540. *Nitration in Sulphuric Acid. Part IX.* The Rates of Nitration of Nitrobenzene and Pentadeuteronitrobenzene.*

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Within the limits of experimental error, the rates of nitration of nitrobenzene in 97·4% and in 86·7% sulphuric acid are identical with the rates of nitration of pentadeuteronitrobenzene in the same media. These results confirm Melander's demonstration (*Arkiv Kemi*, 1950, **2**, 211) that breakage of the C–H bond is not part of the rate-determining step in aromatic nitration, and extend it to more highly acid nitrating conditions.

MELANDER has shown (*Nature*, 1949, **163**, 599; *Arkiv Kemi*, 1950, **2**, 211) that the radioactive intensities in the products of nitration of benzene, toluene, bromobenzene, and naphthalene, each containing one appropriately situated nuclear tritium atom, are consistent only with the supposition that nitration at C–T and C–H bonds takes place at approximately the same speed. Melander derived minimum values for the velocity coeffient ratios k_T/k_H for all stages of the nitrations and found them to lie between 0·74 and 0·85. It follows that the breakage of the C–H bond does not form part of the rate-determining step in aromatic nitration under the conditions of these experiments.

This conclusive result applies, in the first instance, to experimental conditions nearer to those of preparative nitration, with relatively high proportions of nitric acid and aromatic compound to sulphuric acid, and with moderately aqueous nitrating mixtures, than to the conditions of the kinetic nitration experiments in homogeneous systems initiated by Martinsen (*Z. physikal. Chem.*, 1904, **50**, 385; 1907, **59**, 605). In Melander's experiments, naphthalene was nitrated with a nitric acid–water mixture; but mixtures of nitric acid (*d* 1·40—1·42) and sulphuric acid (96—96·6%) were used for the other three compounds, and reaction was continued to the dinitration stage. Calculation from the quantities used gives typical reaction mixtures as approximately: benzene 0·0055, HNO_3 0·043, H_2SO_4 0·099, H_2O 0·085 mole, molar ratio $H_2O/H_2SO_4 = 0·86$; and toluene 0·0046, HNO_3 0·053, H_2SO_4 0·124, H_2O 0·104 mole, molar ratio $H_2O/H_2SO_4 = 0·84$. In these nitrations, only the conversion of nitrobenzene into *m*-dinitrobenzene requires a sulphuric acid–water mixture acid enough to convert a considerable proportion of nitric acid into nitronium ion (Hetherington and Masson, *J.*, 1933, 105; Bonner, James, Lowen, and Williams, *Nature*, 1949, **163**, 955; Williams and Lowen, *J.*, 1950, 3312). The molar ratio H_2O/H_2SO_4 in the acid employed corresponds to a nitration medium considerably more aqueous than the medium ($H_2O/H_2SO_4 \sim 0·58$) giving maximum rate in the homogeneous nitration of nitrobenzene (Bonner *et al.*, *loc. cit.*). Oleum was used in the nitrating acid for bromobenzene but here also the molar ratio H_2O/H_2SO_4 was not less than 0·79.

Nitrating acids with these relatively high water (and nitric acid) contents must contain considerable concentrations of the basic species bisulphate ion; and the conditions of nitration are different from those prevailing in kinetic nitration experiments in homogeneous solution in concentrated sulphuric acid (Part IV, *J.*, 1947, 474; Part VIII, *loc. cit.*). For example, the reaction mixture in 97·4% sulphuric acid (see Table) has the composition: nitrobenzene 0·0075, HNO_3 0·0017, H_2SO_4 0·909, H_2O 0·132 mole, molar ratio $H_2O/H_2SO_4 = 0·145$. It is in the most acid conditions, if anywhere, that the separation of the proton might have kinetic significance in nitration.

In order to put it beyond doubt that Melander's demonstration, that there is no hydrogen isotope effect in nitration, applies also to highly acid conditions, we have compared directly the rates of nitration of nitrobenzene and pentadeuteronitrobenzene, with small reagent concentrations, in homogeneous solution. In the media employed the rates of nitration are given by the equation $-d[HNO_3]/dt = k_2[ArNO_2][HNO_3]$, since $\log\{[ArNO_2]/[HNO_3]\}$ is linear with time (see Figure). The final results for velocity coefficients are given in the Table. The observed identity of nitration rate for nitro-

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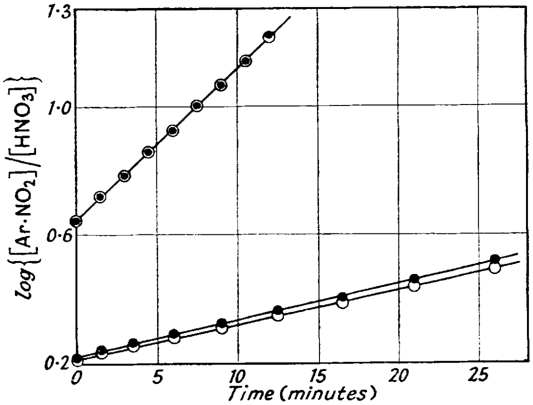
benzene and pentadeuteronitrobenzene, in both media, is not likely to have been simulated through isotope exchange between aromatic compound and nitrating acid; because (*a*) it could only be due *either* to genuine identity of nitration rate at C–H and C–D bonds *or* to complete transfer of deuterium from aromatic ring to nitrating acid before measurements were started; (*b*) rapid deuterium exchange between a nitro-aromatic compound and sulphuric acid is improbable (cf. Ingold, Raisin, and Wilson, *J.*, 1936, 915, 1637); and (*c*) we have found that pentadeuteronitrobenzene does not change its density after exposure to 97·3% sulphuric acid, at 20°, for a longer time than that required for the nitration experiments (see Experimental section).

Rates of nitration at 25° (k_2 in l. mole^{-1} min.$^{-1}$; concentrations in terms of M).

Medium H_2SO_4, %	Expt. No.	Nitrobenzene $[C_6H_5{\cdot}NO_2]$	Nitrobenzene $[HNO_3]$	k_2	Expt. No.	Deuteronitrobenzene $[C_6D_5{\cdot}NO_2]$	Deuteronitrobenzene $[HNO_3]$	k_2
97·4	130	0·1498	0·03402	0·941	129	0·1498	0·03442	0·938
	132	0·1498	0·03419	0·954	131	0·1498	0·03397	0·942
86·7	133	0·05015	0·03040	1·34	135	0·04963	0·03056	1·29
	134	0·05023	0·03205	1·33	136	0·05017	0·02998	1·27



Nitration of: ● *nitrobenzene.*
○ *pentadeuteronitrobenzene.*

Earlier results, with a less exactly characterised specimen of pentadeuteronitrobenzene, pointed to the same general conclusion as the results in the Table. With k_H and k_D referring, respectively, to replacement of protium and deuterium atoms, the results were: in 97·9% sulphuric acid (0·025M-Ar·NO$_2$), k_H = 0·74; k_D = 0·67, 0·69. In 97·6% sulphuric acid (0·15M-Ar·NO$_2$), k_H = 0·87, 0·89; k_D = 0·82, 0·84.

We are indebted to Dr. J. C. D. Brand, of the University of Glasgow, for the results of measurements of nitration velocity (made by following the change in extinction coefficient, Brand and Paton, *J.*, 1952, 281) for the same sample of pentadeuteronitrobenzene in 10% oleum (102·25% H_2SO_4). With excess of nitric acid (0·108 molal) and 9 × 10^{-5} molal concentration of aromatic compound, the first-order nitration velocity coefficients were: for $C_6H_5{\cdot}NO_2$, k_1 = 0·0344, 0·0341; for $C_6D_5{\cdot}NO_2$, k_1 = 0·0320, 0·0323. In this medium, the greater part (75—80%) of the aromatic compound exists as its (cation) conjugate acid. It is not certain that the extent of cation formation is the same for the protium and deuterium compounds.

If the whole of the difference between the zero-point energies of a C–H and of a C–D bond (*ca.* 2 kcal./mole) were to influence nitration rates, then the ratio k_D/k_H could be as low as 0·035. It is clear, even in the most acid media, that the fission of the C–H bond does not help to determine rate of nitration (cf. Melander, *loc. cit.*). The hypothesis of bisulphate-ion catalysis (Part IV, *loc. cit.*) cannot be sustained.

EXPERIMENTAL

Preparation of Pentadeuteronitrobenzene.—Hexadeuterobenzene was prepared by the method of Ingold, Raisin, and Wilson (*loc. cit.*; Best and Wilson, *J.*, 1946, 239). 10 ml. of benzene

(B.D.H. " for molecular weight determinations "; distilled from phosphoric oxide; d_{25}^{25} 0·8760) were shaken for 5 days with 60 g. of deuterosulphuric acid, containing 51 moles % of D_2SO_4 and 49 moles % of D_2O, made by distilling sulphur trioxide (80 g.) into 35 ml. of Norsk Hydro Heavy Water, containing 99·75 atoms % of D, standardising the product by titration with 0·1N-sodium hydroxide, and final adjustment to 83·8% (w/w) D_2SO_4 by distilling in a further 11·4 g. of sulphur trioxide. After this first shaking, the benzene was distilled away and shaken a second time for 5 days with a fresh portion (60 g.) of the same acid. It was then distilled (*a*) on to dry barium oxide, (*b*) after several hours, on to phosphoric oxide, and (*c*) after 3 hr., into a clean receiver. At this stage the benzene had d_{25}^{25} 0·09421, corresponding to a content 92·0 atoms % of D. It was then shaken a third time for 5 days, but this time with 60 g. of 83·8% deuterosulphuric acid prepared from heavy water containing 99·95 atoms % of D. It was then treated with barium oxide and phosphoric oxide as before. It now had d_{25}^{25} 0·9456 corresponding to content 99·3 atoms % of D (Weldon and Wilson, *J.*, 1946, 235); the yield was 5·7 g.

All the benzene distillations referred to were conducted in all-glass apparatus, with oil-pump vacuum, and with appropriate heating baths and refrigerants. In the preparation of deuterosulphuric acid (cf. Best and Wilson, *loc. cit.*), it was found satisfactory to distil sulphur trioxide slowly (without vacuum) from a vessel attached by a ground joint, through a capillary, into two flasks in series, cooled by ice–water, one empty and one containing deuterium oxide, protected from the atmosphere, through a capillary, by a sulphuric acid trap. Sulphur trioxide was driven from the first flask into the heavy water after sealing off the first capillary; and the apparatus was isolated by sealing off the second.

Nitration of Hexadeuterobenzene.—Preliminary experiments with ordinary benzene showed the nitration procedure described by Masson (*Nature*, 1931, **128**, 726) to be the most profitable in yield, though a slightly more aqueous nitrating acid was found to be advantageous in excluding all dinitration. To minimise the (small) risk of isotope exchange during nitration, the nitrating acid was made up with deuterosulphuric acid. The composition was D_2SO_4 (18·4 g.), H_2O (3·14 g.), anhydrous HNO_3 (5·29 g.). Into this were run in, during 70 min., 5·7 g. of hexadeuterobenzene through a capillary, the temperature being kept at 45°, and the reaction flask being shaken throughout. Shaking, still at 45°, was continued for a further 230 min. The temperature was raised to 60° at the end of the reaction, after which the reaction mixture was poured into water, and the product was separated, washed with sodium carbonate solution and then with water, dried with phosphoric oxide and distilled. The yield was 7·7 g. (88·9%). After two distillations a middle fraction (5·5 g.; b. p. 64—65°/5 mm., 215—217°/711 mm.) of very faintly yellow *pentadeuteronitrobenzene* was collected (Found: N, 11·1. $C_6D_5O_2N$ requires N, 10·9%). It had d_{25}^{25} 1·2533 and n_D^{20} 1·5504.

Deuterium Content.—We are very much indebted to Dr. R. I. Reed of the University of Glasgow for a mass-spectrographic examination of the water formed by combustion of our product. The result showed its deuterium content to be $>$99·5 atoms %.

Nitrobenzene.—" AnalaR " material was dried and distilled and purified by fractional crystallisation to constant m. p. 5·82°.

Velocity Measurements.—The rate of nitration was followed by measuring the residual nitric acid concentration at known time intervals. The methods of experiment and of analysis of reaction mixtures and media were as described in Part VIII (Bonner, Bowyer, and Williams, *loc. cit.*).

Test for Deuterium Exchange during Nitration.—A specimen of pentadeuteronitrobenzene (2·3 g.) was dissolved in 97·3% sulphuric acid (5 ml.) and kept at 20° for 1·75 hr. It was then recovered by dilution with 16 ml. of water, repeated extraction with ether, repeated washing with water, drying, and distillation under reduced pressure. The material had d 1·2520 and 1·2518, respectively, before and after exposure to sulphuric acid. Since ordinary nitrobenzene has d^{25} 1·198, deuterium exchange with sulphuric acid during a nitration experiment (requiring $<$30 min.) is evidently inappreciable.

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