The Borderline between the Classical and the Electron Transfer Process in Nitration by the Nitronium Ion

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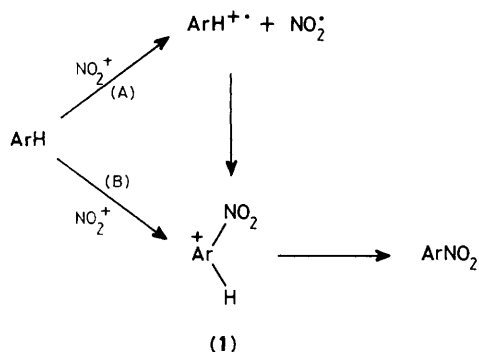[a] Chemistry Department, University College, 20 Gordon Street, London WC1H 0AJ, U.K.

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[15]N N.m.r. studies indicate that the electron transfer process makes a small but significant contribution to the nitration of naphthalene by the nitronium ion.

There has recently been considerable discussion[1] of the relative importance of the electron-transfer path in aromatic nitration (Scheme 1, path A) compared with the 'classical' mechanism (Scheme 1, path B). The earlier evidence[2] for the electron transfer path in the nitration of napthalene has been shown to be invalid by Eberson and Radner[1] and calculations based on Marcus theory suggest that the extent of reaction by this path should be negligible for compounds of the reactivity of naphthalene, mesitylene, and durene.[1] For naphthalene, the calculated rate coefficient[1] for path A is 1.3×10^{-6}
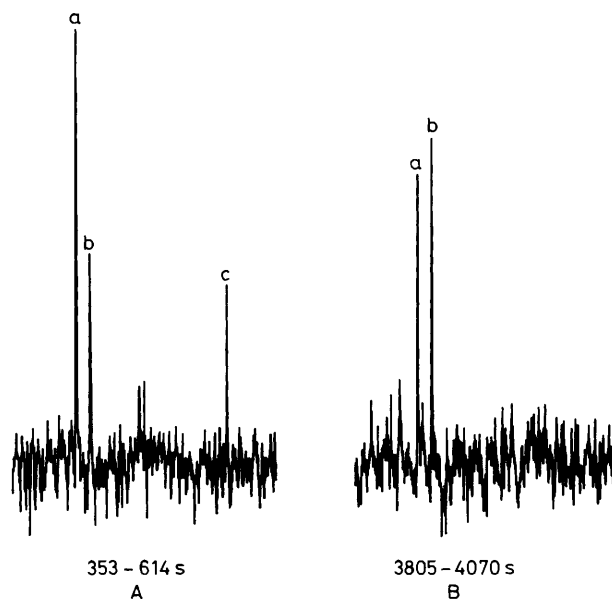
Scheme 1

Figure 1. ^{15}N N.m.r. spectra taken during the nitration of naphthalene (0.252 mol kg^{-1}) by [^{15}N]nitric acid (0.326 mol kg^{-1}) in the presence of sodium azide (0.272 mol kg^{-1}), methanesulphonic acid (0.905 mol kg^{-1}) and [^{15}N]nitrobenzene (standard; 0.281 mol kg^{-1}) at 29 ± 1 °C. Solvent composition: trifluoroacetic acid, 48.9; nitromethane, 50.1; deuterium oxide 1%. Spectrum A *ca.* 1 half-life; spectrum B *ca.* 10 half-lives. Peaks: a 1-nitronaphthalene; b standard; c nitric acid. The spectra involved 24 pulses, pulse repetition time 10.8 s, pulse angle 45°.

mol^{-1} s^{-1} dm^3; the observed rate coefficient for the overall reaction is very near the encounter rate[3] (*ca.* 10^9 mol^{-1} s^{-1} dm^3 in 60% sulphuric acid).

Our previous work on ^{15}N C.I.D.N.P. effects in nitration was in agreement with this for our preliminary studies on naphthalene gave no obvious C.I.D.N.P. effect and the marked effect seen with durene could be ascribed to the homolytic fission of the *ipso*-intermediate formed.[4] However, we have now re-examined the nitration of mesitylene and naphthalene using faster reaction rates (permitting a more sensitive test for C.I.D.N.P. effects) and have found slight but significant nuclear polarisation in the nitration of naphthalene; there is still no evidence for nuclear polarisation in the nitration of mesitylene. The presence of this nuclear polarisation with napthalene is shown clearly by the decrease in the ^{15}N n.m.r. signal for the product (relative to the standard) during reaction (Figure 1).
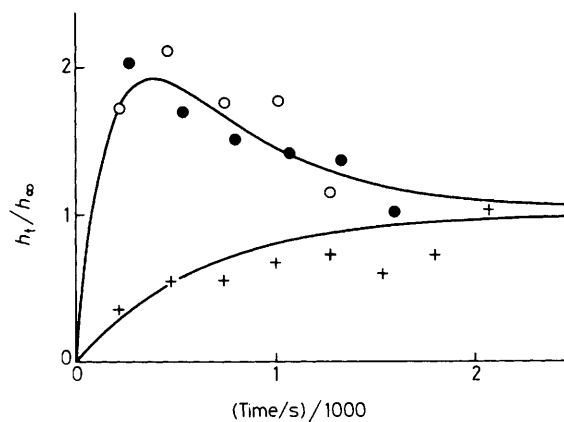
The extent of nuclear polarisation in the nitration of naphthalene has been assessed by fitting the observed result to theoretical curves[5] based on the first-order rate coefficient,† the relaxation time, and an enhancement coefficient (defined as the factor by which the signal is enhanced at the time when the product is first formed[5]). The results for naphthalene (Figure 2) accord with an enhancement coefficient of 10, while those for mesitylene correspond to an enhancement coefficient of unity; *i.e.*, to the absence of nuclear polarisation.

The enhancement coefficient for naphthalene is only *ca.* 2% of that in the rearrangement of 4-methyl-4-nitrocyclohexa-2,5-dienone,[6] a reaction believed to occur entirely through NO$_2$ radicals.[7] This suggests that only a small part of the naphthalene reacts by the electron transfer pathway but this is still very much greater than the amount predicted by the Marcus theory calculations.[1] The discrepancy cannot be explained by the incursion of nitrous acid-catalysed nitration since this gives nuclear polarisation of the opposite phase.[4] The nuclear polarisation cannot be derived indirectly from reactions involving the solvent and the other solutes present since it is absent from the nitration of mesitylene when carried out under the same conditions. The nuclear polarisation does not appear to derive from homolytic fission of the C–N bond in the Wheland intermediate (1) for the extent of such a process, and the consequent C.I.D.N.P. effects, should be greater with [^{2}H$_8$]naphthalene and this is not observed (Figure 2). Molecular orbital calculations (MNDO and MINDO3) suggest that the extent of attack at the bridging carbon atoms of naphthalene is insignificant.

† Under the experimental conditions, the rate of formation of the nitronium ion is rate-determining and so the same rate coefficient (determined from ^{1}H n.m.r. studies) is applicable to all the substrates used.

Figure 2. The experimental peak height ratios (relative to the standard) and the theoretical plots for the nitration of naphthalene, [^{2}H$_8$]naphthalene, and mesitylene under the conditions stated in Figure 1. The theoretical plots are calculated using a rate coefficient of 1.6 × 10^{-3} s^{-1}, a relaxation time of 170 s and an enhancement coefficient of 10 (naphthalene) and 1 (mesitylene). ○ naphthalene, ● [^{2}H$_8$]naphthalene, + mesitylene.

We conclude therefore that the difference between mesitylene (E^0 2.43 V) and naphthalene (E^0 2.08 V) derives from the greater ease of oxidation of the latter and that naphthalene represents the stage at which the electron transfer process (Scheme 1, path A) begins to become significant. The discrepancy with the Marcus theory calculations may come in part from the solvent dependence of E^0 for the nitronium ion and in part because significant interaction between the reactants precedes the electron transfer.

References

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