2O_2$ requires C, 59·2; H, 3·7; N, 17·3%). Bromo(nitro)phenylmethane was prepared by a method based on that of Wieland and Blümich.[9] The sodium salt of phenylnitromethane was obtained by addition of sodium methoxide [made from sodium (1·7 g) in dry methanol (20 ml)] to a solution of α-nitrotoluene (10·0 g) in dry methanol (20 ml) with cooling and stirring. The precipitate was filtered off, washed with cold methanol, and dried under vacuum (53%). The sodium salt (12·8 g) was suspended in dry ether (25 ml) at 0° and bromine (12·8 g) in chloroform (10 ml) was added over 1 h with stirring. Sodium bromide was filtered off and the solvents were removed from the filtrate to leave a pale yellow liquid, b.p. 103° at 3 mmHg (lit.,[9] 122° at 10 mmHg) (40%). Dibromo(nitro)phenylmethane was prepared as described by Ponzio[2] and purified by steam distillation. Dibromo(nitro)-*p*-nitrophenylmethane was obtained by the addition of α,*p*-dinitrotoluene (1·8 g) a little at a time with stirring to a solution of bromine (3·5 g) in 1M-sodium hydroxide (20 ml). A yellow oil formed, which solidified on standing, and was extracted with ether. The extract was washed and dried, and the ether removed to leave a yellow *solid* which was recrystallised from ethanol, m.p. 45° (44%) (Found: C, 25·05; H, 1·2; Br, 46·7. $C_7H_4Br_2N_2O_4$ requires C, 24·8; H, 1·2; Br, 47·1%).

Kinetic Studies.—One drop of a 1% solution of *p*-nitrotoluene in dioxan was added to borax buffer in a spectrophotometer cell, thermostatted at 25°, in a Unicam SP 500 spectrophotometer. The variation of optical density with time (at the wavelengths indicated below) gave good first-order kinetics over at least three half-lives. The wavelengths used were as follows: α-nitrotoluene (295 nm), *p*-methyl- (260 nm), *p*-bromo- (300 nm), *p*-nitro-α-nitrotoluene (380 nm), and bromo(nitro)phenylmethane (300 nm). On dilution of the buffer the ionic strength was kept at 0·1M by addition of KCl.

[2/1333 *Received, 12th June,* 1972]

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[8] N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *J. Amer. Chem. Soc.*, 1955, **77**, 6269.

[9] H. Wieland and E. Blümich, *Annalen*, 1921, **42**, 75.