Electrophilic Aromatic Substitution. Part XII.[1] The Nitration of 1-Acetamidonaphthalene in Acetic Anhydride, in Acetic Acid, and in Sulphuric Acid

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The kinetics and products of nitration of 1-acetamidonaphthalene in the named solvents are presented. In acetic anhydride and in sulphuric acid the behaviour is similar to that observed for acetanilide, but in acetic acid, nitration occurs *via* nitrosation. Earlier results for the nitration of 1-acetamidonaphthalene are discussed.

IN a recent paper we reported the behaviour of various anilides under different conditions of nitration.[2] In acetic anhydride the rates of nitration of acetanilide and, to a lesser extent, of chloroacetanilide and *N*-methylsulphonylaniline are subject to encounter control. The isomer ratios obtained with these reactive compounds exhibit one of two types of behaviour. With *N*-methylsulphonylaniline ($\frac{1}{2}o:p = 0{\cdot}75:1$) the ratio is close to the statistical value, the result to be expected according to one interpretation of the likely behaviour of a compound reacting at, or close to, the encounter limit.[3] Both acetanilide and chloroacetanilide, on the other hand, show a high $\frac{1}{2}o:p$ ratio ($1{\cdot}7:1$ and $2:1$ respectively), a result attributed to the operation of a special mechanism for *o*-nitration.

The nitration of 1-acetamidonaphthalene has been reported in the literature [4] and, as regards the products formed, it differs from the nitration of acetanilide. As has been pointed out [5] the naphthalide gives under a variety of nitrating conditions the 2- and 4-nitro-compounds in a surprisingly constant ratio ($0{\cdot}37:1$ to $0{\cdot}44:1$), whereas acetanilide gives a $\frac{1}{2}o:p$ ratio which depends markedly on the experimental conditions. The near constancy in the product ratio for the naphthalide recalls the behaviour of trifluoroacetanilide, which shows little difference in the $\frac{1}{2}o:p$ ratio for nitration in 80% sulphuric acid and in acetic anhydride, the value [2] in the latter solvent being $0{\cdot}26:1$. Kinetic studies show that trifluoroacetanilide, unlike acetanilide (which reacts at the encounter rate), is relatively unreactive being nitrated in acetic anhydride only *ca.* 6 times faster than benzene. It would be surprising if the similarity between 1-acetamidonaphthalene and trifluoroacetanilide as regards product ratios were a consequence of relative unreactivity of the naphthalide. Indeed, preliminary kinetic studies in acetic anhydride indicated that 1-acetamidonaphthalene reacted at about the same rate as mesitylene, and was therefore being nitrated at the encounter rate. The reported behaviour of 1-acetamidonaphthalene thus stands in marked contrast to that of acetanilide. Of particular interest is the implication that substantial positional selectivity can be maintained in an encounter controlled reaction. We therefore considered it desirable to reconsider the results for the nitration of 1-acetamidonaphthalene and to supplement the product studies with kinetic measurements.

EXPERIMENTAL

Materials.—AnalaR acetic anhydride, glacial acetic acid, and sulphuric acid (98%, *d* 1·84) were used without further purification. Pure nitric acid was prepared by vacuum distillation from a solution of fuming nitric acid in an equal volume of conc. sulphuric acid. Solutions of sulphuric acid for the kinetic measurements were prepared by the dilution of the AnalaR acid with the appropriate amounts of distilled water; the solutions were standardised by density measurements. 1-Acetamidonaphthalene, m.p. 160—161 °C (from aqueous ethanol) (lit.,[6] 160 °C), was prepared by the action of acetic anhydride on 1-naphthylamine in glacial acetic acid. 1-Acetamido-2-nitronaphthalene, m.p. 199—199·5 °C (from absolute ethanol) (lit.,[4] 199—200 °C), 1-acetamido-4-nitronaphthalene, m.p. 189—190 °C (from absolute ethanol) (lit.,[6] 190 °C), and 4-nitro-1-naphthylamine, m.p. 195—196 °C (from absolute ethanol) (lit.,[4] 193—194 °C) were prepared by the method of Hodgson and Walker.[4] 2-Nitro-1-naphthylamine, m.p. 144—145 °C (from absolute ethanol) (lit.,[4] 143—144 °C) was prepared by the hydrolysis of 1-acetamido-2-nitronaphthalene.[5]

Kinetic Measurements.—Changes of the absorbance with time of the reacting solutions were observed in a Unicam SP 800 spectrophotometer fitted with a thermostatted cell

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[1] Part XI, S. R. Hartshorn, J. G. Hoggett, R. B. Moodie, K. Schofield, and M. J. Thompson, *J. Chem. Soc.* (*B*), 1971, 2461.

[2] S. R. Hartshorn, R. B. Moodie, and K. Schofield, *J. Chem. Soc.* (*B*), 1971, 2454.

[3] S. R. Hartshorn, R. B. Moodie, K. Schofield, and M. J. Thompson, *J. Chem. Soc.* (*B*), 1971, 2447.

[4] H. H. Hodgson and J. Walker, *J. Chem. Soc.*, 1933, 1205.

[5] E. R. Ward and R. P. Wells, *J. Chem. Soc.* 1961, 4859.

[6] 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, vol. 4, 1965.

holder (25·0 ± 0·1 °C), as described in earlier papers for acetic anhydride,[7] acetic acid,[3] and sulphuric acid solutions.[8]

Product Studies.—Under the conditions of nitration used, the only major products were 2- and 4-nitro-1-acetamidonaphthalene. The same general methods were used to determine the isomer proportions for each of the different reaction conditions studied. After nitration was complete, the reaction solution was quenched in ice-cold water which was then extracted with ether. The combined ether extracts were evaporated and the solid residue was washed with water and dried. The u.v. extinction curve of the mixture of nitration products was measured in methanol, and the isomer proportions were determined by fitting a curve, calculated from the known spectra of the pure isomers, to that of the reaction mixture over the range 275—400 nm. As a check on this method of analysis, the mixture of nitro-1-acetamidonaphthalenes was hydrolysed, using the procedure of Ward and Wells [5] (ethanol–54% sulphuric acid), to give, in quantitative yield, a mixture of the corresponding nitro-1-naphthylamines. The composition of this latter mixture was determined by u.v. analysis, as described above, but using the range 250—460 nm for the curve fitting. The extraction procedures, the method of hydrolysis, and the methods of analysis were shown to be satisfactory by using synthetic mixtures of the pure isomers. An independent check on the isomer proportions was available from the ^{1}H n.m.r. spectrum of the products measured in [$^2H_6$]DMSO at 60 MHz. The methyl peaks were sufficiently resolved in the spectrum to enable a rough estimate of the product composition to be made.

TABLE 1

First-order rate constants for the nitration of 1-acetamidonaphthalene [a] in acetic anhydride at 25 °C

$[HNO_3]_0$/mol l^{-1}	10^3k_1/s^{-1}	$[HNO_3]_0$/mol l^{-1}	10^3k_1/s^{-1}
0·077	0·448	0·117	1·23
0·098	0·790	0·149	2·61
0·115	1·34	0·151	2·69

[a] [Aromatic] = *ca.* 10^{-4} mol l^{-1}, wavelength for measurement 345 nm.

RESULTS

Nitration in Acetic Anhydride.—An almost quantitative yield (96%) of mononitration product was obtained in a preparative reaction. The isomer proportions, determined by u.v. analysis, were 70 ± 5 and 30 ± 5% of 2-nitro-1-acetamidonaphthalene and 4-nitro-1-acetamidonaphthalene, respectively. The use of fuming nitric acid to prepare the solutions of acetyl nitrate made no appreciable difference, either to the yield or to the isomer proportions. The results obtained from kinetic measurements are shown in Table 1. Good first-order kinetics were observed in all cases and the rate of nitration showed the expected [1,7] third-order dependence on the stoicheiometric concentration of nitric acid. A comparison of rate profiles showed 1-acetamidonaphthalene and mesitylene to be about equal in reactivity [k(mesitylene)/k(acetamidonaphthalene) = 1·37], a result which we take to indicate that 1-acetamidonaphthalene reacts at the encounter rate in this medium.

Nitration in Acetic Acid.—The products of nitration were determined for several different reaction conditions in both glacial acetic acid and aqueous acetic acid. Under all the conditions studied u.v. analysis showed the isomer proportions to be 30 and 70% of 2-nitro-1-acetamidonaphthalene and 4-nitro-1-acetamidonaphthalene, respectively. In glacial acetic acid the nitration was accompanied by the formation of a brown colouration and yields of the mononitration products were low (*ca.* 85%). The same results were obtained using either pure or fuming nitric acid [HNO_3]$_0$ = *ca.* 8 mol l^{-1}), with or without added urea. In aqueous acetic acid solutions (containing 10—25 w/w % of water) the brown colouration did not form during the reaction and the yields of mononitration products were higher (>90%). Kinetic measurements in a solution containing 25 w/w % of water ([HNO_3]$_0$ = 8·10 mol l^{-1}; [urea] = 0·05 mol l^{-1}) showed 1-acetamidonaphthalene to be much more reactive than mesitylene, and the approximate ratio of rate constants, k(1-acetamidonaphthalene)/k(mesitylene) > 10^3, was obtained. In another set of experiments 1-acetamidonaphthalene was nitrated smoothly during 30 min in a medium containing 23 w/w % of water ([HNO_3]$_0$ = 3·0 mol l^{-1}) to give an almost quantitative yield of mononitration products. Repeating the experiment using the identical conditions, but with added urea (0·04 mol l^{-1}), gave no detectable nitration products after 13 h. Addition to this solution of a catalytic amount of sodium nitrite produced a very rapid change in the u.v. spectrum of the reacting solution, giving finally a u.v. spectrum that was consistent with the formation of nitration products. This experiment was repeated using higher concentrations of nitric acid (6—9 mol l^{-1}), but with these concentrations it was not found possible to suppress the nitration by adding urea (up to 0·08 mol l^{-1}). We conclude from these results that under all conditions of nitration in acetic acid, nitration of 1-acetamidonaphthalene occurs *via* nitrosation.

Nitration in Sulphuric Acid.—Product studies were attempted over the range of acidity 70—92% sulphuric acid, but nitration was accompanied by the formation of tarry impurities. Further, both 2- and 4-nitro-1-acetamidonaphthalenes were found themselves to react, presumably undergoing further nitration, over the acidity range studied. The yields of mononitration products that were isolated varied between 50 and 80%, and u.v. analysis of these gave very variable isomer proportions (40 ± 15 and 60 ± 15% of 2-nitro-1-acetamidonaphthalene and 4-nitro-1-acetamidonaphthalene respectively). The further reactions of the mononitration products were not investigated. Despite the lack of success with the product studies, good kinetic results were obtained (Table 2). At the wavelength used for the kinetic measurements (345 nm) there was no appreciable change in the u.v. spectrum for the further reaction of the mononitration products during the time taken for the kinetic measurements. The rate profile was

TABLE 2

Second-order rate constants for the nitration of 1-acetamidonaphthalene [a] in sulphuric acid at 25 °C

H_2SO_4 (%)	$10^3[HNO_3]$/mol l^{-1}	k_2/l mol^{-1} s^{-1}
65·8	2·68	$8·50 \times 10^{-3}$
68·4	3·07	$4·07 \times 10^{-2}$
70·0	36·3	$1·35 \times 10^{-1}$
73·3	1·83	1·89
75·5	0·72	10·7

[a] [Aromatic] = *ca.* 10^{-4} mol l^{-1}, wavelength for measurement 345 nm.

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[7] S. R. Hartshorn, R. B. Moodie, and K. Schofield, *J. Chem. Soc.* (*B*), 1971, 1256.

[8] R. G. Coombes, R. B. Moodie, and K. Schofield, *J. Chem. Soc.* (*B*), 1968, 800.

parallel to those obtained for the acetanilides,[2] and fell close to the rate profile for the nitration of benzene. However, it cannot be argued that for this reason the cation of 1-acetamidonaphthalene (the species probably undergoing mononitration) is about as reactive as benzene because the rate profile is probably composite. This restriction is necessary, not because of the kinetic results (since the further reaction of the mononitro-compounds caused no significant spectral change at the relevant wavelength) but because the source of the deficiency in yield has not been established.

DISCUSSION

Our results for the nitration of 1-acetamidonaphthalene in acetic anhydride, and, within the limitation mentioned above, in sulphuric acid, follow the pattern of behaviour shown by acetanilide.[2] Thus in acetic anhydride, 1-acetamidonaphthalene undergoes nitration at the limiting rate and shows a high 2 : 4 ratio (2·3 : 1); this observation we take to mean that the special mechanism of nitration at the 2-position is operating, as with acetanilide. In sulphuric acid, the overall rate of nitration is about equal to that of benzene and more of the 4-isomer is formed; the 2 : 4 ratio is *ca.* 0·67 : 1. These observations are both consistent with the occurrence of mononitration through the protonated form of the substrate in this medium. The ratio of products formed in acetic anhydride determined by us does not agree with that reported previously (0·44 : 1).[4] However, this may not be a real discrepancy, since in the earlier work $Cu(NO_3)_2$ was used as the nitrating agent.

The nitration of 1-acetamidonaphthalene in acetic acid gives mainly the 4-isomer (the 2 : 4 ratio is 0·43 : 1), and our results are in good agreement with the earlier work. We would expect from our earlier studies[3] that a compound which reacts at the encounter rate in acetic anhydride would also react at the encounter rate in acetic acid. However, the rate of reaction of 1-acetamidonaphthalene in acetic acid was $>10^3$ that of mesitylene; the effect of added urea and of added nitrite (see Results section) demonstrates that nitrosation was occurring. This last observation suggests an explanation of the earlier results; it is, that under all the conditions previously studied nitration was occurring *via* nitrosation, and this was the cause of the constancy of the product ratios.

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