

Review Article

Ingold's Nitration Mechanism Lives!

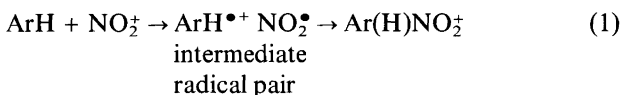
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The proposal that electrophilic aromatic nitration by nitronium ion takes place via an initial electron transfer, followed by recombination of an intermediate radical pair, is critically examined. In particular, recent experimental results from an alleged model reaction, photoexcitation of ArH–tetranitromethane charge transfer complexes to give a triad of ArH^{•+}, trinitromethanide ion and NO₂, are scrutinized, showing that the propensity for adduct formation from the triad invalidates any comparison with the ArH–NO₂⁺ reaction. By conducting the photolysis in the presence of a protic acid, trinitromethanide ion can be removed from the triad by protonation, thus promoting the ArH^{•+}–NO₂ pathway. The isomer ratios of the nitro-substitution products obtained from the latter are different from those of the ArH–NO₂⁺ reaction. Thus the radical pair cannot be an intermediate in electrophilic aromatic substitution, as concluded previously in 1980 from studies of the reaction between electrocrystallized radical cation salts and nitrogen dioxide.

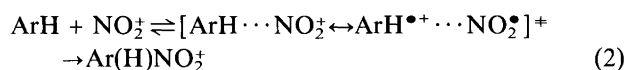
Electrophilic aromatic nitration still holds its position in organic chemistry as a fertile area for finding new phenomena and a testing ground for new mechanisms. A classical problem, formulated nearly 50 years ago,¹ deals with the possible *intermediacy* of a radical pair formed via electron transfer (ET) from the aromatic compound (ArH) to NO₂⁺ on the pathway to the Wheland intermediate [eqn. (1)]. At that time, few facts were available to support such a hypothesis and it was therefore easy for Ingold *et al.*² to refute it immediately. In principle, such a mechanism can be tested experimentally, and much



work has been done along these lines (for reviews, see Refs. 3–5) following Perrin's revival⁶ of the ET hypothesis in 1977.

One must distinguish the mechanism of eqn. (1) from the related hypothesis that the *transition state* for formation of the Wheland intermediate should be written as a resonance hybrid between the ArH–NO₂⁺ and ArH^{•+}–NO₂^{•-} states, as shown in eqn. (2). Such a proposal, force-

fully expounded by Pross and Shaik for nearly all organic



reactions between electrophiles and nucleophiles,⁷ can be tested only by indirect methods, primarily by consideration of structure–reactivity effects and comparison with other mechanisms. Although this is an important task, we will not deal with it in this review, but refer to Ref. 3(a) for a discussion. Instead, the emphasis will be laid on a scrutiny of the ET mechanism of eqn. (1) against the background of present knowledge.

How can one test the mechanism of eqn. (1)? Following Perrin's communication, we sought to develop tests of eqn. (1) along several lines. One was experimental, namely, to generate radical cations and react them with NO₂^{•-} to see if the isomer distribution would be different

* We will consistently write nitrogen dioxide as NO₂, although in most cases one should be aware that the equilibrium mixture 2 NO₂ ⇌ N₂O₄ is the actual source of NO₂. This raises the problem of the reactivity of N₂O₄ toward radical cations, about which little is known. In view of the fact that the equilibrium is fast⁸ and in keeping with current practice, we will assume that NO₂ normally is the kinetically active species in reactions with radicals and that the neutral compound N₂O₄ is much less reactive toward open-shell species than NO₂, a moderately reactive radical.⁹

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Table 1. Values of reorganization energies (λ = the sum of the inner-sphere, λ_i , and outer-sphere, λ_o , reorganization energies) for the redox couples $\text{NO}_2^+/\text{NO}_2$ and NO^+/NO .

Redox couple (solvent)	Method	$\lambda_i/\text{kcal mol}^{-1}$	$\lambda_o/\text{kcal mol}^{-1}$	$\lambda = (\lambda_i + \lambda_o)/\text{kcal mol}^{-1}$	Ref.
$\text{NO}_2^+/\text{NO}_2(\text{CH}_3\text{CN})$	Theory	108	36	144 ^a	15
$\text{NO}_2^+/\text{NO}_2(\text{CH}_3\text{CN})$	Theory	107	36	143 ^a	16
$\text{NO}_2^+/\text{NO}_2(\text{CH}_3\text{CN})$	Theory	78	36	114 ^a	12(b)
$\text{NO}_2^+/\text{NO}_2(\text{CH}_3\text{NO}_2)$	Theory	82	34	116 ^a	12(c)
$\text{NO}_2^+/\text{NO}_2(\text{CH}_3\text{CN})$	Exp.			79	12(b)
$\text{NO}_2^+/\text{NO}_2(\text{CH}_3\text{NO}_2)$	Exp.			95	12(c)
$\text{NO}^+/\text{NO}(\text{CH}_3\text{CN})$	Theory	21	49	70	15
$\text{NO}^+/\text{NO}(\text{CH}_3\text{CN})$	Theory	24	49	73	16
$\text{NO}^+/\text{NO}(\text{CH}_3\text{CN})$	Theory	21	49	70	12(a)
$\text{NO}^+/\text{NO}(\text{CH}_3\text{NO}_2)$	Theory	21	46	67	12(c)
$\text{NO}^+/\text{NO}(\text{CH}_3\text{CN})$	Exp.			87	12(a)
NO^+/NO	Exp.			90	12(c)

^a The difference between these calculated values may seem large, but is entirely due to the choice of a crystallographically obtained value for the N–O–N angle in NO_2^+ [175°; Refs. 12(b) and 12(c)] or the one likely to apply to the solution chemistry of NO_2^+ , 180° (Refs. 15 and 16).

from that of the $\text{ArH}-\text{NO}_2^+$ reaction. It is a well-established mechanistic criterion¹⁰ that a proposed intermediate, if stable enough to be prepared or generated transiently and submitted to the prevailing reaction conditions, should lead to the same product distribution as the reaction under study. If it does, the proposed mechanism may be correct; if it doesn't, the mechanistic hypothesis has been refuted. In practice, this principle for testing mechanisms is seldom upheld on a shorter time-scale, simply because it is difficult to agree on the validity

and outcome of critical experiments and whether they are applicable to the hypothesis under discussion.¹¹

A second approach was theoretical. Experimentally, there is a large difference in the ET properties of NO^+ and NO_2^+ , in spite of the fact that their standard potentials in acetonitrile are almost identical, $E^\circ(\text{NO}^+/\text{NO})$ and $E^\circ(\text{NO}_2^+/\text{NO}_2)$ being 1.52 and 1.56 V vs. NHE, respectively.^{12a,b} However, it should be noted that $E^\circ(\text{NO}_2^+/\text{NO}_2)$ has been reported^{12c} to be >0.6 V more positive than $E^\circ(\text{NO}^+/\text{NO})$ in sulfolane and nitro-

Table 2. Isomer distributions from reactions of relevance for a comparison between the $\text{ArH}^{\bullet+}-\text{NO}_2$ coupling reaction and other nitration processes.

Reaction conditions	Yield ^a of nitro-naphthalenes (%)	Ratio ^a of 1-/2-isomer	Ref.
Solid (naphthalene) ^{•+} PF_6^- under dissolving conditions at $\approx -25^\circ\text{C}$ in dichloromethane	49(4) ^b	43(3)	18
Solid (naphthalene) ^{•+} PF_6^- under dissolving conditions at $\approx -25^\circ\text{C}$ in dichloromethane	119(7) ^c	36(2)	18
(Naphthalene) ^{•+} salt in nitromethane		50	20
Electrolysis in dichloromethane at a Pt anode with NO_2 present at -45°C	100 ^d	65	18
Reaction of solid (naphthalene) ^{•+} PF_6^- with nitrite ion under dissolving conditions at $\approx -50^\circ\text{C}$ in dichloromethane	<0.1 ^e	—	18
(Naphthalene) ^{•+} in the gas phase, calculated ^f		300	21
$\text{NO}_2^+\text{BF}_4^-$ in dichloromethane at -30°C	15 ^g	15(1)	18
$\text{NO}_2^+\text{BF}_4^-$ in dichloromethane at $+20^\circ\text{C}$	49 ^h	12(1)	18

^a Material yield, unless otherwise stated. ^b Theoretical yield, 50%. ^c Theoretical yield, 100%. ^d Current yield. ^e In this case, naphthalene was recovered in 98% yield. ^f The gas-phase reaction between (naphthalene)^{•+} and NO_2 has been found²² to be 'very slow' in relation to other cations, reacting with rate constants around $10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. ^g Reaction period 2 h. ^h Reaction period, 15 h.

methane. NO^+ salts are known as useful one-electron reagents for the preparation of radical cations,¹³ whereas NO_2^+ cannot be used in this way.

Application of the Marcus¹⁴ theory of outer-sphere ET to this problem led to the realization¹⁵ that the reorganization energies (λ) of the NO^+/NO and $\text{NO}_2^+/\text{NO}_2$ redox pairs are vastly different, 70 and 140 kcal mol⁻¹, respectively. Qualitatively, this difference can be expressed as being primarily due to the severe distortion of the NO_2 bond angle that is necessary to reach the transition state of electron transfer. Thus the bond reorganization energy, λ_i , is calculated to be very large, both by using classical Marcus calculations¹⁵ and *ab initio* methods.¹⁶ It is therefore to be expected that NO_2^+ should not engage in reactions leading to weakly bonded transition states (outer-sphere ET) but instead in strongly bonded ones (inner-sphere ET, and in the extreme, polar reactions like direct formation of the Wheland intermediate). This extreme λ_i has no equivalent in the NO^+ ET mechanism.

Experimental tests of this idea have been performed by electrochemical measurement of the heterogeneous rate constants for electron exchange of the NO^+/NO and $\text{NO}_2^+/\text{NO}_2$ redox pairs at platinum electrodes.¹² Such data can be translated into reorganization energies; theoretical and experimental values are compared in Table 1. For $\text{NO}_2^+/\text{NO}_2$ one sees that the theoretical values are considerably larger than the experimental ones which at first sight might seem to contradict the explanation offered above for the lower reactivity of NO_2^+ as an ET reagent. However, one should remember that outer-sphere behaviour is a theoretical concept, whereas experimentally determined λ values might have derived from inner-sphere ET processes.^{17a,b} As an example, determination of $\lambda(\text{O}_2/\text{O}_2^{\bullet-})$ from kinetic studies has given values in the range 22–103 kcal mol⁻¹, depending on the nature of the second redox pair.^{17c} Thus the experimental values determined for $\text{NO}_2^+/\text{NO}_2$ might be influenced by significant orbital overlap between NO_2 and the Pt surface,^{12b} simply because this is the energetically favoured pathway which avoids the consequences of the extremely high outer-sphere λ value. In order to determine a realistic value of $\lambda(\text{NO}_2^+/\text{NO}_2)$ it must be extracted from a study of an ET reaction which is likely to be of the outer-sphere type.

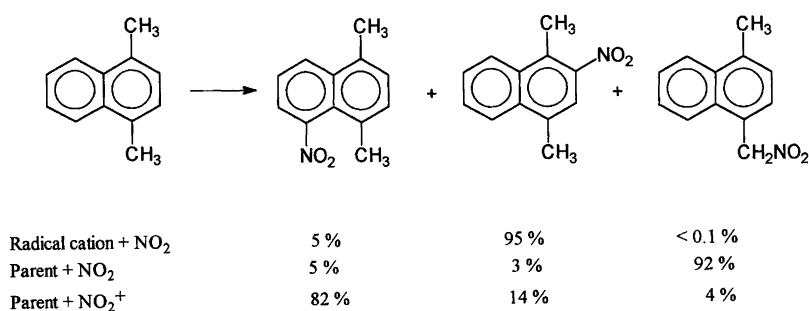
Table 3. Ratio of most abundant α -nitro isomer (in NO_2^+ nitration) to the sum of all other nitro isomers formed in the nitration of naphthalenes and some methylnaphthalenes. Data are from Ref. 19.

Substrate	NO_2^+ ^a	NO_2 ^b	$\text{ArH}^{\bullet+} + \text{NO}_2$ ^c
Naphthalene	11	25	36–65 ^d
1-Methylnaphthalene	1.3	1.9	7.3
2-Methylnaphthalene	1.3	1.9	5.3
1,4-Dimethylnaphthalene	5.8	1.7	0.05
1,8-Dimethylnaphthalene	2.3	7.3	12
2,3-Dimethylnaphthalene	3.3	3.3	9
2,6-Dimethylnaphthalene	3.5	5.3	9

^a Nitration in HNO_3 –acetic anhydride at -10°C . ^b Nitration by NO_2 in dichloromethane at 20°C . ^c Coupling between solid $\text{ArH}^{\bullet+}$ salt and NO_2 in dichloromethane at $\approx -20^\circ\text{C}$. ^d Table 2.

For NO^+/NO the calculated and theoretical λ values are in reasonable agreement.

Reaction of presynthesized radical cation salts with NO_2 . A series of radical cation salts from naphthalene and methyl-substituted naphthalenes were prepared by electrocrystallization and allowed to react with NO_2 (Tables 2 and 3).^{18,19} The resulting mixtures of nitro compounds were analysed and the isomer distributions compared with those from two other nitration procedures, nitration by NO_2 in dichloromethane and by NO_2^+ , the latter being taken as reference reaction for regioselectivity. The results for naphthalene show that the $\text{ArH}^{\bullet+}$ – NO_2 coupling reaction is more selective for 1-substitution than the ArH – NO_2^+ reaction (1-/2-nitronaphthalene ratio ≈ 50 and 15, respectively), and the NO_2 nitration process is somewhere in between in this respect. Analogous results were obtained from methylnaphthalenes, where the regioselectivity was defined as the ratio of the most abundant α -nitro isomer to all other nuclear nitro isomers. 1,4-Dimethylnaphthalene showed the opposite selectivity order, giving a 5-/2-nitro isomer ratio of 0.05 and $< 0.1\%$ of the 4- NO_2CH_2 product in the $\text{ArH}^{\bullet+}/\text{NO}_2$ reaction, a 5-/2-nitro isomer ratio of 5.9 for NO_2^+ nitration, and a high yield (92%) of the 4- CH_2NO_2 product in NO_2 nitration (see Scheme 1). This high sensitivity of 1,4-dimethylnaphthalene to mechanistic changes is a useful diagnostic

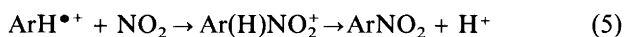
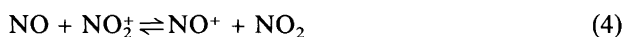


Scheme 1.

property. Finally, it should be emphasized that the reaction between (naphthalene) $^{\bullet+}$ and nitrite ion gives products of ET only, i.e., naphthalene and NO_2^- . Since (naphthalene) $^{\bullet+}$ and NO_2^- must coexist at some stage of this reaction, this result indicates that the coupling between them cannot compete with dimerization of NO_2^- to give N_2O_4 (rate constant $\approx 10^8 \text{ M}^{-1} \text{ s}^{-1}$).¹⁸

The data of Tables 2 and 3 show that the $\text{ArH}-\text{NO}_2^-$ and $\text{ArH}^{\bullet+}-\text{NO}_2^-$ reactions differ significantly with regard to the product distributions observed. On the basis of this criterion, the mechanism of eqn. (1) was considered to be refuted. However, the use of isomer distribution data and their possible significance were questioned later on the basis of studies on the photonitration of ArH by tetranitromethane, as detailed below, and necessitated further studies to validate the $\text{ArH}^{\bullet+}-\text{NO}_2^-$ data. Before we address this problem, a digression into a novel and different way of co-generating these two reactants is of interest.

An alternative method to accomplish the $\text{ArH}^{\bullet+}-\text{NO}_2^-$ reaction: nitrous acid catalysed nitration. A parallel development took place in a different part of the mechanistic spectrum of aromatic nitration, namely nitrous acid catalysed nitration. As shown and summarized by Ridd and coworkers,³ this reaction takes place according to the reaction scheme of eqns. (3)–(5). The key product-forming step is eqn. (5), the coupling between $\text{ArH}^{\bullet+}$ and NO_2^- ,

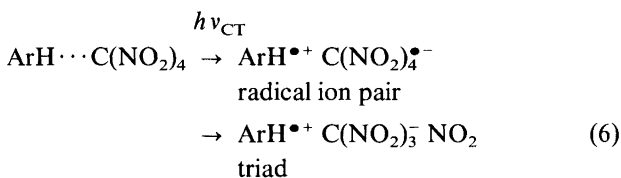


and thus nitrous acid catalysed nitration would be expected to approach the same regioselectivity as that of $\text{ArH}^{\bullet+}/\text{NO}_2^-$ couplings. Because of the possibility of concurrent NO_2^- nitration, the regioselectivity might be somewhat lower. Similarly, reactions run on the assumption that NO_2^- is the nitrating agent might be accompanied by the nitrous acid catalysed mechanism,²³ if precautions

have not been taken to exclude the latter by adding a suitable nitrous acid scavenger.

From the experimental characteristics of nitration by NO_2^- in dichloromethane, it was surmised that this process would simply be a variety of the nitrous acid catalysed reaction, carried out in an aprotic solvent.^{2b} Thus isomer distributions from an additional collection of putative $\text{ArH}^{\bullet+}/\text{NO}_2^-$ reactions are available from the literature, and data for their regioselectivity are given in Table 4, as well as for the corresponding NO_2^- and NO_2^- induced reactions. Since not all of these data were obtained under conditions which rigorously define the mechanism, their interpretation should be made with caution. However, significant differences in isomer ratios are found in cases where one expects them, namely for compounds (anisole, dibenzofuran, PAH:s) which have $E^\circ(\text{ArH}^{\bullet+}/\text{ArH})$ low enough for NO^+ to be a feasible oxidant.

Early work on the photochemical reaction between aromatics and tetranitromethane. Tetranitromethane and ArH form charge transfer (CT) complexes in organic solvents,²⁸ resulting in solutions ranging from faintly yellow to deeply red, depending on the redox potential of the donor molecule. Upon photoexcitation with light of a wavelength matching the band of the CT transition, normally in the range 410–500 nm, such a CT complex undergoes intracomplex ET giving primarily the corresponding radical ion pair [eqn. (6)] which fragments into a triad of $\text{ArH}^{\bullet+}$, trinitromethanide ion and NO_2^- .²⁹

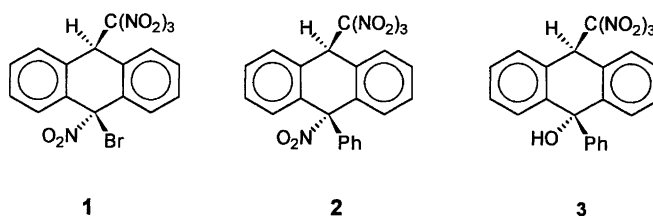


With sufficiently reactive ArH, such as azulene or phenolate ions, the reaction with tetranitromethane is spontaneous.³⁰ Both the photochemical and thermal reactions were found to yield nitro-substitution products, ArNO_2 ,

Table 4. Comparison of isomer ratios from NO_2^- , NO_2^- and nitrous acid catalysed nitration.

Substrate	Isomer ratio measured	NO_2^-	NO_2^-	HNO_2 catalysed	Ref.
Anisole	2-/4-	2.5	0.8	0.6 ^a	23(a)
Phenol	2-/4-	2.4		0.8	23(b),(c)
Dibenzofuran	2-/3-	1.5	0.17	0.11	24, 25
Toluene	2-/4-	2.0		1.52	23(d)
Biphenyl	2-/4-	≈ 2		1.5	23(d)
Perylene	3-/1-	20	100		26
Fluorene	2-/4-	2.4	10		27
Fluoranthene	3-/8-	1.7	2.3		27
Triphenylene	1-/2-	1.2	0.28		27
Chrysene	6-/other	9	32		27

^a The extremely low value of 0.06 sometimes reported for this reaction [Ref. 23(d)] is probably derived from a mechanism involving nitrosation, followed by oxidation.^{23a}

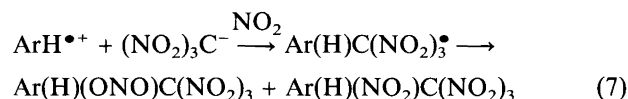


as the ultimate products. For *N*-vinylcarbazole, a reactive substrate, the reaction was of the chain type.³¹

The application of fast kinetic methods showed that the conversion of the radical ion pair into the triad [eqn. (6)] was over within <3 ps, making the formation of the triad a strong competitor with back electron transfer within the radical ion pair.^{5a} Thus a novel source of $\text{ArH}^{\bullet+}$ and NO_2 was available, although with the added complication that trinitromethanide ion, a nucleophile of some strength,³² is a third component of the triad.

Photolysis of the CT complexes between tetranitromethane and anthracene and anthracene derivatives, known for their propensity to add reagents across the weakly aromatic middle ring, initially showed that addition is the favoured pathway.³³ The isolation and X-ray characterization of adducts **1**, **2** and **3** suggested a mechanism in which the trinitromethanide ion first attacks the radical cation, followed by trapping of the neutral trinitromethylcyclohexadienyl radical by NO_2 either via its nitrogen atom (**1**, **2**) or one of the oxygens (**3**, formed by hydrolysis of the initially formed nitrite). This is shown for the general case of ArH in eqn. (7). Adducts of type

2 were unstable in solution and underwent elimination of nitroform to give a nitro-substitution product.^{33a}



Application of reaction (6) to benzene and naphthalene derivatives³⁴ led to the detection and isolation of nitro- and trinitromethyl-substitution products where it appeared that the use of dichloromethane as the solvent favoured trinitromethyl-substitution and acetonitrile led to nitro-substitution. Thus the mechanism was envisaged as a competition between capture of $\text{ArH}^{\bullet+}$ by either trinitromethanide ion or NO_2 [eqns. (8) and (9)] within or outside the triad, directly leading to substitution by ET oxidation-proton loss or proton loss, respectively, notwithstanding the fact that reactions of some

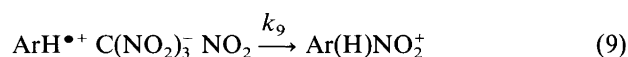
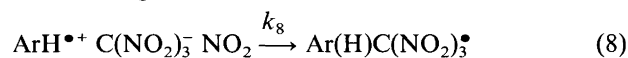


Table 5. Nitro-substitution isomer ratios from the photolysis of ArH-tetranitromethane solutions, compared with those of NO_2^+ substitution.

Substrate ArH	Solvent	Isomer ratio measured	Photolysis of ArH/TNM CT complex	NO_2^+	Ref.
Anisole	AN	2-/4-	0.81	2.5	34(b)
	DCM	2-/4-	0.79 ^a		
2-Methylanisole	AN	6-/4-	0.47		34(b)
	DCM	6-/4-	0.6 ^b		
3-Methylanisole	AN	6-/4-	0.56		34(b)
4-Methylanisole	AN	2-/3-	> 100		34(b)
	DCM	2-/3-	> 100 ^c		
1,2-Dimethoxybenzene	DCM	3-/4-	< 0.01	< 0.01	34(a)
Naphthalene	AN	1-/2-	7.4	16	34(c)
	DCM	1-/2-	3-7		35
	DCM ^d	1-/2-	1-1.5		35
1-Methylnaphthalene	AN	2-/4-	0.17	0.53	34(c)

^a A 40% yield of the 2-trinitromethyl derivative was also formed. ^b A 60% yield of the 4-trinitromethyl derivative was also formed. ^c A 95% yield of the 2-trinitromethyl derivative was also formed. ^d Photolysis performed in the presence of a hindered base.

Table 6. Product distributions from the photolysis of the naphthalene-tetranitromethane CT complex under different conditions. Data were taken from Ref. 36, unless otherwise stated.

Conditions ^a	4	5	6	7	(4+5)/6	1-	2-	Ratio 1-/2-	Ratio adducts/ArNO ₂
DCM at -20 °C	27	17	18	13	2.4	13.5	< 0.5	> 27	6.4
DCM at +20 °C	24	20	17	< 2	2.6	4.4	< 0.5	> 8.8	22
AN at -20 °C	26	19	17	11	2.6	8	0.6	13	11
AN at +20 °C	26	24	17	≤ 2	2.9	12.1	≤ 0.5	≥ 24	7.3
AN at +20 °C	55 ^b				1.8 ^c	10.7	0.5	21.4	4.9
CHCl ₃ at +20 °C	90 ^b				2.8 ^c	4.7	0.6	7.8	17

^a AN=acetonitrile, DCM=dichloromethane. ^b Total adduct yield (Ref. 37). ^c As inferred from the analysis of ArNO₂ formed after elimination of nitroform from the adduct mixture (Ref. 37).

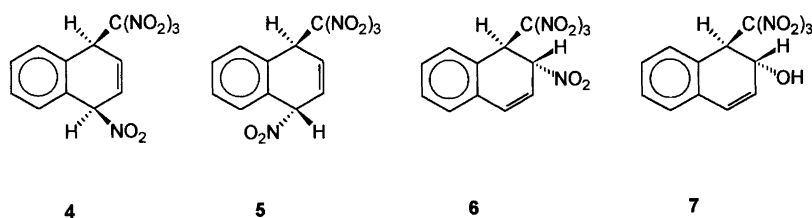
mononuclear ArH gave significant amounts of adducts.^{34b} The isomer distributions (some diagnostic cases are shown in Table 5) indicated a similarity between photonitration and nitration by NO₂⁺, and were different from those obtained from the ArH^{•+}-NO₂ coupling reaction in cases where comparisons were possible. Notably, naphthalene gave a very low 1-/2-nitro isomer ratio, ≈ 5, distinctly different from that determined for the coupling between (naphthalene)^{•+} and NO₂, ≈ 50 (Table 2). However, anisole does not show any large difference in the 2-/4-nitro isomer ratio, at least as long as we accept that the HNO₂-catalysed reaction is a satisfactory model for the ArH^{•+}-NO₂ reaction (0.81 vs. 0.6; see Tables 4 and 5).

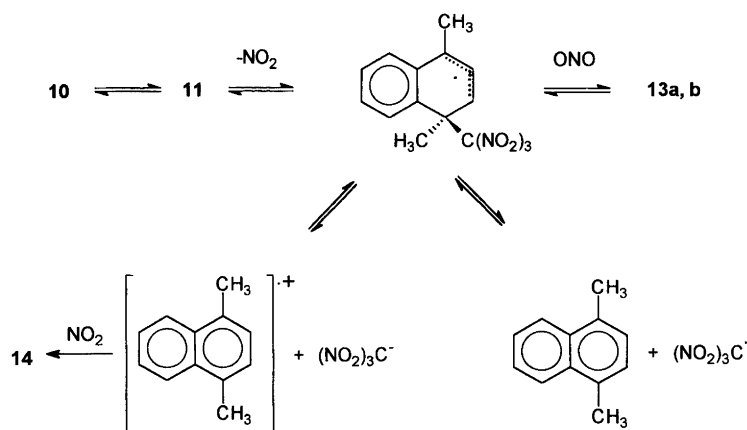
Later work on the photochemical reaction between aromatics and tetranitromethane. The origin of the apparent naphthalene isomer ratio discrepancy became clear when adduct formation was detected³⁵ and indeed found³⁶ to be predominant in the photolysis of the naphthalene-tetranitromethane CT complex in dichloromethane and acetonitrile (Table 6). The adducts were of the nitro/trinitromethyl type (4-6) and the hydroxy(nitro)/trinitromethyl type (7), as was also found for the anthracene adducts 1-3. The structure of 4 was shown by a single-crystal X-ray analysis, whereas the structures of 5-7 were deduced from NMR spectra data. Adducts 4-6 were thermally unstable, readily eliminating nitroform, especially upon GLC, to give nitro-substitution products. Assuming that the efficiency of GLC-induced loss of nitroform from adducts 5 and 6 was comparable to that demonstrated for adduct 4, the (4 + 5)/6 ratios in

Table 6 would lead to a low 1-/2-nitro isomer ratio (2-3), accounting for previous findings where GLC was the analytical method. Thus mild work-up and analysis methods are mandatory in this type of work.³⁶

However, nitronaphthalenes are formed in small amounts along with adducts even from the beginning of the photolysis reaction, and the fact that a higher proportion was formed at -20 than at +20 °C indicated that they had been formed by coupling between ArH^{•+} and NO₂ (elimination from adducts 4 and 5 should be much slower at -20 than +20 °C). The high 1-/2- isomer ratio, 20-30, at low temperature, maximally untainted by elimination from adducts, points in this direction too. It should be noted that the switch from dichloromethane to acetonitrile had little effect upon the adducts/ArNO₂ ratio, contrary to earlier findings for alkoxybenzene systems.^{34b}

The photolysis of tetranitromethane CT complexes of a large number of substrates has later shown that the naphthalene findings represent a general reaction type, formation of nitro/trinitromethyl and/or nitro(hydroxy)/trinitromethyl adducts (Table 7).³⁸⁻⁴⁸ The former type, occurring both by 1,4- and 1,2-addition, has been extensively verified by X-ray crystallographic analysis, whereas the latter type long defied attempts to obtain crystals suitable for this method. However, with the detection⁴⁹ of products from internal 1,3-dipolar cycloaddition of a nitro group (from a trinitromethyl group) to a vinylic bond [8, eqn. (10)] well crystallized derivatives became available and thus verification of the originally proposed hydroxy/trinitromethyl connectivity was possible. Several cases of this cycloaddition reaction are now known and



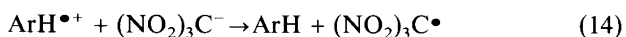
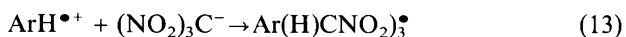


Scheme 2.

minor one [eqn. (12)], whereas at $+20^\circ\text{C}$ **12** predominated. In acetonitrile at -20°C **10–12** appeared in similar proportions but in addition the unstable nitro–trinitromethyl adduct pair **13a,b** was detected. At $+20^\circ\text{C}$ in acetonitrile, the final product mixture consisted of **10–12** and the nuclear nitro compound **14**. The formation of the latter was traced to a rather complex sequence of reactions starting with a polar rearrangement of **10** to **11**, followed by NO_2 loss from **11** and ending with coupling between NO_2 and (1,4-dimethylnaphthalene) $^{\bullet+}$ to give **14**. The latter step was favoured by the acidity built up during the run and accentuated by added acid (Scheme 2). Most of the side-chain product **12** was formed by a polar rearrangement–elimination of **10**.

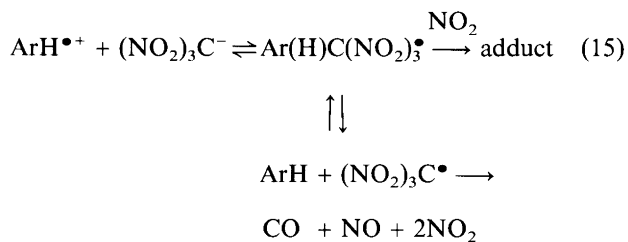
The results above should be compared to those discussed above (Scheme 1 and associated text). The (1,4-dimethylnaphthalene) $^{\bullet+}$ – NO_2 reaction leads only to the nuclear nitro product **14**, whereas the side-chain product **12** originates from other mechanisms.

Competitive reactions of trinitromethanide ion and NO_2 with radical cations. The reactivity of $\text{ArH}^{\bullet+}$ toward nucleophiles Nu^- has been extensively studied,⁵² and it is known that two reactions compete, namely bond formation and ET, exemplified for trinitromethanide ion in eqns. (13) and (14). For two rather stable radical cations,



tris(4-bromophenyl)aminium ion and tris(4-chlorophenyl)aminium ion, it was found⁵³ that ET was the major pathway with trinitromethanide ion, leading to nitro-substitution products instead of the expected trinitromethyl derivatives. For comparison, acetate, chloride and cyanide ion give substitution products with tris(4-bromophenyl)aminium ion whereas bromide and iodide ion give solely ET-derived products.⁵⁴

Thus it appears that eqn. (13) should be rewritten as an equilibrium reaction, with the trinitromethylcyclohexadienyl radical either being trapped by NO_2 to give an adduct or collapsing to $\text{ArH} +$ trinitromethyl radical, presumably a very unstable species (so far only detected by EPR spectroscopy at 77 K),⁵⁵ which appears to fragment to give CO , NO , and 2NO_2 [eqn. (15)].⁵² Additional evidence for such a scheme is described above

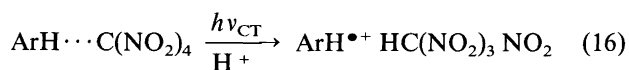


(Scheme 2) where the neutral trinitromethylnaphthalenyl radical, formed in an entirely different way, exhibits reactivity according to eqn. (15). As an example, the trinitromethyl radical could be trapped by a spin trap and thus identified by EPR spectroscopy.⁴⁵

The reactivity of $\text{ArH}^{\bullet+}$ with NO_2 has been less extensively studied. Most quantitative studies^{33b,34a,34b,37,57,58} stem from laser spectroscopy studies on the $\text{ArH}/$ tetranitromethane system, and are hampered by the difficulty of identifying the kinetically active species, except by indirect means. Since it is difficult to identify the reactant pair by inspecting the product distribution — the possibility of adduct formation, even if not explicitly detected, makes such a task ambiguous — there is need for other methods to compare the $\text{ArH}^{\bullet+}/(\text{NO}_2)_3\text{C}^-$ and $\text{ArH}^{\bullet+}/\text{NO}_2$ reactivities.

By Nature's benign intervention, a simple and conclusive method has become available to remove the trinitromethanide ion from the triad, thus avoiding the complicating features of adduct formation, and allowing for detection of the chemical consequences of the change.^{39,59}

By adding trifluoroacetic acid (0.4 M) to the solution of ArH and tetranitromethane, trinitromethanide ion is rapidly protonated as it is formed by photolysis to give the non-nucleophilic nitroform [eqn. (16)], thus



leaving $\text{ArH}^{\bullet+}$ and NO_2 for further reaction. As it happens, the solution *without TFA present* normally does not give any sign of formation of $\text{ArH}^{\bullet+}$, signifying that either or both of reaction (8) and (9) are fast. *With TFA present* to prevent accumulation of trinitromethanide ion, one normally observes (EPR spectroscopy) a rapid build-up of $\text{ArH}^{\bullet+}$, showing that reaction (8) must be faster than reaction (9) ($k_8 \gg k_9$).

Table 8 shows the outcome of these experiments, mostly conducted in dichloromethane at -60°C and

acetonitrile at -40°C (methanesulfonic was used in acetonitrile). The results are defined as the ratio ζ between the radical cation signal intensity in the ArH/tetranitromethane solution with TFA and the intensity in the ArH/tetranitromethane solution without TFA. Control experiments showed that the photolysis of ArH/TFA solutions occasionally gave signals from $\text{ArH}^{\bullet+}$, but not to an extent to influence the validity of the ζ values. Fig. 1 shows a bar chart of $\log \zeta$, illustrating that ζ values are smaller in acetonitrile and could only be measured for systems corresponding to moderately reactive radical cations, presumably due to the fact that the acetonitrile experiments had to be run at -40°C . It may also be that acetonitrile acts as a nucleophile toward more reactive radical cations.

One can distinguish two limiting cases for producing ζ values around 1, namely that the triad reactants are pairwise so reactive that TFA has no effect (naphthalene;

Table 8. Ratio ζ between the EPR spectral intensities of ArH/tetranitromethane solutions in dichloromethane or acetonitrile, if so stated, irradiated at -60°C (in acetonitrile at -40°C), with or without TFA (methanesulfonic acid in acetonitrile) present.^{39,59}

Entry No.	ArH	$E^\circ(\text{ArH}^{\bullet+}/\text{ArH})/V$ vs. NHE ^a	Ratio ζ
1	Naphthalene	2.08	1
2	Naphthalene (at -70°C)		1
3	Naphthalene (at -80°C)		1
4	1-Methylnaphthalene	2.05	1
5	1-Methylnaphthalene (at -70°C)		58
6	1,4-Dimethylnaphthalene	1.99	5
7	1,2-Dimethylnaphthalene	1.98	22
	In acetonitrile		1
8	1,8-Dimethylnaphthalene	1.91	8
9	2,3-Dimethylnaphthalene	1.73	43
10	Acenaphthene	1.82	25
11	Fluoranthene	1.73	17
12	1,3,5,8-Tetramethylnaphthalene		22
13	1,4,6,7-Tetramethylnaphthalene	1.86	74
14	1,4,5,8-Tetramethylnaphthalene	1.56	55
	In acetonitrile		3.5
15	1,4-Dimethoxybenzene	1.56	270
	In acetonitrile		3.3
16	Dibenzo-1,4-dioxin	1.70	2.4
	In acetonitrile		1.4
17	Dibenzo-1,4-dioxin (at -40°C)		1.9
18	Dibenzo-1,4-dioxin (at -20°C)		7.5
	In acetonitrile		7
19	Anthracene	1.61	18
20	9-Phenylanthracene		56
	In acetonitrile		1
21	9,10-Diphenylanthracene	1.44	115
	In acetonitrile		6.3
22	Pyrene	1.60	120
23	Perylene (-70°C)	1.30	106
24	Tris(4-bromophenyl)amine	1.30	9.5
25	9,10-Dimethylanthracene	1.11	600
	In acetonitrile		20
26	1-Methoxynaphthalene (at -50°C)		129
27	1-Methoxynaphthalene (at -40°C)		57
28	2,5-Di- <i>tert</i> -butyl-1,4-dimethoxybenzene (at $+20^\circ\text{C}$)		10

^a Taken from Refs. 14(b), 35, 48 and sources quoted in Ref. 39.

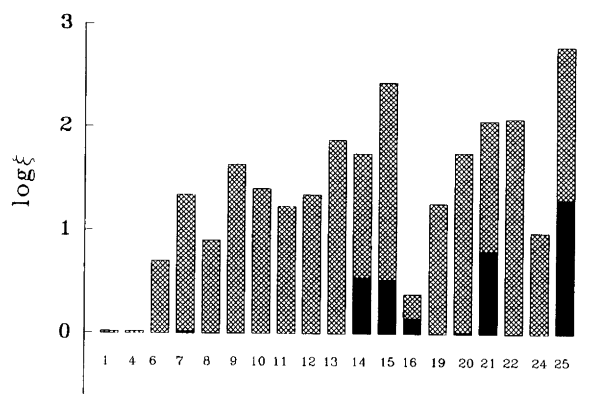


Fig. 1. Bar chart of $\log \zeta$ (see Table 8). The shaded bars are for dichloromethane values and the black bars, superimposed upon the shaded ones, for acetonitrile values. A $\log \zeta$ of '0' is represented by 0.02 in order to become visible and the substrates are from left to right (entry No. of Table 8): naphthalene (1), 1-methylnaphthalene (4), 1,4- (6), 1,2- (7), 1,8- (8) and 2,3-dimethylnaphthalene (9), acenaphthene (10), fluoranthene (11), 1,3,5,8- (12), 1,4,6,7- (13) and 1,4,5,8-tetramethylnaphthalene (14), 1,4-dimethoxybenzene (15), dibenzo-1,4-dioxin (16), anthracene (19), 9-phenyl- (20) and 9,10-diphenylanthracene (21), pyrene (22), tris(4-bromophenyl)amine (24) and 9,10-dimethylantracene (25).

entries 1–3) or that they are so unreactive on the time-scale used that $\text{ArH}^{\bullet+}$ survives intact under both sets of conditions. This would lead to the expectation that ζ should be related to radical cation stability according to a volcano-type relationship. An approximate measure of the latter is available in $E^\circ(\text{ArH}^{\bullet+}/\text{ArH})$, also listed in Table 8. Fig. 2 shows a plot of $\log \zeta$ vs. $E^\circ(\text{ArH}^{\bullet+}/\text{ArH})$ for the dichloromethane data which, however, do not fol-

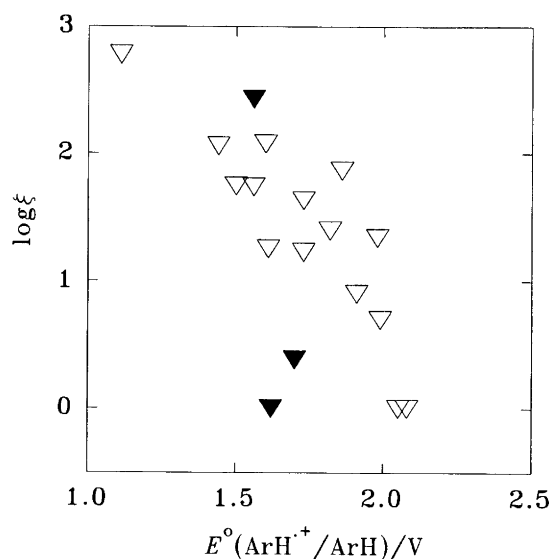


Fig. 2. Plot of $\log \zeta$ vs. $E^\circ(\text{ArH}^{\bullet+}/\text{ArH})$. Empty triangles refer to hydrocarbons, filled triangles to oxy-substituted compounds (see Table 8).

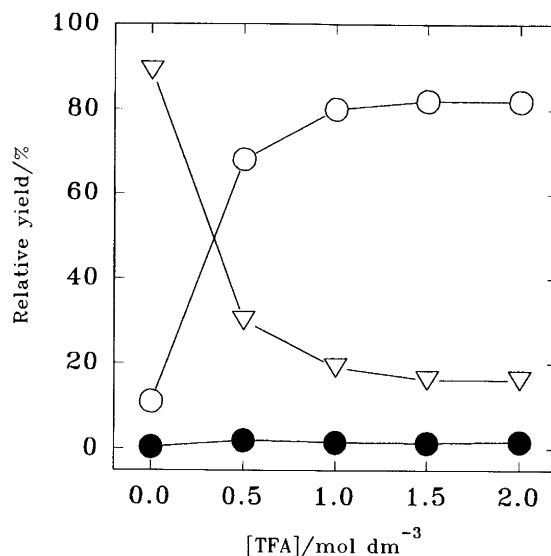


Fig. 3. Dependence of the yields of 1-nitronaphthalene (○), 2-nitronaphthalene (●) and adducts (▽) as a function of [TFA] from the photolysis of naphthalene (0.4 mol dm^{-3}), tetranitromethane (0.8 mol dm^{-3}) and TFA in dichloromethane at -20°C .

low the expected pattern, at least not in the available potential range. This may be due partly to difficulties in comparing reactivities of radical cations which are too different structurally. Alternatively, one and the same substrate should produce a similar relationship of $\log \zeta$ vs. temperature. This is presently being tested.⁶¹

Perhaps the most important chemical consequence of eqn. (16) is the possibility to direct the photolysis of

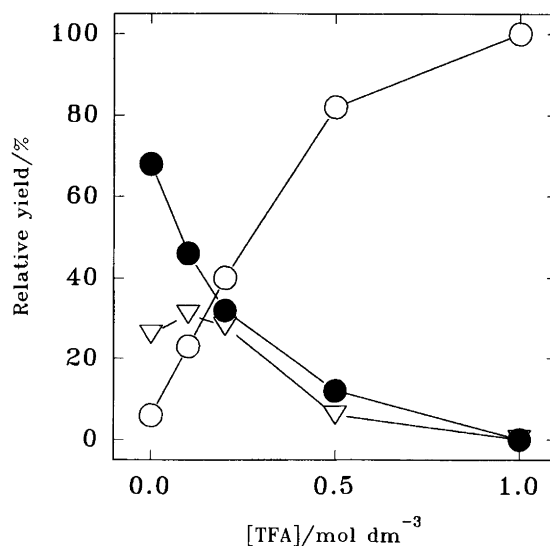


Fig. 4. Dependence of the yields of 2-nitro-1,4-dimethylnaphthalene (○), adducts (●) and 1-methyl-4-nitromethylnaphthalene (▽) as a function of [TFA] from the photolysis of 1,4-dimethylnaphthalene (0.4 mol dm^{-3}), tetranitromethane (0.8 mol dm^{-3}) and TFA in dichloromethane at -20°C .

Table 9. Addition/nitro-substitution product ratios from the photolysis of ArH–tetranitromethane in dichloromethane at $-20\text{ }^{\circ}\text{C}$, unless otherwise stated, and changes in this ratio with addition of TFA.

Substrate	Ratio		Ref.
	No TFA	TFA added	
Toluene	1.7	0 ^a	39
Dibenzofuran	11	0 ^b	24, 25
Naphthalene	8.1	0.19 ^a	39
1-Methylnaphthalene	8.5	0.39 ^d	39
1,4-Dimethylnaphthalene	11	0 ^e	39
1,4-Dimethylnaphthalene	0.6	0 ^e	39, 60
at 23 °C			
1,8-Dimethylnaphthalene	1.1	<0.1 ^d	39
1,4,5,8-Tetramethylnaphthalene	0.7	<0.04 ^f	39

^a In acetonitrile; ^{1f} [TFA]=0.8 mol dm⁻³. ^b Neat TFA.

^c [TFA]=2.0 mol dm⁻³. ^d [TFA]=0.2 mol dm⁻³.

^e [TFA]=1.0 mol dm⁻³. ^f [TFA]=0.4 mol dm⁻³.

ArH–tetranitromethane to give exclusively substitution.^{39,59} By protonation of trinitromethanide ion, the complications of adduct formation are avoided and the inherent high selectivity of the ArH^{•+}–NO₂ reaction can be utilized for preparative purposes (bearing in mind that the same advantage can often be achieved by the much simpler nitration by NO₂ in dichloromethane). Fig. 3 shows the result of adding an increasing [TFA] to the photolysis of naphthalene–tetranitromethane mixtures; the yield of nitro products, with the expected 1-/2-ratio of ≈ 50 , increases strongly whereas the adduct yield levels out at about 15% at high [TFA]. This was taken as evidence that some proportion of the triad reacts fast enough to be untouched by the presence of acid, presumably at the radical cation–trinitromethanide contact ion pair stage. For the less reactive radical cation of 1,4-dimethylnaphthalene, addition of TFA eventually eliminated the adducts **10** and **11** and gave only the nuclear nitro-substitution product **14** (Fig. 4). Further results of a similar nature are given in Table 9.

The kinetics of a large number of triad systems have been probed by fast laser spectroscopy^{33b,34a,34b,37,57,58} and the results interpreted from a consideration of the final products, meaning that the rate constants have been variously ascribed to ArH^{•+}–(NO₂)₃C⁻ or ArH^{•+}–NO₂ reactant pairs. However, the results of Table 8 indicate that the more generally occurring reaction is likely to be ArH^{•+}–(NO₂)₃C⁻ and that a number of the earlier assignments may be erroneous.

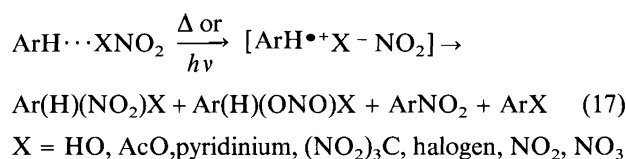
Relationships between electrophilic nitration by NO₂⁺ and photonitration by tetranitromethane. We can now return to the problem of assessing the relevance of the photochemical ArH–tetranitromethane reaction for understanding the possible ET mechanism of electrophilic aromatic nitration. Clearly, adduct formation from the components of the triad is an important, if not predominant, feature

of almost all such reactions. Only in cases where a good electron-releasing group is present in ArH (e.g., alkoxyaromatics) is evidence for adduct formation less pronounced, although it has been detected for anisole,³⁹ 4-methylanisole,^{34b} 4-haloanisoles,^{34b} 4-chloroanisole⁴⁰ and 1-methoxynaphthalene.⁶¹ We propose that adducts in such systems are always formed but are more prone to elimination of nitroform and/or nitrous acid because of the stabilizing influence of the electron-releasing groups upon the transition state leading to elimination.

Secondly, the intermediacy of adducts immediately raises the problem of how to assess the importance of isomer ratios between substitution products. Clearly, one can now cultivate the ArH^{•+}–NO₂ coupling reaction by running the photolysis of ArH–tetranitromethane in the presence of an acid; this fixes isomer ratios for the ArH^{•+}–NO₂ step which so far are in complete agreement with those obtained from earlier studies of the purely thermal reaction. We now claim that these ratios have been shown to be systematically different from those obtained in the ArH–NO₂⁺ reaction, and that electrophilic nitration of ArH by NO₂⁺ occurs predominantly by the classical Ingold mechanism. The radical pair simply does not behave chemically in a way compatible with eqn. (1). The Popperian criterion of falsifying a hypothesis¹¹ has worked!

We note here that Ridd's CIDNP results,³ indicating that a minor part of the ArH–NO₂⁺ reaction proceeds via the radical pair, present little difficulty for the conclusion above. A small proportion of the ET component would be impossible to detect by its effect on isomer ratios.

Future developments. The ArH/tetranitromethane reaction is a special case of the general situation depicted in eqn. (17) where a species NO₂–X reacts spontaneously and/or photochemically with ArH according to an ET mechanism, formally leading to triads of the general type [ArH^{•+} X⁻ NO₂] and generating similar mechanistic problems as those discussed above and no doubt a few additional ones, such as the possibility of the equilibrium XNO₂⁺ \rightleftharpoons X⁻ + NO₂⁺ simply being a source of nitronium ion. Table 10 shows some isomer ratio characteristics of reactions of this type with nitropyridinium ions, chosen because of their possible relationship to an addition/elimination mechanism.⁶² Such a mechanism would be expected to be more favoured than in the tetranitromethane case because of the higher nucleophilicity of pyridines relative to trinitromethanide ion, $n(\text{CH}_3\text{I})$ values⁶³ being 5.2 for pyridine itself and for trinitromethanide ion 2.9 (Ref. 39).

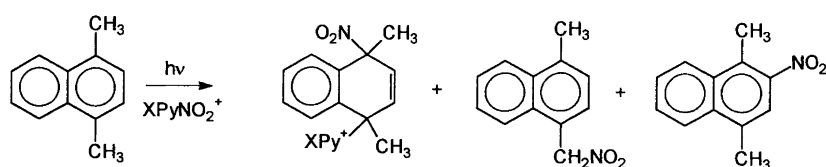
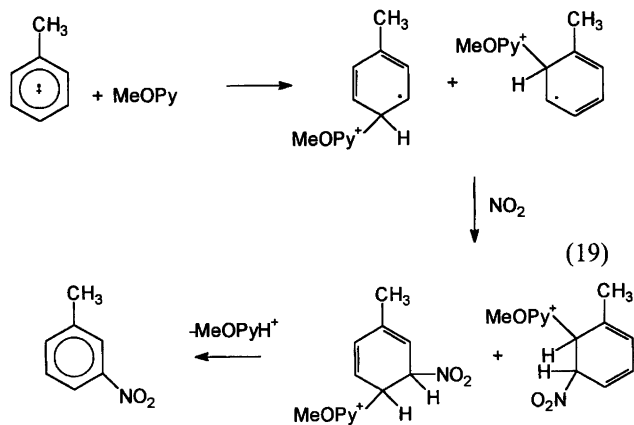
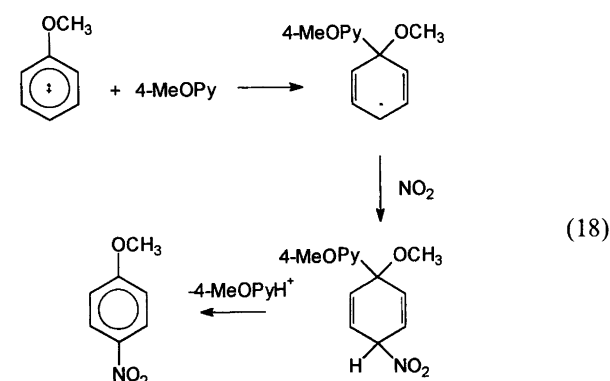


Thus for anisole, it was reasoned^{62c} that the statistical isomer ratio obtained in the 2,6-Me₂PyNO₂⁺ case should

Table 10. Nitro-isomer ratios from reactions between a few X-NO₂ and ArH under thermal or photochemical conditions in acetonitrile, unless otherwise stated. Data were taken from Ref. 62.

Substrate	X	Isomer ratio measured	Ratio	Reaction type
Anisole	2,6-Me ₂ Py ⁺	2-/4-	1.9	Photochemical
Anisole	4-MeOPy ⁺	2-/4-	0.59	Photochemical
Anisole	4-MeOPy ⁺	2-/4-	0.61	Photochemical ^a
Anisole	4-MeOPy ⁺	2-/4-	1.9	Thermal
Toluene	4-MeOPy ⁺	2-/3-/4-	14/59/21	Photochemical
Toluene	4-MeOPy ⁺	2-/3-/4-	28/52/20	Photochemical ^a
Toluene	4-MeOPy ⁺	2-/3-/4-	46/17/28	Photochemical ^b
Toluene	4-MeOPy ⁺	2-/3-/4-	61/3/33	Thermal

^a With TFA added. ^b In dichloromethane and with TFA added.



X = MeOCO	53 %	32 %	5 %
X = H	74 %	11 %	not determined
X = MeO	60 %	29 %	9 %

be a result of ArH^{•+}-NO₂ coupling (no nucleophilic attack by the pyridine because of steric hindrance), whereas the more nucleophilic 4-methoxypyridine would lead to an adduct from *ipso* attack, followed by elimination to give a mixture enriched in the 4-nitro isomer [eqn. (18)]. For toluene, the high proportion of the *meta* isomer was explained in a similar way [eqn. (19)].

1,4-Dimethylnaphthalene also underwent addition upon photolysis together with nitropyridinium ions,⁶⁰ as shown in eqn. (20), where the proportion of adduct is about the same as in the tetranitromethane reaction [eqn. (12)]. The interesting feature with nitropyridinium ions is that they also react thermally with 1,4-dimethylnaphthalene, the products ranging from predominantly adduct-for-4-MeOCOPyNO₂⁺ to mostly side-chain nitration product for MeOPyNO₂⁺. In combination with the fact that nitropyridinium ions are fairly weak ET oxidants, *E*_p for reduction being in the range of 0.14 (4-MeOPyNO₂⁺) to 0.55 V (4-MeOCOPyNO₂⁺), some interesting mechanistic problems clearly await their solution in this area.

Another development lies in the use of zeolites to catalyse the nitration of ArH.⁶⁴ It is generally agreed that some zeolites can oxidize hydrocarbons to their radical cations, and thus one would expect that zeolite-catalysed nitration should have the characteristics of ArH^{•+}-mediated reactions. Thus for toluene radical cation one would expect from the spin densities that the *para* position should be favoured for coupling with NO₂. Indeed it was found that montmorillonite-supported Cu(II) nitrate in acetic anhydride gave a 2-:3-:4-nitro-isomer distribu-

tion of 43:2:55 from toluene instead of 63:3:34 in the homogeneous reaction. While this is not a large effect, this method offers new possibilities of studying $\text{ArH}^{\bullet+}-\text{NO}_2$ reactions and their selectivities with substrates of more discriminating power.

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