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Nitration of Aromatics *via* Electron Transfer; the Relevancy of Experiments Involving Generation of Naphthalene Radical Cation in the Presence of Nitrogen Dioxide

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The electron transfer mechanism for electrophilic aromatic nitration involves an initial electron transfer from the substrate to the nitronium ion thus creating a radical cation/radical (NO_2) pair which eventually collapses to the Wheland intermediate. Experimental evidence for this hypothesis has previously been sought from the oxidative (*e.g.*, anodic) generation of a radical cation in the presence of nitrogen dioxide.

It is now shown that the nitration of naphthalene observed in such an electrochemical experiment is predominantly, if not exclusively, due to the homogeneous nitration of naphthalene by dinitrogen tetroxide, catalyzed by anodically generated acid.

It has been repeatedly suggested [1–5] that electrophilic aromatic substitution reactions in many cases might follow a mechanism involving initial one-electron oxidation of the substrate by the electrophile, followed by radical coupling of the radicals formed. Most recently, Perrin [5] postulated the necessity of initial electron transfer (ET) and ensuing radical pair collapse in the nitronium ion mediated nitration of all aromatics more reactive than toluene (eqn. 1). The energetics of the ET process was determined from the anodic half-wave potentials in acetonitrile of NO_2 (1.82 V *vs.* the Ag/0.01 M Ag^+ reference electrode) and a few typical aromatic compounds (naphthalene 1.34 V, anisole 1.4 V, mesitylene 1.62 V, *o*-xylene 1.68 V, and toluene > 1.9 V). Since ET between species of the type involved in eqn. (1) is known [6] to be diffusion controlled whenever the ET is exothermic, Perrin's proposal is indeed an eminently sound one, capable as it is to resolve the paradox of intramolecular selectivity in aromatic nitration without intermolecular selectivity.[7] This mechanism also provides a simple explanation for many of the side-reactions encountered in aromatic nitration,[8,9] such as side-chain nitrooxylation, acetoxylation, acetamidation and alkoxylation, nuclear oxynitration and biaryl coupling, all reactions known from the anodic chemistry of aromatics and shown to be mediated by radical cations.[10]

While we wholeheartedly concur with Perrin's proposal and in fact have suggested that it might apply to other reactions as well,[11] we have however certain reservations about his key experiment, the controlled potential electrolysis of naphthalene (at 1.3 V) in acetonitrile in the presence of nitrogen dioxide. The rationale of this experiment is to show that $(naphthalene)^{+\cdot}$, generated at an anode potential incapable of oxidizing nitrogen dioxide (with $E_{1/2}$ equal to 1.8 V) couples with nitrogen dioxide to give a mixture of nitronaphthalenes with approximately the same α/β ratio (9.2 ± 1) as that observed in the nitration of naphthalene with nitric acid/sulfuric acid in the presence

$$NO_2^+ + ArH \xrightarrow[\text{controlled}]{\text{Encounter}} \overline{NO_2 + ArH^{+\cdot}} \longrightarrow \overset{+}{Ar}\begin{matrix} H \\ NO_2 \end{matrix} \qquad (1)$$

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of urea on acetonitrile (10.9±1). We now report that the nitration observed in the electrolytic experiment in all likelihood is due to a homogeneous reaction between naphthalene and nitrogen dioxide, catalyzed by anodically generated hydrogen ion.

RESULTS

Since nitrogen dioxide (and/or dinitrogen tetroxide which is the predominant species in acetonitrile solution[12,13d]) is known[13] to cause nitration of aromatics *via* nitrosation we first studied the homogeneous nitration of naphthalene by nitrogen dioxide in acetonitrile; to simulate the electrolysis conditions as closely as possible the experiments were performed in the presence of the supporting electrolyte used, lithium tetrafluoroborate (0.1 M). Initially, the reaction gave erratic results but it was soon established that the water contents of the acetonitrile was a critical factor. In dry acetonitrile[14] a reasonably fast nitration reaction takes place (absolute yields of nitronaphthalenes after 3 and *ca.* 20 h 7±2 and 26±5 %, respectively) but this is slowed down considerably by small concentrations of water,

Table 1. Nitration of naphthalene by nitrogen dioxide in acetonitrile, 0.1 M in lithium tetrafluoroborate; $[NO_2]=[naphthalene]=0.2$ M, temperature 25 °C.

Additive	Yield of nitronaphthalenes, relative to control		Isomer ratio, α/β
	After 1 h	After *ca.* 20 h	After *ca.* 20 h
None	1.0 [a]	1.0 [b]	25±3
Water, 0.005 M	0.7	0.7	31
Water, 0.013 M	0.6	0.7	23
Water, 0.025 M	0.5	0.9	23
CF_3SO_3H, 0.004 M	3.4	1.4	23
CF_3SO_3H, 0.008 M	5.4	1.8	24
Pyridine, 0.01 M	0.3	0.6	21
Pb(II) nitrate, 0.005 M	1.1	1.0	18
Fe(III) nitrate, 0.005 M	0.8	0.7	23
Pt on C (5 %) [c]	0.9	0.9	23

[a] Absolute yield 7±2 % (average of four experiments). [b] Absolute yield 26±5 % (average of five experiments). [c] *Ca.* 50 mg were added to 50 ml of the solution.

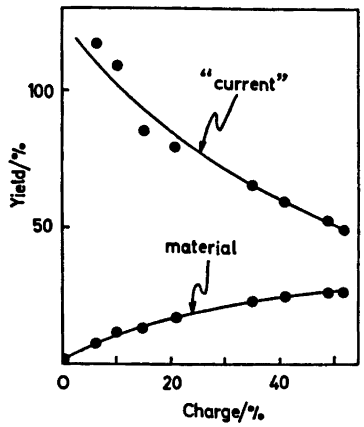

Fig. 1. Yield of nitronaphthalenes *vs.* charge passed through a solution of nitrogen dioxide (0.2 M), naphthalene (0.2 M) and lithium tetrafluoroborate (0.1 M) in acetonitrile at 25 °C.

especially in the initial phase of the reaction (see Table 1) which is the interesting one in view of the normal time-scale of an electrolysis experiment (up to 3 h). Also a base like pyridine has a retarding effect, whereas addition of a strong acid (trifluoromethanesulfonic acid) has a pronounced catalytic effect. The effect of a few other additives, suspected as possible contaminants [Pb(II), Fe(III)] or necessarily present in the electrolysis experiment (Pt) was studied but no significant influence was revealed. The α/β isomer ratio was approximately independent of the added reagents.

Next electrochemical experiments at controlled potential were performed in an undivided cell, using platinum electrodes. The working potential in all cases was chosen to be at least 0.2 V less than that required for oxidation of nitrogen dioxide. Fig. 1 shows the results of such an electrolysis; the material and "current" yield of nitronaphthalenes are plotted *vs.* the amount of charge passed [calculated for 1 F mol^{-1} of naphthalene, corresponding to the stoichiometry of eqn. (1)]. Table 2 gives the corresponding α/β ratios. In the early stages of the run the "current yield" is larger than 100 %, indicative of a homogeneous process which at least in this region is outrunning any possible electrochemical nitration process. In order to show this more clearly, Fig. 2 shows time plots of the "electrochemical" nitration

Table 2. Electrolysis of a solution of nitrogen dioxide (0.2 M), naphthalene (0.2 M) and lithium tetrafluoroborate (0.1 M) in acetonitrile at 25 °C; anode potential 1.4 V *vs.* SCE, undivided cell.

Charge passed [a]/%	Isomer ratio, α/β
6.2	22 ± 3
10.2	20
15.1	20
20.9	19
35.0	18
41.2	18
48.8	17 [b]
51.6	16

[a] Calculated for 1 F mol^{-1} of naphthalene. [b] This value was determined after 3 h and the yield then corresponds to 160 % of that of the homogeneous control experiment (see also Fig. 2).

Table 3. Electrolysis of a solution of nitrogen dioxide (0.2 M), naphthalene (0.2 M), and lithium tetrafluoroborate (0.1 M) in acetonitrile at 5 °C; anode potential 1.6 V *vs.* SCE, undivided cell.

Charge passed [a]/%	Time elapsed/min	Yield of nitronaphthalenes/% Material	"Current"
3	10	1.0	34
10	35	2.8	28
15	60	3.8 [b]	25
20	85	4.8	24
40	160	7.5 [c]	19

[a] Calculated for 1 F mol^{-1} of naphthalene. [b] This yield is *ca.* 160 % of that of the homogeneous control experiment, run parallel with the electrolysis. [c] The yield after electrolysis for this period of time at 25 °C is 26 or 350 % of that obtained at 5 °C.

process and some of the homogeneous ones. It is obvious that during the time-scale of the electrolysis experiment, the control run without any additive gives yields of nitronaphthalenes that correspond to 50 – 60 % of those of the electrolysis experiment.

Since strong acid catalyzes the homogeneous nitration reaction we suspected that anodically produced protons (from, *e.g.*, oxidation of traces of water) might catalyze the homogeneous reaction which might possibly account for the difference between the electrochemical and control run of Fig. 2. Therefore a divided * cell run was set up in which only 1.5 % of the theoretically required charge was passed and the electrolysis discontinued. The solution was then allowed to stand and analyzed at intervals; with the same reaction conditions as those defined in Table 1, the yields in the "electrolysis" experiment was 170 (20 min), 140 (2.5 h) and 120 % (*ca.* 20 h) of those of the control run. Table 3 shows results from an electrolysis run at 5 °C. For this experiment the mechanism of eqn. (1) demands that the yield of nitronaphthalenes as a function of the charge passed should be the same as in the run at 25 °C, since the rate of radical cation production should be controlled by the charge passed and the coupling between radical cation and nitrogen dioxide should have zero activation energy.[5] Clearly, the yields in these two experiments are distinctly different and indeed indicative of a homogeneous nitration process, subject to the normal slow-down by a temperature decrease.

Since the α/β ratios found by us (Tables 1 and 2) consistently were larger than that reported by Perrin,[5] we have also repeated a few homogeneous nitration experiments and compared with values given in the literature for different

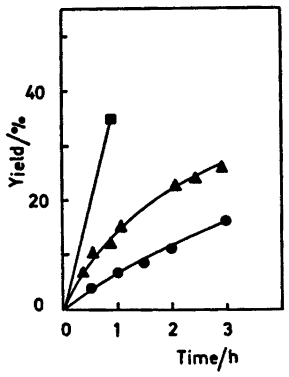

Fig. 2. Yield of nitronaphthalenes *vs.* time in control experiment without additive (0), control experiment with 0.004 M CF_3SO_3H added (□) and electrolysis experiment (△).

* This is necessary since otherwise cathodically generated base would neutralize the acid formed at the anode.

Table 4. Isomer ratios in the nitration of naphthalene under different conditions at 25 °C.

Conditions for nitration	Isomer ratio, α/β	Ref.
HNO_3 in $MeNO_2$	29±4	15
HNO_3 in AcOH	21±4	15
HNO_3/H_2SO_4 in AcOH	22±2	15
HNO_3 in H_2SO_4	35 [a]	15
NO_2BF_4 in sulfolane	10±1	15
HNO_3/H_2SO_4 in acetonitrile [b]	20±3	This work
HNO_3/H_2SO_4 in acetonitrile [c]	16±3	This work
HNO_3/H_2SO_4 in acetonitrile [b]	11±1	5
NO_2BF_4 in acetonitrile	11±1	This work
"Electrochemical"	20±3	This work
"Electrochemical"	9±1	5

[a] Extrapolated value. [b] With urea added. [c] Without urea.

reaction conditions (Table 4). Also these ratios are higher than Perrin's, for reasons that are not easily discernible.

Draper and Ridd [16] recently employed an alternative method, oxidation by cerium(IV) ammonium nitrate, to generate the radical cation of mesitylene in the presence of nitrogen dioxide in acetonitrile at 65 °C. It was claimed that the rate of reaction between 0.19 M nitrogen dioxide and mesitylene (*ca.* 0.2 M) is negligible under these conditions, in spite of a previous report [13b] to the contrary (these experiments were run at 25 °C). We therefore semiquantitatively established that mesitylene does react with nitrogen dioxide in dry acetonitrile at 25 °C, albeit at a rate which is 6 – 8 times slower than that of naphthalene. The mesitylene reaction is retarded by water and catalyzed by trifluoromethanesulfonic acid, just as observed for naphthalene.

DISCUSSION

The results presented above clearly show that the relevancy of electrolysis experiments purporting to demonstrate the reaction between $(naphthalene)^{+\cdot}$ and nitrogen dioxide, is seriously in doubt due to the concurrent homogeneous nitration of naphthalene itself. This reaction accounts unambiguously for 50 – 60 % of the nitronaphthalenes formed in the electrolysis experiment (Fig. 2), and it is likely that all of the product is formed *via* this route, it we allow for the possibility of catalysis by acid formed at the anode. Hydrogen ion will be formed at the anode, irrespective of the reaction taking place there (*e.g.*, water oxidation, oxidation of naphthalene to give 1,1'-binaphthyl [17] or higher oligomers * or even the reaction of eqn. 1 *if* it should occur to a small extent) and thus a hydrogen ion gradient will be set up (far away enough from the anode the acid will of course be neutralized by base formed at the cathode in a nondivided cell). This acid gradient surely must catalyze the homogeneous nitration reaction;[10b] to what extent we cannot establish quantitatively, but it is telling that in a divided cell 1.5 % of the theoretically calculated charge for the complete formation of the radical cation is enough to increase the rate of the homogeneous reaction by 40 – 60 % during the time-scale of the electrolysis experiment.

The electrochemical run at 5 °C is equally informative. It immediately refutes the prediction from the ET mechanism [eqn. (1)] that the same yield should be formed independent of the temperature at which the electrolysis is carried out. Instead, we find the normal rate retardation associated with homogeneous reactions possessing reasonable activation energy.

An alternative way of generating aromatic radical cations, oxidation of a hydrocarbon by cerium(IV) ammonium nitrate,[16] is in principle hampered by the same difficulties as the electrochemical method. Also here acid is generated in the reaction, thus making catalysis of the homogeneous process possible. Moreover, it has by no means been definitely established that a radical cation is an intermediate in this kind of process.[18,19] As an example, there is a large difference between the anodic and cerium(IV) oxidation of anisole, in that nuclear acetoxylation can take place in the latter case even in the absence of acetate

* From the electrolysis run of Fig. 1 were also detected 1,1'-binaphthyl [17] (0.2 % material yield), at least one nitrobinaphthyl (*ca.* 2 %) and an unknown but appreciable amount of high-molecular material thus indicating that dehydrooligomerization of naphthalene is the major source of hydrogen ion at the anode. The homogeneous control run contained none of these products.

ion,[20] whereas anodic nuclear acetoxylation requires its presence.[21] The isomer distribution is different in the two cases too (no *meta* isomer formed from Ce(IV) oxidation *vs. ca* 3 % in the anodic case).

EXPERIMENTAL

Materials. A stock solution of lithium tetrafluoroborate (0.1 M) in acetonitrile (analytical grade) was prepared and kept over molecular sieves (3 Å).[14] Nitrogen dioxide was either of commercial quality or prepared by thermal decomposition of anhydrous lead(II) nitrate, and was bubbled into a suitably sized sample of the stock solution. The amount of nitrogen dioxide was determined by differential weighing.

All other reagents were commercial samples of highest purity possible.

Electrolytic experiments. Non-divided cell electrolyses were performed in a 50 ml water-jacketed cell, equipped with a lid, open to the atmosphere *via* a drying-tube, and with magnetic stirring. The electrodes were pieces of platinum foil (anode area 4 cm^2, cathode area 1 cm^2) and the reference electrode a saturated calomel electrode (SCE). The electrolysis was made with 50 ml of electrolyte, using an Amel model 552 potentiostat as power supply. Samples (1.00 ml) were withdrawn for analysis at suitable intervals. They were analyzed for nitronaphthalenes directly by GLC (Varian 1400 gas chromatograph with a Hewlett-Packard 3380 A integrator) on a 2.5 m × 3 mm 5 % NPGS on Chromosorb W column, using β-naphthyl acetate as an internal standard for naphthalene runs and pentamethylbenzene for mesitylene runs. 1,1-Binaphthyl and nitrobinaphthyl were analyzed on a 0.5 m × 3 mm 3 % OV-1 column.

Homogeneous controls were run parallel with the electrolysis experiments and were treated as closely as possible in the same way as the electrolytes. Experiments with additives on the homogeneous reaction were done similarly.

Divided (by a middle compartment of the type described by Lund and Iversen)[22] cell electrolyses were run in a three-compartment cell of a total volume of *ca.* 500 ml, equipped with lids for both electrolyte compartments. All three compartments were vented to the atmosphere *via* drying-tubes. The middle and cathode compartments were filled with stock solution.

Nitration by conventional nitrating agents (nitric acid and nitronium tetrafluoroborate) was performed in 10 mmol runs as decribed in Ref. 15.

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