

Nitration of Aromatics *via* Electron Transfer. II.* On the Reaction between Naphthalene Radical Cation and Nitrogen Dioxide

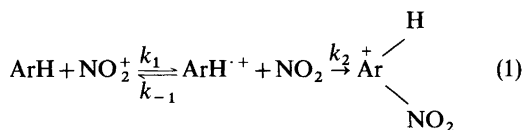
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The electron transfer mechanism for electrophilic aromatic nitration by nitronium ion involves as a crucial step the diffusion-controlled coupling between a radical cation and nitrogen dioxide. This step has now been examined in detail by reacting solid naphthalene^{•+} hexafluorophosphate with a solution of dinitrogen tetroxide in dichloromethane at low temperatures, between -45 and -25 °C. The results show that nitronaphthalenes are formed in very good yields with an α/β ratio of *ca.* 40. Thus it does not seem probable that this reaction can be involved as an elementary step in the naphthalene/ NO_2^+ mechanism (α/β ratio *ca.* 15 at -30 °C).

Naphthalene^{•+} hexafluorophosphate reacts instantaneously with nitrite ion at -50 °C in a 100 % electron transfer process.

The electron transfer (ET) mechanism for nitration of reactive aromatics by nitronium ion encompasses an initial ET step between ArH and NO_2^+ to give a radical pair followed by coupling of the two radicals – a radical cation and a neutral radical – formed (eqn. 1). The ET step is assumed to be encounter-controlled, as are all exergonic ET processes according to current ET theory.² Also the



k_2 step must be extremely fast in order to account for the over-all diffusion-controlled rate.

Experimental evidence for this mechanism was sought in attempts to generate aromatic radical cations anodically¹ or by Ce(IV) oxidation³ in the presence of NO_2 in the hope of finding close similarities (mainly positional isomer ratios) between these reactions and ordinary electrophilic aromatic nitration. For the anodic experiments it was, however, possible to demonstrate⁴ that homogeneous nitration by N_2O_4 (the by far most predominant component of the equilibrium $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$), catalyzed by anodically generated acid was in all probability responsible for the nitration reaction observed.

We now report on a different approach to study this problem, namely to synthesize a radical cation salt of naphthalene and allow it to react with NO_2 at low temperature. If one could demonstrate a close similarity with respect to the α/β ratio between the $\text{ArH}^{\bullet+}/\text{NO}_2$ and ArH/NO_2^+ reactions and be able to exclude interference from the competing proton-catalyzed N_2O_4 nitration process, one would have removed at least one obstacle for the mechanism given in eqn. (1). As pointed out before, the energetics of the ET step makes this mechanism feasible in view of current ET theory,¹ also a recent theoretical study has provided further arguments in favor of a diradicaloid intermediate stage.⁵ Experimental tests of the proposal are, therefore, urgently needed.

* Part I, see Ref. 4.

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Table 1. Reaction of $(C_{10}H_8)_2^+ PF_6^-$ with N_2O_4 in dichloromethane in a non-divided cell.

Experiment No.	Amount of naphthalene/mmol		Current yield of naph $^{\cdot+}$ ^b	Yield of nitronaphthalenes/% ^a		Ratio of α/β isomer
	At start of electrolysis	Anodically "bound"		Material	Current	
1	3.00	1.12	75	46	34	44
2	2.00	0.86	78	45	35	46
3	1.72	0.76	112	36	40	30
4	0.45	0.23	102	57	58	45
5	1.62	0.61	63	59	37	36
6	1.43	0.43	60	51	31	54

^a Based upon the amount of anodically "bound" naphthalene (see column 3). ^b Based upon $(C_{10}H_8)_2^+ PF_6^-$.

RESULTS

The synthesis of a suitable radical cation salt of naphthalene had already been described,⁶ in that anodic oxidation of naphthalene in dichloromethane /0.2 M tetrabutylammonium hexafluorophosphate (TBAHP) at $-45^\circ C$ at low current density causes electrocrystallization of the salt $(C_{10}H_8)_2^+ PF_6^-$. This synthesis was run in a non-divided cell.

Using a slightly different electrode configuration (a cylindrical Pt gauze anode, arranged around a stainless steel cathode) we conducted a number of syntheses of the radical cation salt. The salt, which is insoluble in dichloromethane, was allowed to react with NO_2 (added at $-50^\circ C$; 1 mol of N_2O_4 per mol of naphthalene used). At $-50^\circ C$, no reaction took place between the brown-violet crystals and the NO_2 solution, and the reaction mixture had to be brought up to *ca.* $-25^\circ C$ before any reaction took place. This resulted in a reddish-yellowish solution which was immediately worked up and analyzed.

Table 1 shows the results of six runs in the *non-divided cell*. We have used different concentrations of naphthalene, run the electrolysis at slightly differing conversions, and analyzed for unreacted naphthalene and nitronaphthalenes. In addition a by-product, 1-chloronaphthalene ($5 \pm 2\%$ material yield), was invariably present (see below) in significant amounts. A possible by-product, binaphthyl, was sought for but not found.

Inspection of Table 1 shows a very good agreement between the experiments and expectations based upon the previously⁶ established stoichiometry of the TBAHP salt of naph $^{\cdot+}$. The anodically bound naphthalene, corresponding to a 41(4)* %

* Mean values with their mean errors are given in all cases.

current yield of naph $^{\cdot+}$, reacts with NO_2 to give a 39(3) % current and 49(4) % material yield of α - and β -nitronaphthalene. Ideally one would expect a 50 % material yield of nitronaphthalenes and identical current yields for formation of naph $^{\cdot+}$ and nitronaphthalenes. The results thus indicate that naph $^{\cdot+}$ indeed couples with NO_2 .

However, when we compare the isomer ratio of the $ArH^{\cdot+}/NO_2$ reaction, 43(3), with that obtained in the nitration of naphthalene by $NO_2^+BF_4^-$ in dichloromethane (heterogeneous system), 15(1) at $-30^\circ C$ and 12(1) at $20^\circ C$, there is a significant difference which should not exist if the ET mechanism of eqn. 1 is correct.

A number of runs in a *divided cell* (see Table 2) suggested to us that the simplicity and near perfection of the results obtained in the non-divided cell might be hiding a very complex reaction pattern. We now see more than twice as high a material yield of nitronaphthalenes [119(7)], *i.e.* compared to that expected on the basis of the previously published stoichiometry of the radical cation salt, a slightly lower α/β ratio [36(2)] and a much lower chloronaphthalene yield [0.9(0.3) % material yield]. The current yield for formation of nitronaphthalenes is now higher than that for formation of naph $^{\cdot+}$, 96(9) *vs.* 82(8) %. Especially the higher product yield indicated that either something fundamentally different might take place in the divided cell runs or that the seemingly simple chemistry in the non-divided cell runs might be more complex.

In all the divided cell experiments tributylamine was formed in the catholyte compartment.

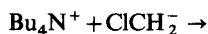
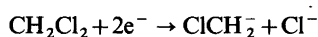
A more detailed consideration of the processes taking place in the non-divided cell shows why the radical cation salt must have the stoichiometry

obtained in the non-divided cell (see eqns. 2 and 3). Combining these reactions, the overall *electrochemistry* is given by eqn. 4, whereas the overall

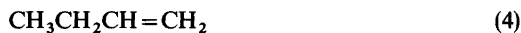
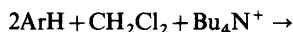
At the anode



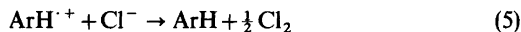
At the cathode



chemistry is only to be understood when one



realizes that Cl^- can diffuse from the cathode to the anode and react with $\text{ArH}^{\cdot+}$ to give ArCl indirectly *via* Cl_2 (eqn. 5). Since one Cl^- is formed per two $\text{ArH}^{\cdot+}$ (eqn. 4) it is immediately realized



why $(\text{C}_{10}\text{H}_8)_2^+ \text{PF}_6^-$ is the product obtained in the non-divided cell. We can also qualitatively explain the formation of chloronaphthalene in relatively high yield under these conditions.

With this chemistry in mind, it is reasonable to assume that the radical cation salt formed in the

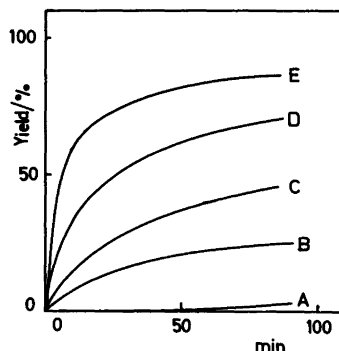


Fig. 1. Yield of nitronaphthalenes *vs.* time in the acid-catalyzed nitration of naphthalene in dichloromethane. A: Trifluoroacetic acid at -20°C ; ratio naph/acid 2:1. B: Methanesulfonic acid at -45°C ; ratio naph/acid 2:1. C: Methanesulfonic acid at -15°C ; ratio naph/acid 4:1. D: Methanesulfonic acid at -15°C ; ratio naph/acid 2:1. E: Methanesulfonic acid at -15°C ; ratio naph/acid 1:1.

divided cell runs has the composition of $\text{ArH}^{\cdot+} \text{PF}_6^-$. In such a case, the current yield of $\text{naph}^{\cdot+}$ is 82(8)%, giving rise to a 96(9) % current and 119(7) % material yield of nitronaphthalenes. It then remains to explain why an extra 15–20 % of nitronaphthalenes is formed in the divided cell runs.

We here suspected that the same complication was present as in our previous study of the anodic oxidation of naphthalene in acetonitrile,⁴ namely that acid-catalyzed nitration by N_2O_4 takes place simultaneously with the $\text{ArH}^{\cdot+}/\text{NO}_2$ reaction. Even if no acid would ideally be formed in the anolyte of a divided cell run (eqn. 2) small amounts might be formed *via* unavoidable side-reactions (like oxidation of traces of water and dehydrooligomeri-

Table 2. Reaction of the radical cation salt of naphthalene with N_2O_4 in dichloromethane in a divided cell.

Experiment No.	Amount of naphthalene/mmol		Current yield of $\text{naph}^{\cdot+}$ ^b	Yield of nitronaphthalenes/%		Ratio of α/β isomer
	At start of electrolysis	Anodically "bound"		Material ^a	Current	
7	1.76	0.76	86	105	91	31
8	1.50	0.73	65	137	90	43
9	1.28	0.53	69	100	69	32
10	1.08	0.64	118	109	129	
11	1.19	0.64	83	141	116	35
12	1.13	0.47	68	119	82	38

^a Based upon the amount of anodically "bound" naphthalene (see column 3). ^b Based upon $\text{C}_{10}\text{H}_8^+ \text{PF}_6^-$.

zation of ArH). Moreover, an ET mechanism according to eqn. 1 would be accompanied by the liberation of acid. Any nitration caused by the catalytic influence of this acid would take place parallel to eqn. 1, however, and thus show a time lag with respect to it. Fig. 1 shows that acid-catalyzed nitration of naphthalene by N_2O_4 takes place in dichloromethane at low temperatures at rates that might explain the formation of the excess of nitronaphthalenes observed in the experiments reported in Table 2. Note, however, that the experiments of Fig. 1 have been run at higher concentrations.

An experiment (at $-45^\circ C$) in which N_2O_4 was present in the anolyte during the whole electrolysis period showed that any electrocrystallized material was rapidly consumed by reaction with the electrolyte under such conditions. A 100% current yield of nitronaphthalenes with an α/β ratio of 65 was obtained.

A different approach was tried in two experiments in which tetrabutylammonium nitrite was added to the radical cation salt made by electrolysis in a divided cell. In these cases the crystal mass dissolved instantaneously already at $-50^\circ C$ and a clear yellow solution was obtained. Naphthalene (>99%) was recovered and no (<0.1%) nitronaphthalene was found.

DISCUSSION

Before we can discuss the results given in Tables 1 and 2, it is necessary to summarize pertinent kinetic and thermodynamic data for the monomer-dimer equilibrium in the dinitrogen tetroxide system (eqn. 6). Equilibrium constants (K_3) and ΔH° values are known for several solvents (cyclohexane,⁷ $K_3 = 1.77 \cdot 10^{-4}$ M at $25^\circ C$, $\Delta H^\circ = 14.6$ kcal mol^{-1} ; carbon tetrachloride,⁷ $K_3 = 1.78 \cdot 10^{-4}$ M



at $25^\circ C$, $\Delta H^\circ = 14.6$ kcal mol^{-1} ; acetonitrile,⁷ $K_3 = 3 \cdot 10^{-5}$ M at $25^\circ C$, $\Delta H^\circ = 16.0$ kcal mol^{-1} ; water,⁸ $1.53 \cdot 10^{-5}$ at $25^\circ C$) and one can see that there is only a 12-fold decrease in K_3 in going from a nonpolar solvent to water. We have, therefore, assumed that K_3 in dichloromethane is the same as in carbon tetrachloride (and cyclohexane) and used the thermodynamic parameters for this system to estimate $[NO_2]$ at 25, 0, -25 , and $-50^\circ C$ at two limiting experimental concentrations of N_2O_4 employed in this investigation, 5 and 10 mM (see Table 3).

Kinetic data for reaction 6 are known for water only,⁸ k_3 and k_{-3} being $6900 s^{-1}$ and $4.5 \cdot 10^8 M^{-1} s^{-1}$, respectively, at $25^\circ C$. Assuming that the frequency factors are of normal magnitude, $10^{13} s^{-1}$ and $10^{11} M^{-1} s^{-1}$ (corresponding to E_a values of 12.5 and 3.2 kcal mol^{-1} , respectively), we can estimate k_3 , k_{-3} and K_3 at 0, -25 and $-50^\circ C$ in aqueous solution. For dichloromethane the corresponding rate constants were simply estimated by multiplying k_3 (water) and dividing k_{-3} (water) by the square root of the ratio between the K_3 values in the two solvents.

Our first study⁴ of the problem at hand was primarily concerned with room temperature electrolysis of naphthalene in the presence of dinitrogen tetroxide, using acetonitrile as solvent. These experiments were marred by relatively low material yields of nitronaphthalenes and relatively fast concurrent *homogeneous* nitration by dinitrogen tetroxide, catalyzed by anodically generated acid. This reaction is well-known from other studies.⁹⁻¹² Thus no firm conclusion regarding the feasibility of the $naph^{+\cdot}/NO_2$ coupling step could be drawn.⁴

In dichloromethane at $-45^\circ C$, the anodic oxida-

Table 3. Estimated equilibrium data for the dinitrogen tetroxide/nitrogen dioxide equilibrium (eqn. 6) in dichloromethane at different temperatures.⁷

Temp.	K_3/M	$[NO_2]/mM$	
		In 5 mM N_2O_4	In 10 mM N_2O_4
25	$1.78 \cdot 10^{-4}$	0.9	1.3
0	$1.87 \cdot 10^{-5}$	0.3	0.43
-25	$1.24 \cdot 10^{-6}$	0.08	0.11
-50	$4.5 \cdot 10^{-8}$	0.015	0.021

tion of naphthalene in the presence of dinitrogen tetroxide does not result in the usual electrocrystallization process. Instead, one can observe how any solid material formed is rapidly consumed by reaction with the electrolyte. A 100% yield of nitronaphthalenes with a very high α/β ratio (65) was secured. Under similar conditions homogeneous nitration by dinitrogen tetroxide at -45°C , catalyzed by methanesulfonic acid (ratio [naph]:[$\text{CH}_3\text{SO}_3\text{H}$]:[N_2O_4]=1.8:1:2.2) produced only *ca.* 25% of nitronaphthalenes during 2 h (see Fig. 1). Keeping in mind that [NO_2] is ≈ 0.02 mM in dichloromethane at -45°C (Table 3) it seems as if $\text{naph}^{\cdot+}$, generated at a rate of $1\text{ nmol s}^{-1}\text{ cm}^{-2}$ (0.1 mA cm^{-2}) can just barely be kept from crystallizing on the electrode by reaction with NO_2 at this concentration level. On the other hand, no visible reaction takes place at -45°C between electrocrystallized $\text{naph}^{\cdot+}$ salt when the dinitrogen tetroxide is added after the electrolysis has been completed.

The experiments in which $\text{naph}^{\cdot+}$ was reacted with nitrite ion are of interest in connection with previously reported radical cation/ NO_2^- induced nitrations (perylene $^{\cdot+}$ ¹³ and certain porphyrin radical cations¹⁴⁻¹⁶). Here the mechanistic discussion has centered upon whether nitration occurs *via* (1) direct bond formation between the radical cation and nitrite ion or (2) if ET, followed by NO_2 (N_2O_4) induced nitration of the parent compound, or (3) NO_2 coupling with the radical cation,¹⁶ takes place. For $\text{naph}^{\cdot+}$ at -50°C we can unambiguously state that ET takes place to at least 99.9%, and it is then obvious that the second mechanism above can be simulated by choosing a higher reaction temperature and longer reaction time. Coupling between NO_2 and radical cation does not occur at -50°C . The ET reaction is extremely fast, even under heterogeneous conditions and at the low [NO_2^-] actually employed

(3 mM), as should be the case for a strongly exergonic ET step according to current theory.² The estimated value of ΔG° for the reaction $\text{naph}^{\cdot+} + \text{NO}_2^- \rightarrow \text{naph} + \text{NO}_2$ is *ca.* -32 kcal mol^{-1} at 25°C in acetonitrile.¹⁷ It can be predicted with reasonable certainty that the perylene $^{\cdot+}$ reaction with NO_2^- should also proceed with initial ET (the reaction is exergonic by -15 kcal mol^{-1} at 25°C in acetonitrile,¹⁷ whereas the porphyrin radical reactions probably occur *via* the same initial step (ΔG° around 0). This can, in principle, be checked experimentally in the same way as done here for naphthalene, *i.e.*, by reacting the radical cation with nitrite ion at such a low temperature that any homogeneous nitration by NO_2 (N_2O_4) is excluded. ET, being diffusion controlled, is very little affected by lowering the temperature.

In the present context, it is interesting to note that the NO_2 formed in the heterogeneous ET reaction between nitrite ion and the $\text{naph}^{\cdot+}$ salt does not couple with $\text{naph}^{\cdot+}$ in competition with its self-coupling reaction (rate constant *ca.* $10^8\text{ M}^{-1}\text{ s}^{-1}$ at -50°C in dichloromethane; see Table 4). This is a hint that the $\text{naph}^{\cdot+}/\text{NO}_2$ reaction might be a relatively slow process and not the diffusion-controlled one demanded by the mechanism of eqn. 1.

Proceeding to the series of reactions carried out in the non-divided cell, it nicely demonstrates that $\text{naph}^{\cdot+}$ coupled with NO_2 at -25°C under "neutral" conditions (note that the acid-base balance of eqns. 4 and 5 should result in "basic" to "neutral" conditions during most of the reaction period for the $\text{naph}^{\cdot+}/\text{NO}_2$ reaction). Thus the acid-catalyzed homogeneous nitration process should be negligibly slow, as is indeed borne out by the observation of a near perfect material yield [49(4) *vs.* 50%] and very good agreement between current yields for $\text{naph}^{\cdot+}$ and nitronaphthalene

Table 4. Estimated rate data for the dinitrogen tetroxide/nitrogen dioxide system (eqn. 6) in water and dichloromethane at different temperatures.⁸

Temp./ $^\circ\text{C}$	k_3/s^{-1}	Water		Dichloromethane	
		$k_{-3}/10^8\text{ M}^{-1}\text{ s}^{-1}$	K_3/M	k_3/s^{-1}	$k_{-3}/10^8\text{ M}^{-1}\text{ s}^{-1}$
25	6900	4.5	1.53×10^{-5}	23500	1.32
0	980	2.8	3.5×10^{-6}	2260	1.22
-25	98	1.5	6.5×10^{-7}	135	1.09
-50	5.7	0.73	7.8×10^{-8}	4.3	0.96

formation [41(4) and 39(3) %, respectively].

The reactions in the divided cell are more difficult to interpret unambiguously. Since it cannot be avoided that some acid is formed *via* side-reactions (oxidation of traces of water, partial dehydrooligomerization of naphthalene, chlorination of naphthalene — note that there always is some leakage through cell membranes of the type used here, as evidenced by the detection of small amounts of chloronaphthalene in the anolyte) acid-catalyzed homogeneous nitration by dinitrogen tetroxide takes place to an extent of at least 10–20 %. This type of reaction has been well documented previously^{9–12} and has considerable interest on its own right since it provides a very mild nitration procedure.

Summarizing, we have presented evidence which almost definitely establishes that the coupling reaction between a solid naph^+ salt and NO_2 takes place at a measurable rate at temperatures $\geq -25^\circ\text{C}$. The α/β ratio of the nitronaphthalenes formed, *ca.* 40, is significantly higher than that observed (15) for nitration with nitronium tetrafluoroborate under similar conditions. Hence we conclude that the $\text{naph}^+/\text{NO}_2$ reaction cannot be an elementary step in the sequence of reactions of eqn. 1.

Unfortunately, it is not possible to obtain a quantitatively reliable estimate of the rate of the $\text{naph}^+/\text{NO}_2$ reaction from the observations reported here. All reactions are heterogeneous, and a comparison between the $\text{naph}^+/\text{NO}_2$ reaction (relatively slow at -25°C) and the $\text{naph}^+/\text{NO}_2^-$ reaction (instantaneous at -50°C) is not meaningful due to the difference in reagent concentrations ($[\text{NO}_2] \approx 0.1 \text{ mM}$ *vs.* $[\text{NO}_2^-] = 3 \text{ mM}$) and possible differences in reaction mechanism. It does, however, point to another possibility of testing the mechanism of eqn. 1, namely to determine the rate of the $\text{naph}^+/\text{NO}_2$ step in homogeneous medium. If the reaction is slower than a diffusion-controlled process it cannot be an elementary step of the sequence of reactions of eqn. 1, all of which must proceed at a diffusion controlled rate. It is a sad fact that the experimental difficulties of such experiments seem almost unsurmountable; one of the few consoling aspects is that naph^+ has been reported to be a rather stable species at room temperature toward meticulously purified propionitrile.¹⁸ We are presently studying the possibilities to study the kinetics of the $\text{naph}^+/\text{NO}_2$ reaction.

EXPERIMENTAL

Materials and methods. Dichloromethane was distilled and stored over molecular sieves (3Å). Tetrabutylammonium hexafluorophosphate (Fluka AG, Buchs, Switzerland), tetrabutylammonium nitrite (Aldrich, Milwaukee, USA), nitronium tetrafluoroborate (Aldrich), and naphthalene (*p.a.* quality, Merck, Darmstadt, FRG) were used without further purification. Solutions of nitrogen tetroxide were made up as described previously.⁴

The power source was an AMEL model 552 potentiostat, operated in the galvanostatic mode. GLC analyses were performed by a Varian 1400 gas chromatograph, equipped with an HP 3380 A integrator (column: 2.5 m \times 3 mm 5 % neopentylglycol succinate on Chromosorb W). Internal standards were durene (for naphthalene) and 2-naphthyl acetate (for nitronaphthalenes).

All operations involving synthesis and reactions of the radical cation salt were performed in a glovebox, as were also the nitronium tetrafluoroborate experiments.

*Synthesis of naph^+ hexafluorophosphate.*⁶ The anodic oxidation of naphthalene was performed in a jacketed 400 ml cylindrical vessel, equipped with a glass lid with four necks. Cooling was effected by circulating ethanol from a cryostat (Haake). The anode was a cylindrical platinum gauze (geometric area 50 cm^2), concentrically placed around the cathode, a steel rod of about 20 cm^2 effective area. For divided cell runs the cathode was placed inside a glass tube, sealed at the lower end by a glass frit (1G4). The catholyte was dichloromethane, 0.02 M in TBAHP.

In a typical experiment naphthalene (1–2 mmol) was accurately weighed in and dissolved in the electrolyte (300 ml of dichloromethane, 0.02 M in TBAHP). A trace of trifluoromethanesulfonic acid (*ca.* 20 μl) was added to provide a slight initial acidity of the electrolyte. Identical control experiments, except that electrolysis was omitted, demonstrated that less than 1 % nitration occurred with this amount of acid present during the following reaction with dinitrogen tetroxide. The cell contents were cooled to -45°C and a constant current of 5 mA (anode current density = 0.1 mA cm^{-2}) was passed until 50–70 % of the theoretically necessary charge for formation of naph^+ had been passed. At the end of the electrolysis period a brown-reddish crystal mass had collected on the anode.

This procedure is essentially the same as that used by Fritz *et al.*⁶ in a nondivided cell. We did, however, find it necessary to decrease the current density to half their value in order to get the electrocrystallization to proceed well.

Reaction between naph^+ hexafluorophosphate and nitrogen dioxide. After withdrawing as much as

possible of the electrolyte (generally ca. 100 ml); this is a difficult procedure since the crystal mass on the anode is very fragile) an equivalent volume of precooled dichloromethane containing dinitrogen tetroxide (molar ratio of naphthalene to dinitrogen tetroxide 1:1) was added. Magnetic stirring was commenced whereupon the crystal mass disintegrated and formed a suspension. The temperature of the solution was allowed to rise to -25°C where a yellowish to reddish solution was obtained. This was immediately removed from the dry-box and subjected to workup (washing with water). Analyses were performed for unreacted naphthalene, nitronaphthalenes and chloronaphthalene. No binaphthyl was detectable.

The lapse between the addition of the dinitrogen tetroxide solution at -45°C to the start of the work-up procedure was generally ca. 30 min.

Reaction between naph⁺ hexafluorophosphate and tetrabutylammonium nitrite. After synthesis of the radical cation salt in a divided cell, tetrabutylammonium nitrite (1 mmol) was added to the electrolyte which resulted in an instantaneous dissolution of the radical cation salt with formation of a yellow solution. Work-up and analysis showed that $<0.1\%$ (= limit of detection) of nitronaphthalenes was formed and a high recovery of naphthalene (98–99%). The same result was obtained by adding a large excess of powdered sodium nitrite and running the reaction under heterogeneous conditions at -25°C .

Anodic oxidation of naphthalene in dichloromethane at -45°C in the presence of dinitrogen tetroxide. This reaction was run in a divided cell as described above with an equivalent amount of dinitrogen tetroxide present in the electrolyte. Very little electrocrystallized material was visible during the run. The yield of nitronaphthalenes was ca. 100%, and the α/β ratio was 65.

Acid-catalyzed nitration of naphthalene by dinitrogen tetroxide. A solution of naphthalene (ca. 2 mmol), acid (amount and nature of, see Fig. 1) and dinitrogen tetroxide (ca. 1 mmol) in dichloromethane (25 ml) was allowed to stand at a selected temperature (see Fig. 1). Samples were withdrawn at intervals and analyzed by GLC.

Nitration of naphthalene by nitronium tetrafluoroborate. Nitronium tetrafluoroborate (2.0 mmol) was suspended in a solution of naphthalene (1.9 mmol) in dichloromethane (30 ml). The reaction was run at several temperatures with the following results [temperature/ $^{\circ}\text{C}$, yield/% (reaction period/h), α/β ratio]: -70 , 2(2), –; -30 , 15(2), 15 ± 1 ; 20 , 49(15), 12 ± 1 .

The sluggishness of the reaction is due to the extremely low solubility of nitronium tetrafluoroborate in dichloromethane.

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REFERENCES

1. Perrin, C. L. *J. Am. Chem. Soc.* 99 (1977) 5516.
2. Schuster, G. B. *J. Am. Chem. Soc.* 101 (1979) 5851.
3. Draper, M. R. and Ridd, J. H. *Chem. Commun.* (1978) 445.
4. Ebersson, L., Jönsson, L. and Radner, F. *Acta Chem. Scand. B* 32 (1978) 749.
5. Takabe, T., Takenaka, K., Yamaguchi, K. and Fueno, T. *Chem. Phys. Lett.* 44 (1976) 65.
6. Fritz, H. P., Gebauer, H., Friedrich, P., Ecker, P., Artes, R. and Schubert, U. *Z. Naturforsch. Teil B* 33 (1978) 498.
7. Redmond, T. F. and Wayland, B. B. *J. Phys. Chem.* 72 (1968) 1626.
8. Grätzel, M., Henglein, A., Lilie, J. and Beck, G. *Ber. Bunsenges. Phys. Chem.* 73 (1969) 646.
9. Bonner, T. G., Hancock, R. A., Yousif, G. and Rolle, F. R. *J. Chem. Soc. B* (1969) 1237.
10. Underwood, G. R., Silverman, R. S. and Vanderwalde, A. *J. Chem. Soc. Perkin Trans. 2* (1973) 1177.
11. Norman, R. O. C., Parr, W. J. E. and Thomas, C. B. *J. Chem. Soc. Perkin Trans. 1* (1974) 369.
12. Olah, G. A., Malhotra, R. and Narang, S. C. *J. Org. Chem.* 43 (1978) 4628.
13. Ristagno, C. V. and Shine, H. J. *J. Org. Chem.* 93 (1971) 1811.
14. Shine, H. J., Padilla, A. G. and Wu, S.-M. *J. Org. Chem.* 44 (1979) 4069.
15. Smith, K. M., Barnett, G. H., Evans, B. and Martynenko, Z. *J. Am. Chem. Soc.* 101 (1979) 1979.
16. Johnson, E. C. and Dolphin, D. *Tetrahedron Lett.* (1976) 2197.
17. Ebersson, L. and Nyberg, K. *Acta Chem. Scand. B* 32 (1978) 235.
18. Gschwind, R. and Haselbach, E. *Helv. Chim. Acta* 62 (1979) 941.

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