

Nitration of Aromatics *via* Electron Transfer. IV.* On the Reaction between Perylene Radical Cation and Nitrogen Dioxide or Nitrite Ion

LENNART EBERSON** and FINN RADNER

Division of Organic Chemistry 3, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden

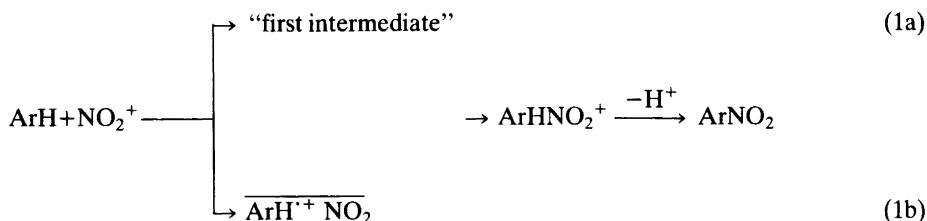
The electron transfer mechanism for aromatic nitration by nitronium ion involves as a crucial step the diffusion-controlled coupling between a radical cation and nitrogen dioxide. We now report that the reaction between (perylene)^{•+} hexafluorophosphate or trifluoromethanesulfonate with nitrogen dioxide does not lead to the clean formation of mononitroperylene. This militates against the possibility of the nitronium ion acting as an electron transfer oxidant in all practical cases of aromatic nitration, perylene being one of the most easily oxidizable aromatics available. These results are in accordance with earlier presented calculations based on the Marcus theory. The observation of radical cations under conditions of aromatic nitration is suggested to be the result of either homolytic dissociation of the σ complex under strongly acidic conditions or oxidation by nitrosonium ion impurities.

(Perylene)^{•+} reacts instantaneously with nitrite ion in a 100 % electron transfer process, yielding perylene and dinitrogen tetroxide. The reaction between the two latter species leads to the formation of mononitroperylene in excellent yields with high 3-/1- isomer ratio in neutral or slightly acidic media or with low 3-/1- ratio under basic conditions or in media of low ionizing power.

The mechanism of aromatic nitration has remained an area of major interest for many decades.¹ Two important discussion points are presently the possible involvement of an electron transfer (ET) step prior to σ -complex formation²⁻⁸ and the role of N(III) species as catalysts in the nitration of reactive aromatics.⁹⁻¹³ As stressed by Olah,^{1b} the necessity of a "first intermediate" [eqn. (1a)] constitutes a widely accepted conclusion. The "first intermediate" has been suggested to be a non-bonded encounter pair,¹⁶ a π complex,¹⁷ a charge transfer (CT) complex¹⁸ and, on the extreme of the CT representation, a radical/radical cation pair, formed in an ET step as originally proposed by Kenner^{2a} and Weiss^{2b} [eqn. (1b)].

* Part III, see Ref. 21c.

** To whom correspondence should be addressed.



The latter possibility was recently revived by Perrin.³ The ET mechanism (1b) has a least one unique feature relative to the others, namely the capability of explaining most of the common side-reactions in aromatic nitration,¹⁹ such as oxidative substitutions and biaryl coupling, reactions known to be mediated by radical cations in many other cases.²⁰ Evidence for the ET formalism includes thermochemical calculations,^{3,4} observation (UV/ESR) of radical cations and/or NO_2 under conditions of aromatic nitration,⁷ and the similarity of products arising from the reactions of ArH with NO_2^+ and of ArH^+ with NO_2 .⁸ On the other hand, the non-involvement of ET has been clearly demonstrated from CIDNP studies on the NO_2^+ mediated nitration of mesitylene,^{13c} and inferred from studies on the reactions between radical cations and NO_2 ,^{21,22} making the overall picture of the ET mechanism somewhat confused.

Traditionally, the catalytic effect of N(III) species upon nitration of reactive aromatics has been explained as nitrosation followed by oxidation of ArNO ,²³ a hypothesis that has been questioned in later years. Ridd *et al.* have presented kinetic and spectral (CIDNP) evidence of the intermediacy of radical cations in the nitrous acid catalyzed (NAC) nitration of *N,N*-dimethylaniline and interpreted this according to eqns. (2)–(4).⁹ Further evidence of the possible ET catalyzing effects of HNO_2 , NO^+ or the lower oxides of nitrogen has been demonstrated in the nitration of phenol,¹⁰ 1,2,3-trimethoxy-5-nitrobenzene,¹¹



naphthalene,¹² 4-nitrophenol^{13a,b} and mesitylene.^{13c} In the latter study the feasibility of eqn. (3) was questioned since NO_2^+ formation was suspected to be slower than the oxidation step of eqn. (2).

Treatment of an excess of phenothiazine with nitric acid in perchloric acid leads to the autocatalytic formation of phenothiazine radical cation.⁶ The proposed reaction steps are shown in eqns. (5) and (6).



We recently applied the Marcus theory to elucidate the properties of NO^+ and NO_2^+ as ET oxidants, and predicted the former species to be by far the most effective one, despite the fact that $E^\circ(\text{NO}^+/\text{NO})$ and $E^\circ(\text{NO}_2^+/\text{NO}_2)$ are almost identical. The difference resides in

the very large difference in reorganization energies of the NO^+/NO and $\text{NO}_2^+/\text{NO}_2$ self-exchange reactions (70 vs. 140 kcal mol⁻¹). It was thus concluded that aromatic substrates with $E^\circ(\text{ArH}^+/\text{ArH}) \geq \text{ca. } 0.2 \text{ V vs. NHE}$ will react with NO_2^+ via direct bond formation. On the other hand, NO^+ , with an *electrophilic* reactivity of ca. 10^{-14} of that of NO_2^+ ,¹⁴ was predicted to undergo non-bonded ET with aromatics having $E^\circ(\text{ArH}^+/\text{ArH})$ lower than that of chrysene (1.8 V).

In this paper we study the rather complex reaction pattern in the nitration of an easily oxidizable model aromatic hydrocarbon, perylene ($E^\circ=1.30 \text{ V}$), by different nitrogen oxide species. The results are discussed in relation to the predicted ET oxidizing properties of NO^+ and NO_2^+ .

RESULTS

Nitration of perylene by nitric acid or dinitrogen tetroxide. Earlier reports²⁴⁻³⁰ on the nitration of perylene (PeH) are summarized in the upper part of Table 1. Since also bromination, formylation and sulfonation³¹ initially occur almost exclusively at the 3-position, the formation of a large proportion of 1-nitroperylene (1-PeNO₂) upon treatment of PeH with HNO₃ in aqueous dioxane,²⁸ although properly documented, seems a bit peculiar. Our own attempts to reproduce this experiment have repeatedly failed; treatment of PeH with HNO₃ in a variety of solvents regularly gave less than 5 % of 1-PeNO₂ in the presence or absence of stronger acids. Some representative examples are included in Table 1.

Treatment of reactive aromatics with N(IV) species, *i.e.*, NO₂/N₂O₄ has been shown earlier to yield nitrated products.³² We recently reported³³ that the method of choice for the mononitration of a large number of polycyclic aromatic hydrocarbons (PAH:s) is simply to mix solutions of the PAH and N₂O₄ in dichloromethane. The general features of this

Table 1. Nitration of perylene under different conditions.

Conditions for nitration	Product (yield/%) ^a	Ratio of 3-/1-mononitro isomers ^a	Ref.
NaNO ₂ , H ₂ SO ₄ , 100 °C	Perylene-3,10-quinone		24
HNO ₃ , reflux	3,4,9,10-Tetra-nitroperylene		25
HNO ₃ , CCl ₄ , 0 °C	3,10-Dinitroperylene		26
HNO ₃ , Ac ₂ O, 15 °C	Nitroperylene (35) ^b	>20 ^e	27
HNO ₃ , aq. dioxane, 100 °C	Nitroperylene (80) ^c	2.3	28
AgNO ₂ , I ₂ , CH ₃ CN, rt	Nitroperylene (66) ^c	(∞) ^e	29
N ₂ O ₄ , CH ₂ Cl ₂ , rt	Nitroperylene (97) ^c	124	30
HNO ₃ , aq. dioxane, 100 °C	^d		This work
Aq. HNO ₃ , dioxane, rt	Nitroperylene (60) ^c	39	This work
HNO ₃ , Ac ₂ O, rt	Nitroperylene (70) ^c	20	This work
HNO ₃ , CH ₂ Cl ₂ , rt	Nitroperylene (36) ^c	100	This work
Aq. HNO ₃ , H ₂ SO ₄ , CH ₂ Cl ₂ , rt	Nitroperylene (17) ^c	24	This work

^a Experimental values in this work determined by GLC. ^b Based on HNO₃. ^c Based on perylene. ^d No mononitroperylene detected; complex mixtures containing some di- and polynitrated perylene observed. ^e No 1-PeNO₂ was identified.

Table 2. Nitration of perylene by N_2O_4 at 20 °C in dichloromethane. $[PeH]=0.01$ M; $[N_2O_4]=0.075-0.080$ M. Reaction period 8 min, unless otherwise stated.

Additive (concentration/M)	Yield of PeNO ₂ /% ^a	Ratio of 3-/1- mononitro isomers	Additive (concentration/M)	Yield of PeNO ₂ /% ^a	Ratio of 3-/1- mononitro isomers
None ^c	98 ^b	82	TBAOAc ^c (0.001)	96	3.1
TBACF ₃ SO ₃ (0.005)	97	75	TBANO ₂ (0.002)	92	2.5
CH ₃ COOH (0.001)	95	63	TBAI ^d (0.016)	20 ^f	2.5
CH ₃ COOH (0.3)	20 ^f	100	TBAI (0.0015)	97 ^b	2.3
CF ₃ COOH (1.5)	10 ^g	100	TBAI (0.0003)	90	4.9
CF ₃ COOH (7.7)	3 ^h	100	TBAI (0.0002)	90	5.2
CF ₃ COOH (12.8)	— ⁱ	—	TBAI (0.0001)	90	7.4
MSA (0.025)	54 ^k	19	TBAI (0.00005)	90	15.7
Satd. H ₂ O	98	27	DBMP (0.001)	98	3.0
TBAF (0.001)	90	2.7	DBMP (0.008)	54 ^l	2.0
TBABr (0.001)	86	3.0			

^a Determined by GLC, unless otherwise stated. ^b Isolated yield. ^c Reaction period 1 min. ^d Reaction period 7 days. ^e As TBA(AcO)₂H. ^f PeH (70 %) recovered. ^g PeH (30 %) recovered. ^h PeH (6 %) recovered. ⁱ No PeH recovered. ^j PeH (3 %) recovered. ^k Yield of PeNO₂ approximately equal to amount of PeH consumed.

reaction were presented in the preceding paper,¹⁵ and we here report only those results of the PeH/N₂O₄ reaction that are of interest for the mechanistic discussion (see Tables 2 and 3). In Fig. 1 the yield of mononitroperylene vs. equivalents of N₂O₄ added is plotted. The observed stoichiometry is 0.75 mol N₂O₄/mol of PeH, and upon addition of excess N₂O₄ dinitration and side-reactions take place, thus lowering the yield of mononitro product. The reaction is very fast; 3-PeNO₂ is formed in virtually quantitative yield after 1 min upon treatment of perylene (10 mM) with N₂O₄ (7.5 mM), the 3-/1- ratio being of the order of 10². The addition of a strong acid such as methanesulfonic acid prior to addition of N₂O₄, earlier shown to have a beneficial catalytic effect upon nitration of less reactive aromatics, e.g. naphthalene, lowers the yield considerably and to some extent, the 3-/1- ratio. Addition of the tetrabutylammonium (TBA) salt of a strong acid, such as TBACF₃SO₃, has no effect in contrast to TBA salts with basic/nucleophilic anions. Addition of TBACl causes formation of chloroperylene and was not further investigated, while the addition of 10 mol-% of, e.g., TBANO₂ or TBABr, leads to the formation of nitroperylene in a 3-/1- ratio of 2–3. The stoichiometry remains unaffected, and the same results are obtained upon adding silver nitrite when acetonitrile, but not dichloromethane, is used as solvent. This is a result of the insolubility of Ag(I) salts in dichloromethane. Low $\frac{3}{1}$ ratios are also found when a hindered base such as 2,6-di-*t*-butyl-4-methylpyridine (DBMP) is added and when carbon tetrachloride, pentane or benzene are used as solvents (Table 3). Addition of TFA is detrimental, in that the amount of PeH as well as PeNO₂ (solely 3-) present after work-up decreases with increasing TFA/CH₂Cl₂ ratio (Table 2).

1-PeNO₂ or 3-PeNO₂ was partly recovered after treatment overnight with methanesulfonic acid in dichloromethane at 20 °C with no sign of isomerization to the other isomer. No dramatic difference in the rates of further nitration was observed, treatment of approximately equimolar mixture by N₂O₄ in dichloromethane revealed a relative rate of disappearance, $k_{1\text{-PeNO}_2}/k_{3\text{-PeNO}_2}$, of ca. 1.1.

Table 3. Nitration of perylene by N₂O₄ in different solvents^a at 20 °C. Reaction period 16 h. [PeH]=0.00058 M; [N₂O₄]=0.00044 M.

Solvent	Yield of PeNO ₂ /%	Ratio of 3-/1-mononitro isomers	Additive	
CH ₂ Cl ₂	95	100		
Dioxane	52	100		
Tetrahydrofuran	61	44		
CHCl ₃	88	40		
CH ₃ CN	95	39		
CH ₃ CN	90	4.9		5 mol % AgNO ₂
CH ₃ NO ₂	89	23		
Diethyl ether	4	9.2		
CH ₃ COOH	90	7.3		
CH ₃ COOH	70 ^c	13		1 mol % CH ₃ SO ₃ H
C ₆ H ₆	100	2.9		
Pentane	15	2.4		
CCl ₄	100	1.8		

^a PeH was initially dissolved in CH₂Cl₂; all runs therefore performed in the presence of 5 vol % CH₂Cl₂.

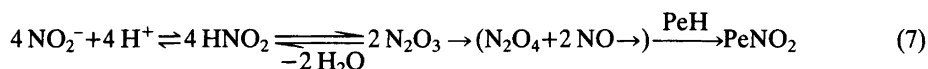
^b Only approximate GLC yields, measured without internal standard; accuracy ± 15 %. As a rule PeH corresponding to ca. 100 % material balance was recovered, unless otherwise stated. ^c No PeH recovered.

Table 4. Reactions of perylene with silver- or tetrabutylammonium nitrite in the presence of acid or iodine at 20 °C.

Source of NO ₂ ⁻	Solvent	Additive	Molar ratio PeH:NO ₂ ⁻ : additive	Yield of PeNO ₂ / % ^a	Ratio of 3-/1- mononitro isomers
TBANO ₂	CH ₂ Cl ₂	—	1:10:—	—	—
TBANO ₂	CH ₂ Cl ₂	I ₂	1:4:2	5	1.5
TBANO ₂	CH ₂ Cl ₂	TFA	1:2:1.3	85	2.0
TBANO ₂	CH ₃ CN	I ₂	1:4:2	30	1.9
AgNO ₂	CH ₂ Cl ₂	TFA	1:1.2:1.2	95	45
AgNO ₂	CH ₂ Cl ₂	I ₂	1:>4:0.5	80	100
AgNO ₂	CH ₃ CN	I ₂	1:1.8:0.5	85	2.1

^a Determined by GLC.

The reactions between PeH and (initially) N(III) species are summarized in Table 4. No reaction takes place when PeH is treated with TBANO₂ in dichloromethane or with silver nitrite in acetonitrile, but the addition of acid to these mixtures (or iodine, as discussed below) causes nitration. Since low 3-/1- ratios only are observed under conditions where nitrite ions is easily soluble, it is reasonable to assume that nitration is effected *via* the same route as observed for N(IV) [eqn. (7)].



Reactions of PeH with nitrosonium salts have been shown³³ to give the radical cation salt (*e.g.*, PeH^{•+}BF₄⁻ from NOBF₄).

Preparation and analysis of (perylene)^{•+} salts. Any study of PeH^{•+} reactions is complicated by the presence of PeH in preparations of PeH^{•+} salts. Since PeH reacts rapidly with N₂O₄ it is important to a) minimize the proportion of PeH in the PeH^{•+} salt and b) develop a good method for determining the PeH^{•+}/PeH ratio. None of these problems is trivial. The most thoroughly documented method of preparation of PeH^{•+} is electrocrystallization;^{34,35} the passage of very weak currents through PeH solutions of TBAX (X=BF₄, PF₆, ClO₄) in dichloromethane causes the formation of beautiful black needles of (PeH)₂X at the anode. However, the use of these salts introduces 1 mol of PeH per mol of PeH^{•+} to be studied.

Iodine and PeH form molecular complexes of various compositions, *e.g.*, PeH(I₂)_{1.5}³⁶ and PeHI_{2.92}.³⁷ The latter has been shown to be partially oxidized with the schematic representation (PeH^{•+})_{0.4}(I₃⁻2I₂)_{0.4} so here the PeH/PeH^{•+} ratio is even less favourable. The addition of Ag⁺ (*e.g.*, as AgClO₄) to PeH/iodine mixtures causes separation of the PeH^{•+} salt, suggested by elementary analysis³⁸ and iodometric titration³⁴ to have the composition PeHClO₄, AgI.

Another method for the preparation of PeH^{•+} is oxidation of PeH by NOBF₄ but also here the index *n* in (PeH)_{*n*}BF₄ is unknown.

In order to determine the PeH/PeH^{•+} ratio, we applied the following method to the iodine-silver ion system, assuming that the solubility of (PeH)_{*n*}X in dichloromethane is negligible relative to that of PeH and that the internal standard used, triphenylene, remains unaffected under the reaction conditions.²⁹ Solutions of PeH (10 mM), triphenylene and

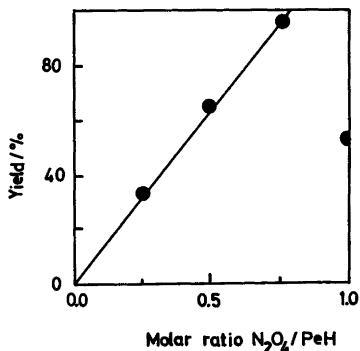


Fig. 1. Yield of mononitroperylene vs. equivalents of N_2O_4 added to perylene (0.0065 M) in acetonitrile at 20 °C; reaction period 30 min.

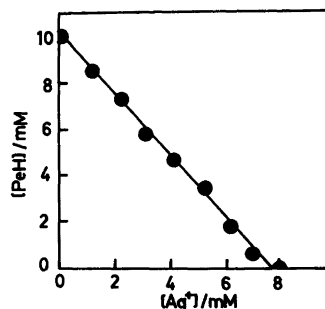


Fig. 2. Concentration of perylene remaining in solution vs. amount of AgTFMS ($[Ag^+] = 2[I_2]$) added. $[PeH]_0 = 0.01$ M. Average of three determinations.

silver trifluoromethanesulfonate (AgTFMS, initially dissolved in a small amount of acetonitrile) (10 mM) in dichloromethane were treated with solutions of iodine in dichloromethane [formal concentration 0–5 mM, 0–1 equivalents based on the stoichiometry given in eqn. (8)].



After mixing the solid was allowed to precipitate and after 3 min $[PeH]$ in the supernatant was determined by GLC. A plot of $[PeH]$ vs. formal $[I_2]$ is given in Fig. 2, revealing a composition of the solid of $(PeH)_{1.33}TFMS, AgI$.

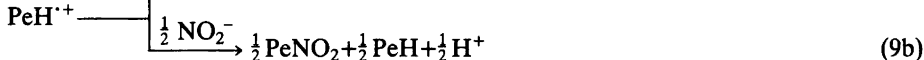
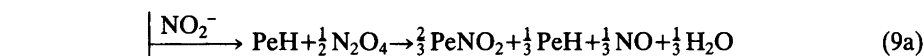
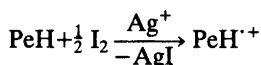
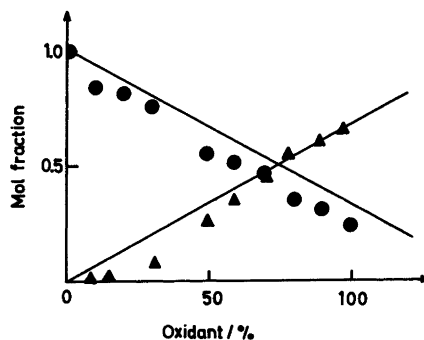
Reaction between (perylene)⁺⁺ and nitrite ion. In Table 5 the reactions between PeH^{++} and nitrite ion are summarized. To obtain comparable values of the amount of $PeNO_2$ formed from the various PeH^{++} preparations, the total amount of perylene added had to be accounted for. Therefore the $(PeH)_2PF_6$ preparations are listed as consisting of 100 % PeH and 100 % PeH^{++} while $(PeH)_{1.33}TFMS$ was assumed to contain 33 and 100 %, respectively. On addition of sodium nitrite to a suspension of the PeH^{++} salt in dichloromethane the initial violet colour immediately changed into orange, and within 1 min into red. With $TBANO_2$ the 3/-1- ratio was considerably lowered. Therefore the reaction must proceed *via* initial ET followed by $PeNO_2$ formation *via* reaction of PeH with N_2O_4 . As inferred from the stoichiometry of eqn. (9a) below, the theoretical yield of $PeNO_2$ is 67 %, based on the amount of PeH^{++} ; in Table 5 the yields range from 5 to 79 %. However, if the results from the reaction of $PeHTFMS$ with excess $TBANO_2$ and $AgNO_2$ in acetonitrile are omitted (here the ET step apparently proceeded but the follow-up reaction was slowed down due to the presence of a large excess of dissolved nitrite ion) the average yield from the five remaining experiments is 65 %. The low material balances for $(PeH)_2PF_6$ can partially be explained by the formation of chloroperylene (as observed with naphthalene^{21b}) whereas in the experiments with the preparations of the formal composition $PeHTFMS$ excess I_2 and AgTFMS may interfere. Upon treatment of PeH with 10, 20, ..., 100 % of the required [eqn. (8)] amounts of I_2 and AgTFMS in dichloromethane, followed by a large excess of $NaNO_2$, the amount of PeH and $PeNO_2$ detected after work-up nicely corresponded to the stoichiometry of eqn. (9a), as shown in Fig. 3, apart for some PeH consistently being lost.

Table 5. Reactions of perylene radical cation with nitrite ion at 20 °C.

Nature of PeH ^{•+} salt	Source of NO ₂ ⁻	Solvent	No. of equivalents of NO ₂ ⁻ ^a	Yield/% ^b			Ratio of 3-/1- Mononitro isomers
				PeH ^c	PeNO ₂ ^d	Sum ^e	
(PeH) ₂ PF ₆ ^{f,i}	{ TBANO ₂ TBANO ₂ NaNO ₂	CH ₂ Cl ₂	1	95	51 ^k	146	2.1
		CH ₂ Cl ₂	2	96	68	164	2.4
		CH ₂ Cl ₂	>10	98	79	177	30
PeHTFMS ^g	{ TBANO ₂ AgNO ₂ NaNO ₂	CH ₃ CN	>10	87	5	92	4.2
		CH ₃ CN	>10	45	38	83	10
		CH ₃ CN	>10	25	64	89	100
(PeH) _{1.33} TFMS	TBANO ₂	CH ₂ Cl ₂	1	68	64	132	3.1

^a Based on [PeH^{•+}]. ^b Determined by GLC, unless otherwise stated. ^c Theoretical yield of PeH: For (PeH)₂PF₆, 133 %, PeHTFMS 33 %, (PeH)_{1.33}TFMS 67 %. ^d Theoretical yield 67 %. ^e Theoretical sums of yields 200, 100 and 133 %, respectively. ^f Prepared by electrocrystallization. ^g Prepared from 1 eq. PeH, 1 eq. AgTFMS, 0.5 eq. I₂. ^h Prepared from 1 eq. PeH, 0.75 eq. AgTFMS, 0.375 eq. I₂. ⁱ Chloroperilyenes were also formed in these experiments (presumably from the electrocrystallization process ^{21b}). ^k Isolated yield.

Fig. 3. Plot of mol fraction of PeNO_2 (based on initial $[\text{PeH}]$) (triangles) and PeH (circles) resulting from the reaction of $\text{PeH}^+\text{TFMS}^-$ with NaNO_2 in dichloromethane vs. percentage oxidant added (based on initial $[\text{PeH}]$). Solid lines represent theoretical amounts.



It should be noted that the nitration taking place when treating PeH with I_2 and AgNO_2 in acetonitrile is not radical cation mediated in the way suggested by Ristagno and Shine^{29,34} (9b) since with an excess of AgNO_2 the observed 3/-1- ratio is much lower in acetonitrile than in dichloromethane (Table 4, last two entries) as a consequence of dissolved nitrite ion being present. Moreover, mixing solutions of I_2 and AgNO_2 in the absence of PeH produces a brown solution plus solid AgI . This solution after filtration shows the same nitration characteristics vs. PeH as solutions of N_2O_4 prepared by other methods. Moreover, the yield of N_2O_4 from I_2 and AgNO_2 has been shown to be almost quantitative in carbon tetrachloride.³⁹

Reaction between (perylene)^{•+} and nitrogen dioxide. The similarity of the reactions of perylene and naphthalene radical cation (NpH^+) with nitrite ion (both exhibiting 100 % initial electron transfer) is shifted into dissimilarity in their respective reactions with nitrogen dioxide. With NpH^+ rapid coupling of the two radicals to give 100 % NpNO_2 (α/β ratio=60) was observed, while for PeH^+ neither clean coupling nor any other clear reaction pattern can be discerned. The main problems encountered are the following: (1) The very low solubility of the PeH^+ salts (once crystallized) in non-acidic solvents, (2) concurrent $\text{PeH}/\text{N}_2\text{O}_4$ nitration and (3) if any coupling takes place protons are eventually formed, and are likely to induce unwanted reactions.

In the upper part of Table 6 some of the results from the reactions between electrochemically prepared $(\text{PeH})_2\text{PF}_6$ and N_2O_4 are summarized. As in Table 5, a 100 % PeH and PeH^+ content is assumed, the theoretical yields for the reaction between equimolar amounts of PeH^+ and NO_2 according to eqn. (1b) then being 100 % of PeH and PeNO_2 , respectively. For this to be true, the rate of coupling must be $\geq 10^2$ times greater than the rate of $\text{PeH}/\text{N}_2\text{O}_4$ nitration. Invariably, on N_2O_4 addition the blue-fluorescent violet suspension gradually turned brown or black and the formation of tarry solids, partly consisting of di- and polynitroperylene, was noticed. The brown-black colour instan-

Table 6. Reactions of perylene radical cation with N₂O₄ at 20 °C. Reaction period >2 h.

Nature of PeH ^{•+} salt	Solvent	No. of equivalents of NO ₂ and DBMP (in parentheses)	Yield/% ^b			Ratio of 3-/1- mononitro isomers
			PeH ^c	PeNO ₂ ^d	Sum ^e	
(PeH) ₂ PF ₆ ^{f,i}	C ₂ H ₅ CN	1.3	102	15	117	>100
	CH ₂ Cl ₂	2.1	81	3	84	>100
	C ₂ H ₅ CN	1.0	106	47	153	>100
	CH ₂ Cl ₂	1.0	96	45	141	>100
	CH ₂ Cl ₂	1.3	40	52	92	>100
(PeH) _{1.33} TFMS	CH ₂ Cl ₂	1.0	48	10	58	>100
	CH ₂ Cl ₂	1.3	26	16	42	>100
	CH ₂ Cl ₂	1.0 (1.0)	36	54	90	19
	CH ₂ Cl ₂	1.0 (2.0)	26	56	82	20
	CH ₂ Cl ₂	1.3 (1.3)	1	74	74	9

^a Based on [PeH^{•+}]. ^b Determined by GLC. ^c Theoretical yield of PeH. For (PeH)₂PF₆ 100%, (PeH)_{1.33}TFMS 33%. ^d Theoretical yield 100%. ^e Theoretical sums of yield 200 and 133%, respectively. ^f Prepared by electrocrystallization. ^g Prepared from 1 eq. PeH, 0.75 eq. AgTFMS, 0.38 eq. I₂. ^h No 1-PeNO₂ observed when 3-/1- >100.

taneously shifted into orange on the addition of dithionite, indicating that the brown/black colouration is due to the radical cation or another long-lived easily reducible species.

Using the (PeH)_{1.33} TFMS preparation (Table 6, lower part, theoretical yield 33 % PeH and 100 % PeNO₂) very much the same behaviour was observed.

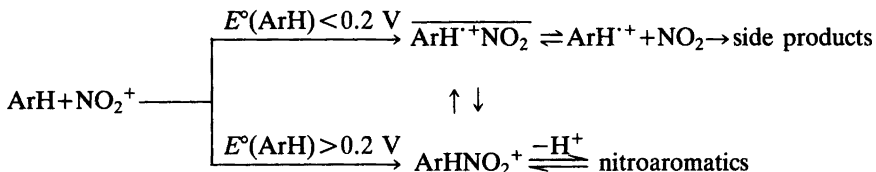
These results seem to fall somewhere between those obtained for naphthalene ($E^\circ=2.08$ V) and for ferrocene (FcH). For FcH, being more readily oxidizable than PeH ($E^\circ=0.60$ and 1.30 V, respectively), no successful NO₂⁺ nitration has ever been achieved⁴⁰ (only FcH^{•+} is formed, and this species is slowly destroyed in the presence of N₂O₄). Treatment of FcH with N₂O₄ in dichloromethane leads to the consumption of FcH without any formation of nitroferrocene (FcNO₂). Reaction of ferricinium ion, *e.g.*, FcHPF₆ with N₂O₄ in the presence or absence of a base (DBMP) does not yield detectable amounts of FcH or FcNO₂.

DISCUSSION

Omitted from the results presented above are those from the reactions of NO₂BF₄ with PeH in various solvents. Commercial samples of NO₂BF₄ are invariably contaminated with NOBF₄⁴¹ and even after careful purification the presence of small amounts of NO⁺ and hence the formation of PeH^{•+}BF₄ and NO in the reaction mixture cannot be excluded. Any NO formed will rapidly be oxidized by NO₂⁺ leading to the formation of NO⁺ and NO₂ and therefore in principle the presence of catalytic amounts of NO⁺ can induce a chain reaction leading to the net formation of PeH^{•+} and NO₂. At our present state of knowledge care must be taken when analyzing results from the reactions of very reactive aromatics with NO₂⁺; our preliminary findings using NO₂BF₄ containing small amounts of NO⁺ show the formation of 3-PeNO₂ in low yield in nitromethane as well as in dichloromethane.

In their studies on CIDNP effects under conditions of aromatic nitration by NO₂⁺, Ridd and co-workers nicely demonstrated that the "normal" nitronium ion mediated nitration of compounds like mesitylene and naphthalene is not a radical pair-mediated process.^{13c} We recently presented a theoretical study on the ET oxidizing properties of NO⁺ and NO₂⁺,⁵ and predicted the former to be far more effective than NO₂⁺, despite their almost identical E° values (1.51 and 1.56 V, respectively). This remarkable and unexpected difference is entirely due to an extremely high reorganization energy of the NO₂⁺/NO₂ self-exchange reaction.

Thus, while NO⁺ was predicted and shown to be an effective non-bonded ET oxidant toward substrates with an E° up to *ca.* 1.8 V, NO₂⁺ was suggested to undergo non-bonded ET from substrates with $E^\circ \leq 0.2$ V only. It therefore cannot be considered an ET oxidant in virtually all cases of aromatic nitration of any practical interest. Any radical cation actually detected from ArH/NO₂⁺ must therefore be formed *via* another route (see Scheme 1 and discussion). Even such readily oxidizable compounds as perylene and ferrocene are predicted to react *via* a direct bonding pathway as shown in Scheme 1, radical cation formation being encountered when deprotonation of the σ -complex is slow relative to its homolysis to give the radical pair, followed by its dissociation to free radicals.



Scheme 1.

Let us now examine in detail the various consequences of Scheme 1. The demanded slowness of the deprotonation step is supported by the observation of a primary kinetic hydrogen isotope effect in the nitration of anthracene ($k_H/k_D=2.25$) but not naphthalene ($k_H/k_D=1.05$) with NO_2PF_6 ,⁴² indicating the possibility of a reversible deprotonation step for sufficiently reactive aromatics.

Moreover, 9-nitroanthracene has been found to nitrate substrates like mesitylene in the presence of superacids *via* a transfer nitration mechanism.⁴² The original interpretation suggests *ipso* protonated 9-nitroanthracene to be the nitrating agent. However, assuming that anthracene radical cation is sufficiently stable under superacidic conditions, formation of the radical pair from the σ -complex and subsequent radical-pair dissociation would yield NO_2 which readily nitrates mesitylene in strongly acidic media. The observation that nitromesitylene does not act as a transfer nitrating agent under the same conditions merely demonstrates, apart from differences in base strength, that the position of the equilibrium $\sigma\text{-complex} \rightleftharpoons \text{radical pair}$ in this case lies strongly to the left, formation of the mesitylene radical cation being thermodynamically unfavourable.

For the nitration of sufficiently reactive aromatics in strongly acidic media, deprotonation becomes slow enough relative to radical pair formation to account for the impossibility of obtaining mononitro products in a clean reaction. Thus, in the case of ferrocene, deprotonation cannot compete with radical pair and subsequent ferricinium ion formation even in weakly acidic media. Mixed acid nitration of reactive aromatics will be even less predictable since sulfuric acid itself may act as an oxidizing agent towards *e.g.*, perylene.⁴³ As shown above, the reaction between PeH^+ and N_2O_4 in TFA yielded no identifiable products.

Let us consider the energetics of Scheme 1. From the schematic energy diagram given in Fig. 4 the differences between the reactions of PeH^+ and NpH^+ with NO_2 are readily understood. Using the E° values given earlier the reaction $\text{ArH} + \text{NO}_2^+ \rightleftharpoons \text{ArH}^+ + \text{NO}_2$ is found to be exergonic (0.26 eV) in the PeH case and endergonic (0.52 eV) in the NpH case. Since the σ -complex necessarily is higher in energy than the ArH/NO_2^+ couple (by Δ_{PeH} and Δ_{NpH} eV, respectively), formation of the σ -complex from PeH^+ and NO_2 must be

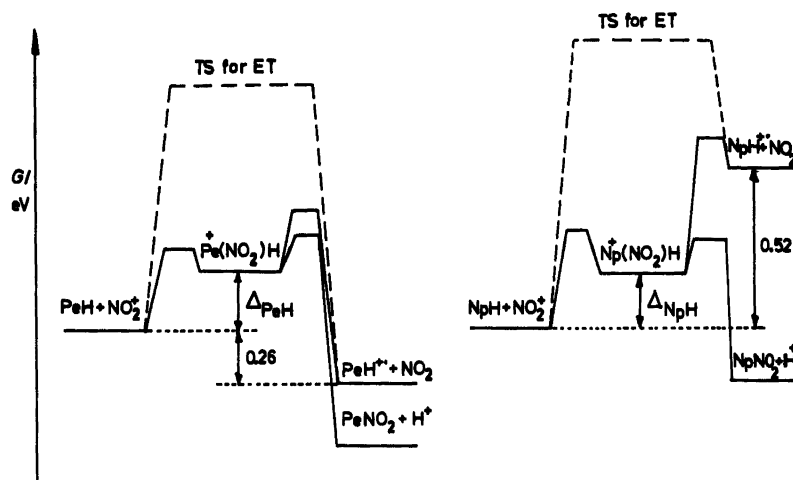
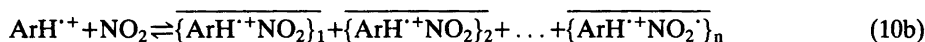
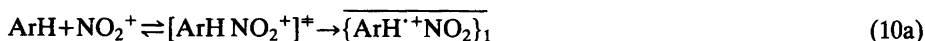


Fig. 4. Schematic free energy diagrams for the reaction $\text{ArH} + \text{NO}_2^+ \rightarrow \text{ArH}^+ + \text{NO}_2$ for (a) perylene and (b) naphthalene.

endergonic by $[\Delta_{\text{PeH}}+0.26]$ eV, while the same process from $\text{NpH}^{\cdot+}$ and NO_2 has ΔG° equal to $[\Delta_{\text{NpH}}-0.52]$ eV.

Since Δ_{NpH} is of the order of 0.1 eV⁴⁴ (the NpH/NO_2^+ reaction is diffusion controlled), the reaction $\text{NpH}^{\cdot+} + \text{NO}_2 \rightleftharpoons \text{NpHNO}_2^+$ must be *exergonic*. This might explain why $\text{NpH}^{\cdot+}$ and NO_2 couple to give virtually 100 % nitration product and why the $\text{PeH}^{\cdot+}/\text{NO}_2$ reaction predominantly gives by-products. A detailed interpretation of the results from the latter reaction is presently not fruitful, but clearly the reaction(s) taking place is(are) not very fast. Any coupling is likely to occur at the 3-position since it has the highest spin density in the radical cation.²⁹ Some of the PeNO_2 must be formed *via* nitration of PeH with N_2O_4 at least when DBMP is added, as is evident from the lowering of the 3-/1- ratio (Table 6).

The observation of a slow coupling step is not necessarily evidence against the ET mediated mechanism proposed in eqn. (1b). Spatial restrictions might be demanded in the transition state, leading to a radical pair (cage 1) suitable for radical coupling [eqn. (10a)] whereas individually pre-formed $\text{ArH}^{\cdot+}$ and NO_2 can in principle upon encounter yield different cages 1, 2, 3, . . . , n [eqn. (10b)], out of which only cage 1 is capable of proceeding to the σ -complex. In spite of this difficulty, we are convinced that Scheme 1 gives the



most accurate picture of the reactions of NO_2^+ with easily oxidizable aromatic and heteroaromatic compounds that can presently be given. Even if NO_2^+ for some reason is capable of acting as an ET oxidant toward substrates with somewhat higher E° values than estimated from our calculations,¹⁵ the limiting E° value will be found among compounds likely to yield stable radical cations, expected to couple slowly with NO_2 .

We have earlier predicted that radical cations of aromatics with E° values >1.0 V should react *via* initial ET with nitrite ion to yield ArH and NO_2 .⁴⁵ For naphthalene this was easily demonstrated since NpH was quantitatively recovered and no NpNO_2 formed upon treatment of $\text{NpH}^{\cdot+}\text{PF}_6^-$ with NO_2^- .^{21b} As shown in Table 5 $\text{PeH}^{\cdot+}$ also reacts *via* initial ET, but here PeNO_2 is formed from the rapid follow-up reaction of PeH with N_2O_4 . Therefore any mechanistic proposal for aromatic nitration involving nucleophilic attack of NO_2^- upon an aromatic radical cation should be avoided. For the same reason, NO_2 cannot be considered an ET oxidant toward aromatics with E° values >1.0 V since for these compounds the equilibrium $\text{ArH} + \text{NO}_2 \rightleftharpoons \text{ArH}^{\cdot+} + \text{NO}_2^-$ will be displaced to the left.¹⁵

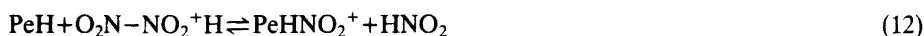
We finally proceed to discuss the N_2O_4 nitration of perylene. In the preceding paper the reactions of PAH:s with N_2O_4 were discussed and the general similarity of these reactions with nitrous acid catalyzed (NAC) nitrations pointed out.¹⁵ This is exemplified here by the similar results obtained from the reactions of perylene with N_2O_4 and AgNO_2/TFA , respectively. In view of the fact that nitrogen oxides at different oxidation levels are readily interconvertible [*e.g.*, in this case *via* eqn. (17)], this similarity is not surprising. It is however not trivial to put together a consistent mechanistic picture of the N_2O_4 induced nitrations, but we suggest that one which is reconcilable with most experimental findings might be formulated along the following lines.

We have earlier shown that N_2O_4 induced nitration of naphthalene and mesitylene is catalyzed by strong acid and similar findings have been reported by others.³² In the case of perylene, one can see (Tables 1 and 2) that strong acid and/or high acid concentrations have a detrimental effect upon the yield of $PeNO_2$. We propose that this effect is caused by acid promoted enhancement of the concentration of the $NO^+NO_3^-$ isomer of N_2O_4 .⁴⁶ The NO^+ can oxidize PeH to PeH^{++} via ET, and thus we run into the previously noted reluctance of PeH^{++} to react cleanly with NO_2 (Table 6; cf. discussion of these data in text).

The second case of N_2O_4 nitration is the one taking place in initially neutral medium [eqn. (11)], at least formally. In practice, the solution will be slightly on the acidic side due



to the difficulty of avoiding the presence of traces of water, causing hydrolysis of some of the N_2O_4 . At this low acid concentration it is reasonable to assume that a weakly electrophilic reagent can be formed by protonation or nitrosation (as discussed in the preceding paper) of N_2O_4 . This reagent attacks perylene selectively at the 3-position [eqn. (12)] and is in general the species that is responsible for the remarkably mild, efficient and selective nitration of PAH:s by N_2O_4 reported earlier.³⁰



But this mechanism is not sufficient to explain the effect of solvent polarity and addition of bases/nucleophiles. This is clearly brought out in the plot of the $\log[3\text{-}/1\text{-isomer ratio}]$ vs. the E_T^N solvent polarity parameter.⁴⁷ A very distinct non-linearity is strongly indicative of a change in mechanism as less polar solvents are employed (Fig. 5). In the region of low polarity, PeH nitration by N_2O_4 is characterized by sluggishness and low 3-/1- isomer ratios. The same effects are achieved in CH_2Cl_2 by adding bases which drastically reduce the proton concentration or remove protons completely. Under these conditions we propose that NO_2 attacks perylene in a free-radical type process [eqn. (13)] with the usual characteristics of such: Low selectivity, favoured in solvents of low polarity, relatively slow in this particular case because of the low reactivity of NO_2 .⁴⁸

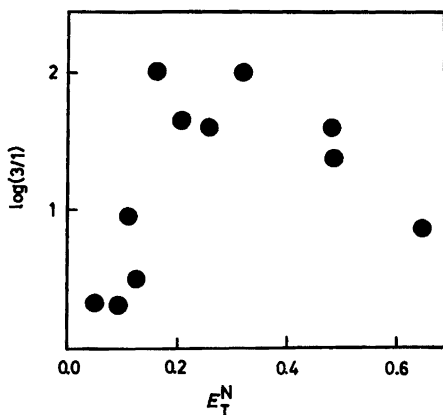
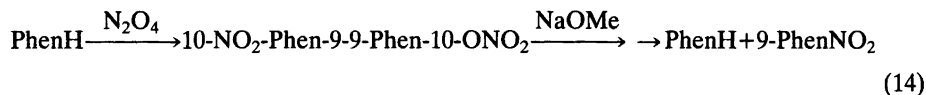


Fig. 5. Plot of $\log [3\text{-}/1\text{- isomer ratio}]$ vs. the E_T^N solvent polarity parameter.



To complete eqn. (13) one can either invoke an oxidation step (since cyclohexadienyl radicals are very easily oxidized, NO_2 and/or N_2O_4 would be sufficiently strong as ET oxidants to effect this step) or an addition-elimination mechanism where a second NO_2 couples at a ring position to give a dinitro- or nitro-nitritodihydroperylene. Such a compound would be expected to rearomatize rapidly by loss of HNO_2 . Alternatively, the nitroperylene radical might dimerize, followed by coupling with a second NO_2 to give a nitrotetrahydroperylene nitrate. This species would instantaneously decompose to PeNO_2 in the presence of a base, similarly to what has been observed for phenanthrene (PhenH)⁴⁹ as shown schematically in eqn. (14).



There are some precedents for low-selectivity NO_2 mediated nitrations. Olah and Overchuck⁵⁰ have shown that under conditions of "free radical nitration" (high temperature and irradiation by UV light) toluene reacts with NO_2 to give nitrotoluenes in nearly statistical *o:m:p* proportions. As a result of reactions under similar conditions, 2-nitropyrene has been observed in environmental samples⁵¹ whereas NO_2^+ as well as N_2O_4 in dichloromethane without added base very selectively yields 1-nitropyrene, no detectable amounts of the 2-isomer being formed.

Summarizing, if we assume that Looker²⁸ in his high temperature HNO_3 /aqueous dioxane nitration of perylene (see Table 1) somehow established conditions for a radical pathway, we think we have proposed plausible explanations for what at a first glance appears to be a rather complex and perplexing nitration pattern of a typical PAH. For such easily oxidizable substrates, ET oxidation appears to be a source of by-products.

EXPERIMENTAL

Materials and methods. Perylene (EGA Gold Label, 99 %) was used without further purification. Dichloromethane (Merck zur Rückstandsanalyse), carbon tetrachloride, dioxane, chloroform and benzene (Merck zur Analyse) and nitromethane (MCB Spectro-quality) were dried over 3 Å molecular sieves. Acetic acid, tetrahydrofuran, diethyl ether and pentane were distilled prior to use. Acetonitrile (Merck Uvasol) was distilled from potassium permanganate and Ar-flushed through a column packed with alumina. Propionitrile (EGA) was purified according to a literature procedure.⁵² Solutions of dinitrogen tetroxide were made up as described previously^{21a} and concentrations determined by acid-base titration after treatment with hydrogen peroxide. 2,6-Di-*t*-butyl-4-methylpyridine⁵³ and ferricinium hexafluorophosphate⁵⁴ were prepared according to literature procedures. All other reagents were commercial samples of highest purity available.

The power source was an AMEL model 552 potentiostat, operated in the galvanostatic mode. GLC analyses were performed on a HP 5380 A gas chromatograph equipped with a HP 18850 integrator and a glass insert in the injection port (column: 0.5 m × 1.8 mm glass-lined 5 % OV 1701 on Chromosorb W) using triphenylene as the internal standard. ¹H NMR spectra were recorded at a Nicolet Model 360 WB spectrometer.

Synthesis of (PeH)₂PF₆. The anodic oxidation of perylene was performed in close resemblance to the literature procedure;³⁵ however a 250 ml three-compartment cell and platinum wires as electrodes were used. The growth of black needles at the anode was

continued until GLC showed consumption of 90 % of the starting material. After washing with dichloromethane, the crystals were stored under Ar.

Reactions between PeH^+ salts and nitrogen dioxide/nitrite ion. The PeH^+ salt (Tables 5 and 6) was suspended in the solvent, yielding a violet, intensely blue-fluorescent colour. On the addition of nitrite ion, the suspension immediately disintegrated, turning orange and later red. After filtration and washing with water yields were determined by GLC. Alternatively, work-up was conducted as described below.

On the addition of nitrogen dioxide, the dark colour persisted indefinitely, whereas the fluorescence gradually disappeared. When adding dithionite or DBMP the dark colour vanished within 0.5 and 10 min, respectively. After filtration and washing by water yields were determined by GLC.

Nitration with dinitrogen tetroxide, general procedure. Additives, if required, were weighed into tightly stoppered Erlenmeyer flasks. Perylene (generally 10 ml of a 0.010 M solution) and triphenylene (internal standard, 0.02 mol) were added followed by, at time=0, the required amount (see Tables 2 and 3) of dinitrogen tetroxide. After the appropriate reaction period the solutions were analyzed by GLC.

Synthesis of 3-nitroperylene. Perylene (1 mmol) in dichloromethane (50 ml) and dinitrogen tetroxide (0.80 mmol) in dichloromethane (8 ml) were mixed and allowed to stand for one min. One g of silica gel was added and the resulting mixture was evaporated to dryness and placed on top of a column packed with silica gel. Carbon tetrachloride eluted small amounts of perylene and 1-nitroperylene. Elution with carbon tetrachloride-dichloromethane (90:10) led to the collection of brick-red 3-nitroperylene (0.98 mmol), m.p. 218–219 °C. 1H NMR ($CDCl_3$) δ 7.53 (2 H, t, $J=8.0$ Hz, 8-H+11-H), 7.66 (1 H, dd, $J=7.8$ and 8.6 Hz, 5-H), 7.75 (1 H, d, $J=8.0$ Hz, 10-H), 7.81 (1 H, d, $J=8.0$ Hz, 9-H), 8.10 (1 H, d, $J=8.2$ Hz, 1-H), 8.19 (1 H, d, $J=8.2$ Hz, 2-H), 8.21 (1 H, d, $J=8.0$ Hz, 12-H), 8.23 (1 H, d, $J=8.0$ Hz, 7-H), 8.25 (1 H, d, $J=7.8$ Hz, 6-H), 8.46 (1 H, $J=8.6$ Hz, 4-H).

Synthesis of 1-nitroperylene. Using carbon tetrachloride instead of dichloromethane the method above led to the isolation of 3-nitroperylene (0.62 mmol) and 1-nitroperylene (0.35 mmol), respectively. M.p. 177–179 °C. 1H NMR ($CDCl_3$) δ : 7.43 (1 H, t, $J=7.8$ Hz, 11-H), 7.54 (1 H, d, $J=8.4$ Hz, 2-H), 7.54 (1 H, t, $J=8.0$ Hz, 8-H), 7.61 (1 H, t, $J=8.0$ Hz, 5-H), 7.70 (1 H, d, $J=8.4$ Hz, 3-H), 7.71 (1 H, d, $J=7.8$ Hz, 10-H), 7.77 (1 H, d, $J=8.0$ Hz, 4-H), 7.80 (1 H, d, $J=8.0$ Hz, 9-H), 7.82 (1 H, d, $J=7.8$ Hz, 12-H), 8.22 (1 H, d, $J=8.0$ Hz, 7-H), 8.25 (1 H, d, $J=8.0$ Hz, 6-H).

Nitration of perylene by other nitrating agents. Nitration with HNO_3/Ac_2O has been described previously.³⁰ Nitration with HNO_3 /aqueous dioxane was performed with the closest possible adherence to the method of Looker.²⁸ For the other systems included in Table 1, perylene was suspended in the reaction medium (containing a slight excess of HNO_3) for 30 min. After extraction from dichloromethane/water the yields were determined by GLC.

Reactions of ferrocenylferrocene radical cation with nitrogen dioxide. These reactions were performed essentially by the methods presented above. In all experiments brown, tarry reaction mixtures were produced, containing no detectable amounts of ferrocene or nitroferrocene.

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