Nitration of Polycyclic Aromatic Hydrocarbons by Dinitrogen Tetraoxide. II.* Synthetic and Mechanistic Aspects

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Treatment of polycyclic aromatic hydrocarbons by dinitrogen tetraoxide in dichloromethane solution leads to the clean production of mononitro derivatives with high positional selectivity in almost quantitative yields. For substrates less reactive than chrysene the addition of catalytic amounts of acid is required for the reaction to proceed at convenient rates. Being very easily performed, the method should be regarded as the best yet found for the synthesis of small amounts of these, in many cases, mutagenic mononitro compounds.

From studies on relative reactivities, isomer distributions, and the effect of acid, base and nitrosonium ion on the reaction, a mechanism involving initial attack of a novel electrophile, nitrosated dinitrogen tetraoxide, is proposed. The initially formed σ-complex is suggested to be transformed into the nitro σ-complex _via_ a pathway involving radical pairs, thus explaining the observation by others of CIDNP effects on the reaction path of nitrous acid catalyzed nitration, a reaction proposed to follow the same reaction scheme.
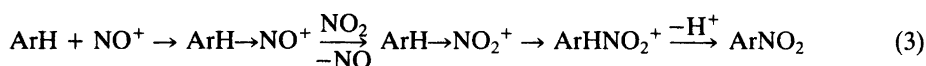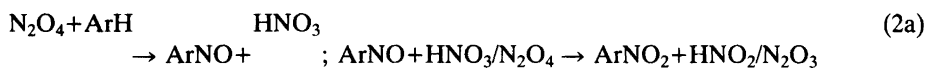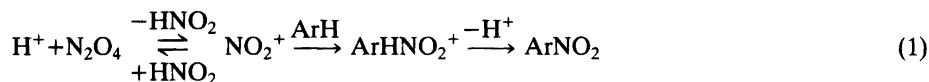
In recent years the reaction between dinitrogen tetraoxide or its monomer, nitrogen dioxide, with polycyclic aromatic hydrocarbons (PAH:s) has received considerable interest as a possible route to the formation of, in many cases mutagenic, nitro derivatives of PAH:s in airborne matter and exhausts from combustion engines.[1] Earlier work includes studies on the reaction between N_2O_4 and individual PAH:s in organic solvents, _e.g._ acenaphthylene,[2] acenaphthene,[3] fluorene,[3] anthracene,[4-6] naphthalene[4,5,7] and phenanthrene.[4,8-10] However, no study directed at the general behaviour of a series of PAH:s toward N_2O_4 comparable to the work by Dewar _et al._[11] on HNO_3/acetic anhydride nitration has been performed. Very recently Nielsen[12] reported on the nitration of 30 PAH:s under environmentally relevant conditions, _i.e,_ in aqueous solution containing HNO_3, HNO_2 and N_2O_4. Here the reaction was demonstrated to be of an electrophilic nature, and an annotation of the possible involvement of electron transfer from the PAH to NO_2, N_2O_4 or NO^+ was made.

Earlier proposals for the mechanism of the N_2O_4 nitration of reactive aromatics include "normal" nitronium ion mediated nitration in strongly acidic media[7,13,14] or in the presence

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of Lewis acids[14] [eqn. (1)] and initial nitrosation followed by rapid oxidation of the nitroso derivative[15-17] [eqn. (2a)]. Recently Milligan[18] reported on the nitration of toluene and benzene with nitrite ion or N_2O_4 in TFA, summarizing some older work and proposing the reaction not to proceed *via* initial nitrosation, but rather *via* NO_2 oxidation of an intermediate arene-NO^+ π-complex [eqn. (3)].

$$H^+ + N_2O_4 \underset{+HNO_2}{\overset{-HNO_2}{\rightleftharpoons}} NO_2{}^+ \xrightarrow{ArH} ArHNO_2{}^+ \xrightarrow{-H^+} ArNO_2 \qquad (1)$$

$$N_2O_4 + ArH \qquad\qquad HNO_3$$
$$\qquad\qquad \to ArNO + \qquad ; ArNO + HNO_3/N_2O_4 \to ArNO_2 + HNO_2/N_2O_3 \qquad (2a)$$
$$NO^+ + ArH \qquad\qquad H^+ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (2b)$$

$$ArH + NO^+ \to ArH{\to}NO^+ \underset{-NO}{\overset{NO_2}{\longrightarrow}} ArH{\to}NO_2{}^+ \to ArHNO_2{}^+ \xrightarrow{-H^+} ArNO_2 \qquad (3)$$

The catalytic effect of nitrous acid or the lower oxides of nitrogen on mixed acid nitrations has traditionally been interpreted by initial nitrosation[19] [eqn. (2b)], a representation that has been demonstrated to be invalid for a number of substrates.[20-26] An alternative mechanism, involving NO^+ as a one-electron oxidant in the key step has been proposed[20] [eqns. (4)–(6)]. In a recent study, Clemens and Ridd provided strong evidence (CIDNP)

$$ArH + NO^+ \to ArH^{\cdot +} + NO \qquad (4)$$

$$NO + NO_2{}^+ \to NO^+ + NO_2 \qquad (5)$$

$$ArH^{\cdot +} + NO_2 \to ArHNO_2{}^+ \qquad (6)$$

in favour of the existence of a radical cation-radical pair along the reaction path for ArH=mesitylene. However, the feasibility of eqn. (5) was questioned since the overall rate of nitration greatly exceeded the rate of formation of $NO_2{}^+$ under the reaction conditions employed.[26]

During the course of our investigations on the possible involvement of an electron transfer step in the $NO_2{}^+$ mediated nitration of reactive aromatics [eqn. (7)] by studying the coupling reaction between nitrogen dioxide and radical cation salts of suitable PAH:s, *e.g.* naphthalene[27] and perylene,[28] we became aware of the clean and rapid production of

$$ArH + NO_2{}^+ \to \overline{ArH^{\cdot +} NO_2{}^{\cdot}} \to ArHNO_2{}^+ \xrightarrow{-H^+} ArNO_2 \qquad (7)$$
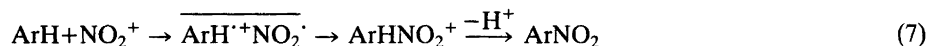
mononitro PAH:s from the reaction between N_2O_4 and the parent PAH:s. For substrates less reactive than chrysene, catalytic amounts of a strong acid had to be added in order to obtain reasonably fast nitration. A preliminary account on the synthetic utility of this reaction has been published.[29] The principal purpose of this paper is to further elaborate on

Table 1. Nitration of polycyclic aromatic hydrocarbons by dinitrogen tetraoxide in dichloromethane at 20 °C.

Substrate	Reaction period[a,b]/min	Mononitro isomers[a] isolated (isomer distribution/%)	Half-life/s[f]	Relative reactivity[f]	$\log (k_2/M^{-1}s^{-1})$[f]	$E°/V$[31]	Reaction with NOBF$_4$[g]	Relative nitration rates h	i
Perylene	5[c]	3–(99.2);1–(0.8)	10	390	1.21	1.30	RC formed	11000	37
Pyrene	40[c]	1–(100)	45	84	0.56	1.60	RC formed	4	7
Anthracene	15[d,e]	9–(100)	60	65	0.43	1.61	RC formed	200	
Chrysene	15[d]	6–(>97)	$3.9 \cdot 10^3$	1	−1.38	1.88	<1 % RC formed	1	1
Naphthalene	180[d]	1–(96);2–(4)	$1.4 \cdot 10^5$	0.028	−2.94	2.08	No reaction	0.1	0.2
Triphenylene	180[d]	1–(22);2–(78)	$2.2 \cdot 10^5$	0.018	−3.13	2.12	No reaction		1

[a] Molar ratio PAH:N$_2$O$_4$=1:0.8. [b] Time after which >98 % of the starting material has been consumed. [c] Uncatalyzed. [d] Molar ratio PAH:CH$_3$SO$_3$H=10:1. [e] 5–7 % of 9,10-anthraquinone was also formed. [f] [PAH]=10 mM; [N$_2$O$_4$]=7.5 mM, no acid added. [g] From Ref. 32. The reactions were performed in dichloromethane, NOBF$_4$ in sulfolane being added to the PAH. RC=radical cation. [h] From Ref. 11. Nitrating agent HNO$_3$/acetic anhydride. [i] From Ref. 12. Nitrating agent HNO$_3$/NaNO$_2$/N$_2$O$_4$/H$_2$O/dioxane/methanol.

the synthetic usefulness and possible mechanism of the reaction. Also, the similarities between N_2O_4 nitration in aprotic media with nitrous acid catalyzed (NAC) nitration in protic media will be commented upon.

RESULTS

Synthetic aspects. In the preliminary report [29] yields and isomer distributions for the nitration of a number of PAH:s with N_2O_4 were presented. For all substrates examined, N_2O_4 in dichloromethane exhibits higher selectivity and produces better yields than does HNO_3 in acetic anhydride or acetic acid.[11] After a very simple work-up procedure that minimizes handling of these hazardous compounds, essentially pure samples (99 %) of the major isomers (in the case of triphenylene both isomers) can be isolated, as summarized for six representative PAH:s in Table 1. However, when samples with purities in the 99.9 % range are required, *e.g.* for mutagenic assays, neither our separation technique (column chromatography) nor method of analysis (GLC on a short, glass-lined column) are powerful enough; procedures for the essentially complete purification (HPLC) of most of these nitro PAH:s have recently been reported.[30]

Further examples of PAH:s that can be successfully nitrated *via* the present method include fluorene, binaphthyl, fluoranthene, 9-phenylanthracene and 1-methoxynaphthalene (2-nitro/4-nitro=0.17), while for a few substrates, *i.e.* phenanthrene and acenaphthylene unclean reactions were observed.

Mechanistic aspects. In order to obtain a semiquantitative picture of the relative nitration rates, half-lives for the reactions of stoicheiometrically [according to eqn. (8) below] equivalent amounts were measured. Solutions of the PAH (10 mM) were treated with N_2O_4 (7.5 mM) and samples withdrawn at appropriate intervals. From plots of the yield of nitro-PAH (determined by GLC) *vs.* reaction time, $t_{\frac{1}{2}}$ values and the corresponding approximate second-order rate constants (k_2) were evaluated. These are listed in Table 1 together with $E°$ values [31] (*vs.* the normal hydrogen electrode; all potentials given are referred to this standard) and qualitative results from the reactions of these PAH:s with $NOBF_4$ in dichloromethane.[32] Included in Table 1 are also relative nitration rates for HNO_3/acetic anhydride [11] and $HNO_3/NaNO_2/N_2O_4$/water/methanol/dioxane,[12] respectively.
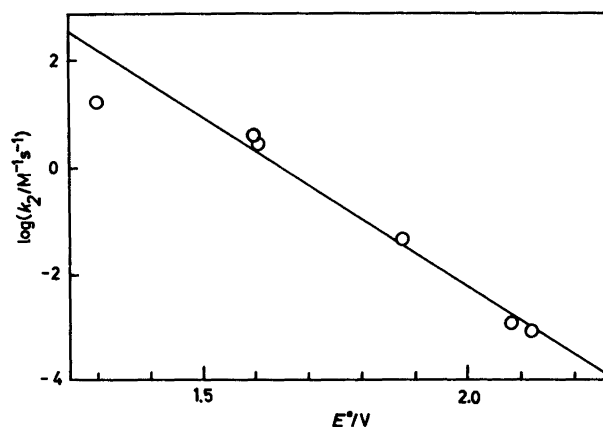

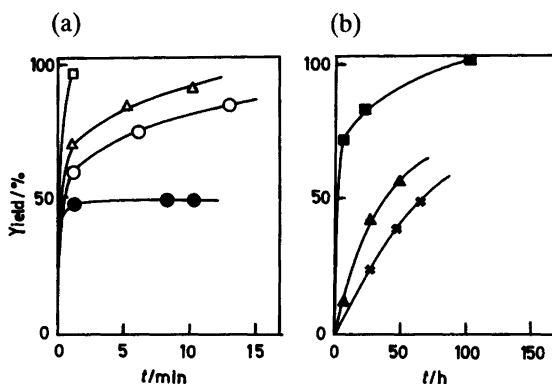*Fig. 1.* Plot of log k_2 *vs.* $E°$ (Table 1).

Fig. 2. Plot of yield of mononitro PAH:s *vs.* time in the nitration of PAH:s by N_2O_4 in dichloromethane at 20 °C. (a) Perylene (□), pyrene (△), anthracene (●) and anthracene in the presence of 10 mol % CH_3SO_3H (○). (b) Chrysene (■), naphthalene (▲) and triphenylene (★).

The $t_{\frac{1}{2}}$ and k_2 values should be regarded as indicative of magnitude rather than exact. Thus perylene (PeH) is too rapidly nitrated for the reaction to be reliably monitored by GLC. A plot of log k_2 *vs.* $E°$ gives a straight line of slope -5.8 with a correlation coefficient of 0.975 (see Fig. 1). As obvious from Fig. 2, showing the rate profiles of the reactions, anthracene exhibits special behaviour in the non-catalyzed reaction, and will therefore be the subject of a separate study.

In the following paper some of the peculiarities of the reaction between PeH and N_2O_4 are presented. The observed stoicheiometry of the reaction, 0.75 mol N_2O_4 per mol of PeH is identical to that found for pyrene (PyrH) (Table 5, expts. 21−27) and, in the presence of a catalytic amount of acid, for chrysene (ChrH). Using a 0.77 molar ratio of N_2O_4:ArH in TFA, Milligan[18] obtained mononitrotoluenes in 80 % yield, while a ratio of 3.9 was required to achieve total conversion. In the same study nitric oxide was detected as a reaction product.[18]

Treatment of a concentrated solution of PyrH in dichloromethane with N_2O_4 led to the formation of 0.5 mol NO/mol N_2O_4. By GLC the amount of water formed upon treatment of PeH with N_2O_4 was estimated at 0.35 ± 0.05 mol/mol PeH. Based upon eqn. (8) the yields of NO and H_2O in the two experiments were 75 and 70 %, respectively.

$$4\,ArH + 3\,N_2O_4 \rightarrow 4\,ArNO_2 + 2\,NO + 2\,H_2O \tag{8}$$

In order to further disentangle the effect of added acid on the reaction, a series of experiments with ChrH were performed (Table 2, expts. 2−10). The results parallel those earlier reported for naphthalene (NaphH)[27] in that TFA or weaker acids only have a limited effect at the catalytic level, whereas stronger acids, *e.g.* methanesulfonic acid (MSA), exhibit a very pronounced catalytic effect. Thus the addition of 5 mol % of MSA causes a decrease in the $t_{\frac{1}{2}}$ value from 65 to 3 min. An even more powerful catalytic influence is exhibited by NO^+, $t_{\frac{1}{2}}$ on the addition of 5 mol % $NOBF_4$ being reduced to approximately 30 s. Neither the addition of acid nor NO^+ alters the isomer distribution (>97 % 6-ChrNO_2, the other isomers were not identified). Similar results for the acid- and NO^+-catalyzed N_2O_4 nitration of NaphH are presented in Table 3. For the more reactive substrates, PyrH (Table

Table 2. Nitration of chrysene (ChrH) by N_2O_4 at 20 °C in dichloromethane. [ChrH]=0.01 M; [N_2O_4]=0.0075 M. Reaction period 3 min (expts. 1−11) or 40 min (expts. 12−17).

Expt. no.	Additive[a] (concentration/M)	Yield of ChrNO$_2$/%[b]
1	None	3
2	MSA (0.0001)	12
3	MSA (0.0005)	55
4	MSA (0.002)	96
5	MSA (0.005)	100
6	MSA (0.010)	99
7	CH_3COOH (0.002)	4
8	CF_3COOH (0.002)	12
9	p-$CH_3C_6H_4SO_3H$ (0.02)	94
10	CF_3SO_3H (0.002)	100
11	$NOBF_4$ (0.0005)	97
12	None	37
13	DBMP (0.0025)	31
14	DBMP (0.010)	0.1
16	$TBANO_2$ (0.001)	9
17	$TBANO_3$ (0.001)	13

[a] MSA=methanesulfonic acid; DBMP=2,6-di-t-butyl-6-methylpyridine. [b] In all experiments, ChrH corresponding to *ca.* 100 % material balance was recovered. Determined by GLC.

4, expts. 44−45) and PeH (following paper) the catalytic influence is accompanied by a decrease in the yield of mononitro product.

In Table 4 the results from the N_2O_4 nitration of PyrH in the presence of some representative bases/nucleophiles are presented (expts. 30−40). Upon addition of 20 mol % of 2,6-di-t-butyl-6-methylpyridine (DBMP) an increase in $t_{\frac{1}{2}}$ from 0.75 to 10 min was observed. Similar results were obtained when adding tetrabutylammonium nitrite ($TBANO_2$) or nitrate ($TBANO_3$), the weakest base, nitrate ion, exhibiting the smallest retarding effect. The anticatalytic influence of TBAI can to some extent be explained by reduction of N_2O_4, the iodine thus formed being unreactive towards PyrH under the reaction conditions. No simple explanation can presently be offered to the observation that the addition of TBABr causes the consumption of PyrH without formation of neither mononitro- nor monobromopyrene. Some analogous results for the base-retarded N_2O_4 nitration of ChrH are included in Table 2 (expts. 13−17). For neither substrate was any change in the isomer distribution observed, 1-PyrNO$_2$ (100 %) and 6-ChrNO$_2$ (>97 %) being formed.

Table 3. Nitration of naphthalene by N_2O_4 at 20 °C in dichloromethane. [NaphH]=0.010 M; [N_2O_4]=0.0075 M. Reaction period 20 min.

Expt. no.	Additive (concentration/M)	Yield of NaphNO$_2$/%[a]
18	None	1
19	CH_3SO_3H (0.01)	82
20	$NOBF_4$ (0.0005)	53

[a] Determined by GLC.

Table 4. Nitration of pyrene by N_2O_4 at 20 °C in dichloromethane. [PyrH]=0.010 M.

Expt. no.	N_2O_4/M	Additive (concentration/M)	Reaction period/min	Yield[a] of 1-PyrNO$_2$/%	Recovered[a] PyrH/%
21	0.001	None	180	14	83
22	0.0025	None	180	38	57
23	0.005	None	180	74	21
24	0.0075	None	180	101	0
25	0.010	None	180	97	0
26	0.015	None	180	73	0
27	0.050	None	180	50	0
28	0.0075	None	1	72	18
29	0.0075	None	10	93	6
30	0.0075	DBMP (0.001)	10	70	25
31	0.0075	DBMP (0.002)	10	54	43
32	0.0075	DBMP (0.004)	10	25	71
33	0.0075	DBMP (0.006)	10	13	82
34	0.0075	DBMP (0.008)	10	9	85
35	0.0075	TBANO$_3$ (0.001)	10	76	20
36	0.0075	TBANO$_3$ (0.005)	10	51	46
37	0.0075	TBANO$_3$ (0.010)	10	16	78
38	0.0075	TBANO$_2$ (0.005)	10	29	66
39	0.0075	TBABr (0.005)	10	< 1	55
40	0.0075	TBAI (0.005)	10	3	92
41	0.0075	CCl$_4$ as solvent	10	< 1	100
42	0.0075	CCl$_4$ as solvent	1200	71	28
43	0.0075	CH$_3$SO$_3$H (0.003)	10	92	0
44	0.0075	CH$_3$SO$_3$H (0.005)	10	81	0
45	0.0075	CF$_3$COOH (7.7)[b]	10	19	0

[a] Determined by GLC. [b] CH$_2$Cl$_2$:CF$_3$COOH 50:50 (v/v).

DISCUSSION

Before embarking on mechanistic considerations, some remarks on the state of N_2O_4 in different solvents are relevant. Massive information[33,34] is available on the homolytic dissociation $N_2O_4 \rightleftharpoons 2 NO_2$. A 0.01 M solution in dichloromethane contains 6.5 % of the monomer at 25 °C.[28] Two routes are possible for heterolytic dissociation; extensive reviews on these reactions have been given by Addison.[34] Formation of NO_2^+/NO_2^- in liquid N_2O_4 has only been observed upon the addition of strong Lewis acids, *e.g.* BF$_3$. Also, the assumption of the simultaneous presence of a fairly good reductant and a strong oxidant is thermodynamically questionable.[35] On the other hand, dissociation[36] into NO^+/NO_3^-, although occurring to a very small extent only in the pure liquid, is appreciable in media of higher dielectric constant and complete in dilute nitric acid.[34] Solutions of N_2O_4 in dichloromethane therefore must contain the following species: N_2O_4, NO_2, NO^+ and NO_3^-, the latter two within all likelihood as the ion pair $NO^+NO_3^-$. On addition of acids stronger than nitric acid, the formation of the ion pair will become increasingly favoured.

Many examples of initial radical attack by NO_2 (especially on olefins) are included in the literature on reactions between N_2O_4/NO_2 and organic compounds.[37–39] Obviously, the radical pathway is not prevalent here, as demonstrated by the high positional selectivities encountered. Interestingly, the PAH:s that are unsuitable for, or at least not cleanly nitrated by the present method are those containing bonds of more or less pronounced olefinic

character. Thus phenanthrene in our hands does not exhibit the general behaviour of PAH:s towards N_2O_4 as judged from preliminary studies on relative reactivity and product composition. Earlier reports are in accordance with an at least partially radical mediated pathway, a tetrahydromononitrobiphenanthryl nitrate [9,10] or very complex reaction mixtures being observed. Analogous observations have been made for anthracene [5,6] and acenaphthylene. [2]

As shown in Table 1 and Fig. 1, log k_2 fairly nicely correlates with $E°$ which can be considered as a measure of the reactivity toward one-electron oxidation of the PAH. We then must ask ourselves if NO_2 or N_2O_4 are powerful enough as ET oxidants toward PAH for an initial rate-determining ET step to be feasible. This problem can be addressed by application of the Marcus theory to eqn. (9). We need only consider NO_2 as ET oxidant

$$ArH + NO_2 \rightleftharpoons ArH^{+\cdot} + NO_2^- \qquad (9)$$

since it must be stronger as such than N_2O_4. The $E°$ value of NO_2/NO_2^- in aqueous solution has been calculated to be 1.0 V,[40–44] and by estimating ΔG_{tr}° from water to dichloromethane for the appropriate species of eqn. (10), we can get an approximate $E°(NO_2/NO_2^-)$ in dichloromethane.

$$NO_2(aq) + \tfrac{1}{2} H_2(g) \rightarrow NO_2^-(aq) + H^+(aq) \qquad (10)$$

Very few data of this type are known for dichloromethane,[44] however, and therefore data for transfer to the related, much more studied solvent, 1,1-dichloroethane, were used as a starting point.[45] We have previously[46] equated $\Delta G_{tr}^\circ(NO_2^-)$ with $\Delta G_{tr}^\circ(SCN^-)$ or $\Delta G_{tr}^\circ(I^-)$ in the absence of any data for NO_2^- and still have to resort to this approximation. In this particular case we have used $\Delta G_{tr}^\circ(I^-) = 7.4$ kcal mol^{-1} as an approximation for $\Delta G_{tr}^\circ(NO_2^-)$. In order to estimate $\Delta G_{tr}^\circ(H^+)$ a slightly different procedure was used: Available[45] $\Delta G_{tr}^\circ(H^+)$ were plotted vs. $\Delta G_{tr}^\circ(Na^+)$ (see Fig. 3) and $\Delta G_{tr}^\circ(H^+)$ was obtained at 10 kcal mol^{-1} for transfer to 1,1-dichloroethane by interpolation to $\Delta G_{tr}^\circ(Na^+) = 6.9$ kcal mol^{-1} determined for this solvent. $\Delta G_{tr}^\circ(H_2)$ is 0 by definition and $\Delta G_{tr}^\circ(NO_2)$ was assumed to be 0 in the absence of
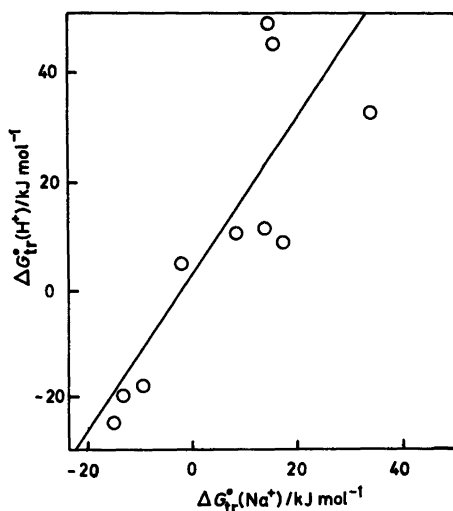

Fig. 3. Plot of $\Delta G_{tr}^\circ(H^+)$ vs. $\Delta G_{tr}^\circ(Na^+)$.[47]

relevant data. Since NO_2 is a neutral species, no serious error is introduced by this assumption. Thus $E^\circ(NO_2/NO_2^-)$ in 1,1-dichloroethane becomes equal to $1.0-(7.4+10)/23.06=0.25$ V, and the same value is considered to be valid in dichloromethane.

E° values of $ArH^{\cdot+}/ArH$ have been determined [31] in acetonitrile and thus should be corrected for solvent change in the same way. Considering the similarity of $\Delta G^\circ_{tr}(H^+)$ of the two media (10 and 11 kcal mol^{-1}, respectively, for transfer from water) and the diffuse charge distribution of the $ArH^{\cdot+}$ involved, implying little change in solvation upon transfer from acetonitrile to 1,1-dichloroethane, no correction was deemed necessary.

It is of course unsatisfactory that more accurate estimates are not available, but yet we consider the E° values thus obtained good enough for discussing the problem at hand, namely to see if ET from ArH to NO_2 [eqn. (9)] is feasible. Treatment of the log k_2 values of Table 1 according to the Marcus theory now becomes possible (for details, see Ref. 42) and we have chosen to fit the data to equation (70) of Ref. 42, putting log $k_d=10.30$ and $A=0.2$ and with the reorganization energy, λ, as the adjustable parameter. Table 5 shows the results of this analysis, using different assumptions about E°, chosen to probe the borderline toward the ET domain.

The electrostatic term of column 2 is the change in free energy upon transfer of the electron in the transition state; the dielectric constant was taken to be that of dichloromethane, 8.9, and the distance between $ArH^{\cdot+}$ and NO_2^- in the transition state$=3.5$ Å, giving an electrostatic term of -10.6 kcal mol^{-1}.

Table 5 shows that the starting data set, with the presently best estimate of $E^\circ(NO_2/NO_2^-)$, cannot at all be fitted to the Marcus equation. Only by assuming that $E^\circ(NO_2/NO_2^-)$ is too low by 0.65 V – or any other possible error(s) of the same magnitude – do we reach the domain where the reorganization energy becomes similar to that expected, $0.5 [\lambda(NO_2/NO_2^-)+\lambda(ArH^{\cdot+}/ArH)]=0.5(70+10)=40$ kcal mol^{-1}.[32]

In keeping with this result, reaction (9) has been demonstrated to be rapid and quantitative in the *reverse* direction for both naphthalene[27] and, more importantly, perylene[28] which is the most easily oxidizable compound of the set. Hence, the only reasonably strong ET oxidant available is NO^+ ($E^\circ=1.51$ V). However, any reaction of electrophilic nature would exhibit the same relative order of reaction rates for the substrates used (Table 1).

With NO_2^+ and NO_2 omitted from the group of conceivable attacking species, the discussion in the following will deal with three possibilities, namely: 1) NO^+ attacking as an ET oxidant followed by radical/radical cation coupling; 2) NO^+ attacking as an electrophile followed by formal oxygen transfer oxidation of the intermediate $PAH-NO^+$ complex; 3) N_2O_4, or a modification thereof, attacking as an electrophile.

Table 5. Fit of log$(k_2)/E^\circ$ data to eqn. (70) of Ref. 42.

$E^\circ(NO_2^-/NO_2^-)$/V	Electrostatic term/kcal mol^{-1}	λ/ kcal/mol^{-1} [a]	Remark
0.25	-10.6	28(30)	No fit possible!
0.70	-10.6	30(17)	
0.90	-10.6	40(10)	
1.10	-10.6	52(6)	

[a] Number within parentheses corresponds to the parameter interval at the 95 % confidence level.

At this stage, let us draw some parallels between NAC and N_2O_4 nitrations. Nitrous acid in nitric acid exists to some extent as NO^+,[27] and hence an equivalent to N_2O_4 (NO^+ and NO_3^-) is invariably present. NAC nitrations differ markedly from nitronium ion nitration in the relative reactivities observed. All aromatics more reactive than xylene are nitrated by NO_2^+ at the same, encounter-controlled rate, whereas the rates of NAC nitration, being very low for benzene and toluene, increase with increasing reactivity of the substrate.[19] As for positional selectivities, NaphH on treatment with NO_2BF_4 yields mononitronaphthalenes with an α/β ratio of 10;[47] while under NAC nitration conditions the ratio is of the order of 20,[25] similar to that of acid-catalyzed N_2O_4 nitration in dichloromethane.[27] Based on these observations, we suggest that NAC nitration and nitration by N_2O_4 merely are variations on a common theme.

Taking into account recent observations of radical pairs on the reaction path of NAC nitration,[24,26] it is tempting to consider 1) to be the route of choice. Moreover, the data on the relative reactivities are in better accordance with initial ET than electrophilic attack.[48] However, some major obstacles prevent us from supporting this proposal. Mesitylene and other substrates with $E°$ values much higher than what is energetically feasible for reasonably fast ET oxidation by NO^+ are nitrated *via* a NAC pathway by nitric/nitrous acid in TFA as well as by N_2O_4/CH_3SO_3H in dichloromethane. We have earlier[32] questioned whether it is reasonable to assume that the oxidizing power of NO^+ can be raised by the required extent in acidic media since naphthalene was not affected by treatment with $NOBF_4$ in dichloromethane. Moreover, the almost complete absence of by-products in the N_2O_4 nitration of NaphH is not in agreement with a mechanism involving the intermediacy of such an unstable and reactive species as the naphthalene radical cation, $NaphH^{+\cdot}$. We have earlier demonstrated that coupling between $NaphH^{\cdot+}$ and NO_2 yields mononitronaphthalenes with an α/β ratio >40.[28]

On the other hand, substrates yielding radical cations upon treatment with $NOBF_4$[49] in dichloromethane (*i.e.* those with $E°$ values lower than that of chrysene)[32] do not couple in any clean manner with NO_2 as shown and discussed in the following paper. Since NO^+ is a poor electrophile, it is reasonable to assume that it preferentially acts as an ET oxidant whenever possible. We therefore conclude that treatment of reactive aromatics with NO^+ results in the formation of either $ArH^{\cdot+}$ and NO or, for less easily oxidizable substrates, an $ArH \rightarrow NO^+$ π-complex.[50] Note that the addition of NO^+ or H^+ actually lowers the yield of mononitro product in the N_2O_4 nitration of PyrH and PeH. Substrates extremely susceptible to electrophilic attack will on the other hand be nitrosated by NO^+. In the case of phenol the isomer distribution ($o:p=0.03$) is significantly different from those observed in NO_2^+ ($o:p=2$) or NAC ($o:p=0.78$) nitrations.[21]

We may therefore conclude that NO^+ cannot be the attacking species, and hence both 1) and 2) can be eliminated. Left to be discussed is then only 3); electrophilic attack by N_2O_4, not as such but in some modified shape, since N_2O_4 itself is too weak an electrophile. In order to obtain a more reactive attacking species, N_2O_4 must be subjected to either protonation[36] or nitrosation, leading to the formation of species *1* or *2* shown in Scheme 1. The action of either species on an aromatic substrate leads to the formation of nitroaromatics in accordance with the overall stoicheiometry of eqn. (8). Although protonation at a first glance appears as the most likely of the two possibilities, no simple explanation for a) the catalytic action of NO^+ and b) the CIDNP effects observed is readily available. We therefore propose that the electrophile operating under NAC nitration conditions is $N_2O_4NO^+$ despite the fact that there is presently no physical evidence in favour of its existence. This suggestion is based upon the following reasoning.

$$\overset{+}{HO_2NNO_2} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} O_2NNO_2 \quad\begin{cases} \xrightarrow{\text{catalytic } H^+ \text{ or high } D} NONO_3 \\[2em] \xrightarrow[NONO_3]{NO^+ \text{ or}} O_2N\overset{+}{N}\text{—}ONO \\ \qquad\qquad\qquad\; \downarrow \\ \qquad\qquad\qquad\; O \end{cases}$$

$$1 \qquad\qquad\qquad\qquad\qquad\qquad\qquad 2$$

$$\overset{+}{Ar}(H)NO_2HNO_2 \underset{}{\overset{1}{\rightleftharpoons}} ArH \overset{2}{\rightleftharpoons} \overset{+}{Ar}(H)\overset{\overset{ONO}{|}}{N}ONO_2 \rightleftharpoons \overset{+}{Ar}(H)\overset{\overset{O^\cdot\;NO^\cdot}{|}}{N}ONO_2$$

$$\underset{+}{\uparrow\downarrow}\; 3a \qquad\qquad\qquad \downarrow\; 3b \qquad\qquad\quad \underset{+}{\uparrow\downarrow}\; 3c$$

$$\overset{+}{Ar}(H)NO_2 + HNO_2 \qquad \overset{+}{Ar}(H)NO_2 + N_2O_3 \qquad \overset{+}{Ar}(H)NO_2 + NO + NO_2$$

$$\uparrow\downarrow \quad N_2O_4 \qquad\qquad\qquad \downarrow \qquad\qquad\qquad\qquad\qquad 3d$$

$$HNO_2 + 1 + ArNO_2 \qquad ArNO_2 + NO^+ + HNO_2$$

$$\downarrow \qquad\qquad\qquad\qquad\qquad \downarrow$$

$$\tfrac{1}{2}NO + \tfrac{1}{2}NO_2 + \tfrac{1}{2}H_2O \qquad\qquad \tfrac{1}{2}NO + \tfrac{1}{2}NO_2 + \tfrac{1}{2}H_2O$$

Scheme 1.

Firstly, the equilibrium $N_2O_4 \rightleftharpoons NONO_3$ is assumed not to rest completely to the left in dichloromethane in order to account for the possibility of nitrating PeH or PyrH without added catalyst (H^+). With carbon tetrachloride as solvent, formation of $NONO_3$ is almost completely inhibited and nitration according to Scheme 1 becomes very slow (the influence of the ionizing power of the solvent is discussed in more detail in the following paper). Addition of acid either directly or indirectly catalyzes $NONO_3$ formation (indirectly by creating a medium of higher ionizing power), whereas the addition of base causes a considerable decrease in the rate of formation of $NONO_3$. The high positional selectivity of the reaction is in accordance with the relative bulkiness of 2 relative to NO_2^+, explaining the preference for substitution at the less reactive but less hindered 2-position in triphenylene.

Secondly, Scheme 1 allows for the formation of a radical pair on the reaction path without the involvement of direct electron transfer to NO^+. Assuming that formation of the initial σ-complex (*3b*) is a very rapid process, the rate determining step will be found on the pathway from *3b* to the nitro σ-complex. Deprotonation of the σ-complex is not slow for substrates less reactive than anthracene even in strongly acidic media.[51] We presently have no clues as to the nature of the break-down of *3b* into the nitro σ-complex. The route involving radical pairs *3c* and *3d* is only one possibility, attractive since the radical cationic species (*3c*) is further transformed intramolecularly, thus minimizing the possibility of by-product formation. Although *3c* is not a conventional aromatic radical cation, its stability may parallel that of the substrate radical cation. If then transformation *3b→3c* is rate-determining, the relative reactivities should correlate with E° values, expressing the ease of oxidation of the substrate.

Thirdly, NO^+ is known to form fairly strong complexes (bond energy mostly in the

interval 30−50 kcal mol^{-1}) in the gas phase with many types of organic bases, such as alcohols, aromatics, esters, ethers and ketones.[52] Also NO itself acts as a base, and the bond dissociation energy of NO−NO$^+$ has been determined to be *ca.* 14 kcal mol^{-1}.[53] Moreover, dinitrogen tetraoxide in nitric acid has been suggested (on the basis of Raman spectroscopic studies) to exist partly as a molecular compound of the composition NO_2NO^+.[54] Thus, there is nothing intrinsically wrong with the assumption that NO$^+$ might form a complex of the type discussed above with N_2O_4.

EXPERIMENTAL

Materials. The PAH:s used were of highest commercial quality available and used without further purification. Dichloromethane (Merck zur Rückstandsanalyse) and carbon tetrachloride (Merck *pro analysi*) were dried and stored over 3 Å molecular sieves. Solutions of N_2O_4 were made up as described previously[55] and concentrations determined by acid-base titration after treatment with hydrogen peroxide. 2,6-Di-*t*-butyl-6-methylpyridine was prepared according to a literature procedure.[56] All other reagents were commercial samples of highest purity available.

Warning 1. Some of the PAH:s and most of the nitro PAH:s included in this study are strongly mutagenic.

Warning 2. Solutions of N_2O_4 in organic solvents have been noted[57] to be potentially explosive. During the course of the present work, however, no incidents have occurred.

Nitrations with N_2O_4. Additives, if required, were weighed into tightly stoppered Erlenmeyer flasks. The PAH (generally 10−20 ml of a 0.010 M solution) and internal standard (0.02−0.04 mmol) were added followed by, at time=0, the required (see Tables) amount of N_2O_4. After the appropriate reaction period the solutions were analyzed by GLC using the conditions described previously.[29] The best results were obtained when using a glass insert in the injection port; estimated reproducibility ±5 %.

Synthesis of mononitro PAH:s. Solutions of the PAH (1 mmol) in dichloromethane (50 ml), CH$_3$SO$_3$H (0.1 mmol, if required, see Table 1) and N_2O_4 (0.8 mmol) in dichloromethane were mixed and allowed to stand for the appropriate reaction time. Most of the solvent was evaporated and 1 g of silica gel 60 (Merck, 230−240 mesh) was added. After completed evaporation the yellowish powder was placed on top of a column packed with silica gel and eluted with CH$_2$Cl$_2$ (containing up to 10 % CCl$_4$). The main isomers were recrystallized and identified by GLC retention times, MS, melting point and, for the mononitroperylenes, ^{1}H NMR.[28]

Determination of water. Using a Varian 3700 gas chromatograph equipped with a Varian CDS 111 integrator and a 3 m Porapak P column, the water contents of the following dichloromethane solutions were determined relative to water saturated benzene as external standard. Solution (water contents/mM): As received (5.5); dried (1.3); 0.0075 M N_2O_4 (5.0); 0.0075 M N_2O_4+0.005 M H$_2$O (9.3); 0.0075 M N_2O_4+0.010 M perylene, after complete conversion (8.1). From this the increase in water concentration due to nitration was estimated at 0.0035±0.0005 M.

Determination of nitric oxide. Pyrene (3 mmol) was treated with N_2O_4 (2 mmol) in a minimum of dichloromethane (*ca.* 5 ml). The flask was connected *via* rubber tubing to a measuring cylinder immersed under water, leading to the collection of 22 ml (*ca.* 1 mmol) of NO. Theoretical yield [eqn. (8)]: 1.33 mol.

REFERENCES

1. Nielsen, T., Ramdahl, T. and Björseth, A. *Environ. Health Perspec. 47* (1983) 103; Nielsen, T., Seitz, B. and Ramdahl, T. *Atmos. Environ. In press;* DiPaolo, J.A., De Marinis, A.J., Chow, F.L., Garner, R.C., Martin, C.N. and Doniger, J. *Carcinogenesis 4* (1983) 357 and references therein.
2. Cantrell, T.S. and Shechter, H. *J. Org. Chem. 33* (1968) 114.
3. Monti, L., Martello, V. and Valente, F. *Gazz. Chim. Ital. 66* (1936) 31.
4. Shorygin, P.P., Topchiev, A.V. and Ananina, V.A. *J. Gen. Chem. USSR 8* (1938) 981.
5. Wieland, H. *Ber. Dtsch. Chem. Ges. 54* (1921) 1776.
6. Barnett, E.B. *J. Chem. Soc.* (1926) 2040.
7. Pinck, L.A. *J. Am. Chem. Soc. 49* (1927) 2536.
8. Barlas, H., Parlar, H., Kotias, D. and Korte, F. *Z. Naturforsch. Teil B 37* (1982) 486.
9. Gray, G.W. and Bavin, P.M.G. *Chem. Ber. 96* (1963) 1277.
10. Heaney, H., Jones, A.J. and Millar, I.T. *J. Chem. Soc.* (1965) 2587.
11. Dewar, M.J.S., Mole, T. and Warford, E.W.T. *J. Chem. Soc.* (1956) 3576, 3581.
12. Nielsen, T. *Environ. Sci. Technol. In press.*
13. Norman, R.O.C., Parr, W.J.E. and Thomas, C.B. *J. Chem. Soc. Perkin Trans. 1* (1974) 369.
14. Olah, G.A., Malhotra, R. and Narang, S.C. *J. Org. Chem. 43* (1978) 4628.
15. Bonner, T.G. and Hancock, R.A. *J. Chem. Soc. Chem. Commun.* (1967) 780.
16. Underwood, G.R., Silverman, R.S. and Vanderwalde, A. *J. Chem. Soc. Perkin Trans. 2* (1973) 1177.
17. Bonner, T.G., Hancock, R.A., Yousif, G. and Rolle, F.R. *J. Chem. Soc. B* (1969) 1237.
18. Milligan, B. *J. Org. Chem. 48* (1983) 1495.
19. Schofield, K. *Aromatic Nitration,* Cambridge Univ. Press, London, New York 1980, p. 79 and references therein.
20. Giffney, J.C. and Ridd, J.H. *J. Chem. Soc. Perkin Trans. 2* (1979) 618.
21. Ross, D.S., Hum. G.P. and Blucher, W.G. *J. Chem. Soc. Chem. Commun.* (1980) 532.
22. Main, L., Moodie, R.B. and Schofield, K. *J. Chem. Soc. Chem. Commun.* (1982) 48.
23. Ross, D.S., Malhotra, R. and Ogier, W.C. *J. Chem. Soc. Chem. Commun.* (1982) 1353.
24. Clemens, A.H., Ridd, J.H. and Sandall, J.P.B. *J. Chem. Soc. Chem. Commun.* (1983) 343.
25. Ross, D.S., Moran, K.D. and Malhotra, R. *J. Org. Chem. 48* (1983) 2118.
26. Clemens, A.H., Ridd, J.H. and Sandall, J.P.B. *J. Chem. Soc. Perkin Trans. 2* (1984) 1659.
27. Eberson, L. and Radner, F. *Acta Chem. Scand. B 34* (1980) 739.
28. Eberson, L. and Radner, F. *Acta Chem. Scand. B 39* (1985) 357.
29. Radner, F. *Acta Chem. Scand. B 37* (1983) 65.
30. Svendsen, H., Rønningsen, H.-P., Sydnes, L.K. and Greibrook, T. *Acta Chem. Scand. B 37* (1983) 833.
31. Parker, V.D. *J. Am. Chem. Soc. 98* (1976) 98.
32. Eberson, L. and Radner, F. *Acta Chem. Scand. B 38* (1984) 861.
33. Redmond, R.F. and Wayland, B.B. *J. Phys. Chem. 72* (1968) 1626; Grätzel, M., Henglein, A., Lilie, J. and Beck, G. *Ber. Bunsenges. Phys. Chem. 73* (1969) 646.
34. a. Addison, C.C. *Chemistry in Nonaqueous Ionizing Solvents,* Friedr. Vieweg & Sohn GmbH, Braunschweig 1967, Vol. III/I; b. Addison, C.C. *Chem. Rev. 80* (1980) 21.
35. Wartel, M., Boughriet, A. and Fischer, J.-C. *Anal. Chim. Acta 110* (1979) 211.
36. Effenberger, F., Kurtz, W. and Fischer, P. *Chem. Ber. 107* (1974) and references therein.
37. Titov, A.I. *Tetrahedron 19* (1963) 557.
38. Rees, Y. and Williams, G.H. *Advances in Free Radical Chemistry,* Logos Press, London 1969, Vol. III/4, p. 214.
39. Pryor, W.A., Lightsey, J.W. and Church, D.F. *J. Am. Chem. Soc. 104* (1982) 6685.
40. Berdnikov, V.M. and Bazhin, N.M. *Russ. J. Phys. Chem. 44* (1970) 395.
41. Malone, S.D. and Endicott, J.F. *J. Phys. Chem. 76* (1972) 2223.
42. Eberson, L. *Adv. Phys. Org. Chem. 18* (1982) 79.

43. Stanbury, D.M. and Lednicky, L.A. *J. Am. Chem. Soc. 106* (1984) 2847.
44. Stanbury, D.M. *Personal communication.*
45. Marcus, Y. *Pure Appl. Chem. 55* (1983) 977.
46. Eberson, L. and Nyberg, K. *Acta Chem. Scand. B 32* (1978) 235.
47. Olah, G.A., Narang, S.C. and Olah, J.A. *Proc. Natl. Acad. Sci. U.S.A. 78* (1981) 3298.
48. Pryor, W.A. *Personal communication.*
49. Bandish, B.K. and Shine, H.J. *J. Org. Chem. 42* (1977) 561.
50. Reents, W.D., Jr. and Freiser, B.S. *J. Am. Chem. Soc. 102* (1980) 271.
51. Olah, G.A., Narang, S.C., Malhotra, R. and Olah, J.A. *J. Am. Chem. Soc. 101* (1979) 1805.
52. Reents, W.D., Jr. and Freiser, B.S. *J. Am. Chem. Soc. 103* (1981) 2791.
53. Ng, C.Y., Tiedemann, P.W., Mahan, B.H. and Lee, Y.T. *J. Chem. Phys. 66* (1977) 3985.
54. Goulden, J.D.S. and Millen, D.J. *J. Chem. Soc.* (1950) 2620.
55. Eberson, L., Jönsson, L. and Radner, F. *Acta Chem. Scand. B 32* (1978) 749.
56. Andersson, A.G. and Stang, P.J. *J. Org. Chem. 41* (1976) 3034.
57. *Chem. Eng. News Nov. 23* (1964) 53.