KEYNOTE ARTICLE

Photochemical Nitration by Tetranitromethane. Part XIX. The Competitive Reactions of Trinitromethanide and Nitrogen Dioxide with Radical Cations and their Use for Selective Nitrations

Lennart Eberson,*[a] **Michael P. Hartshorn,**[b] **Finn Radner**†[a] **and Jan O. Svensson**[a]
[a] *Chemical Center, Lund University, PO Box 124, S-221 00 Lund, Sweden*
[b] *Department of Chemistry, University of Canterbury, Christchurch, New Zealand*

The photolysis of the charge-transfer complex between an aromatic compound (ArH) and tetranitromethane is known to form initially a triad of the aromatic radical cation, trinitromethanide ion and NO_2 [eqn. (i)]. For reactive and moderately reactive radical cations, the chemical follow-up

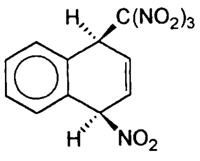
$$\underset{\text{CT complex}}{ArH \cdots C(NO_2)_4} \xrightarrow{h\nu_{CT}} \underset{\text{triad}}{ArH^{\bullet+} (NO_2)_3C^- \; NO_2} \qquad \text{(i)}$$

reactions from the species of the triad are fast at −60 °C, as shown by the fact that the solutions are EPR-silent during photolysis. However, by conducting the photolysis in the presence of a protic acid, the trinitromethanide ion is rendered unreactive by protonation, resulting in the build-up of a detectable (EPR) concentration of $ArH^{\bullet+}$ or $(ArH)_2^{\bullet+}$. This shows that the initial chemical step from the triad is the nucleophilic attack of trinitromethanide ion upon $ArH^{\bullet+}$, and that the rate of the reaction between the latter and NO_2 must be significantly lower. Preparative experiments support this conclusion, in that the predominant *adduct* formation from ArH–tetranitromethane photolysis is diverted into nitro *substitution* in the presence of a protic acid, the latter reaction occurring *via* $ArH^{\bullet+}$–NO_2 coupling.

These findings also establish that results obtained from the photonitration of aromatics by tetranitromethane are not relevant for judging the possible electron transfer nature of electrophilic aromatic nitration by nitronium ion.

The photolysis of the charge-transfer (CT) complex of an aromatic compound (ArH) and tetranitromethane in an aprotic organic solvent, such as dichloromethane or acetonitrile, leads in most cases to *addition* of the elements of tetranitromethane (nitro–trinitromethyl and/or nitrito–trinitromethyl) to the aromatic ring.[1–4] The adducts, in many cases isolated and characterized by X-ray crystallography, are more or less labile in solution and undergo thermal reactions to give *substitution* products or products of intramolecular *cycloaddition.* A small proportion of nitro substitution products also appears to be formed directly by coupling of nitrogen dioxide and $ArH^{\bullet+}$ (see below), but it is difficult to assess the exact contribution from this route because of predominant adduct formation and uncertainty as to how the thermal elimination of nitroform from adducts influences this yield.

Naphthalene is a typical representative of this behaviour.[2,3b] Upon photolysis of its CT complex in dichloromethane or acetonitrile at −20 or +20 °C, the nitro–trinitromethyl adducts **1**–**3** and hydroxy–trinitromethyl adduct **4** together amounted to 85–95% of the product mixture, the remaining products being 1- and 2-nitronaphthalene. The structure of adduct **1** was confirmed by single-crystal X-ray analysis, whereas the other structures were deduced from NMR spectral analysis. It was assumed that adduct **4** was not a primary product but was formed by hydrolysis of the corresponding nitrite during photolysis and/or work-up. Adduct **1**, dissolved in dichloromethane, readily eliminated nitroform upon treatment with a weak base (2,6-di-*tert*-butylpyridine) and also underwent the same reaction slowly in neat acetonitrile. GLC analysis led to instantaneous elimination and quantitative formation of 1-nitronaphthalene at moderate injection-port temperatures. The thermal sensitivity of the adducts thus



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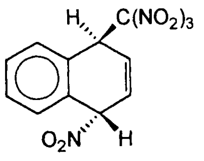

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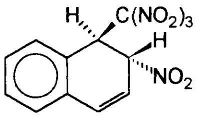

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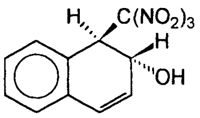

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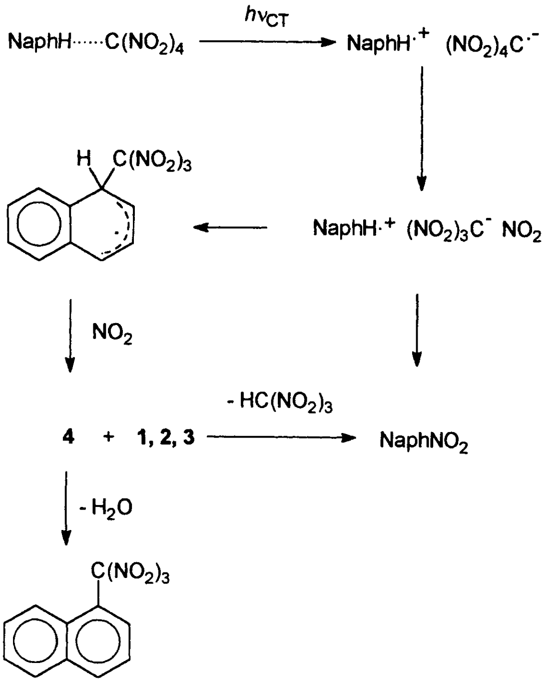
† *Present address:* Nycomed Innovation AB, Ideon-Malmö, S-205 12 Malmö, Sweden.

necessitates work-up at low temperature ($\leqslant 0$ °C) and analysis by a non-destructive technique, such as NMR spectroscopy.

It was assumed that the naphthalene–tetranitromethane photo-reaction would follow the same mechanism as that proposed for similar additions in the anthracene series:[1a,b] formation of the radical ion pair, followed by fast fragmentation of the tetranitromethane radical anion (Scheme 1) to give a triad of naphthalene radical cation, trinitromethanide ion and NO_2. The initial chemical process was assumed to be trinitromethanide attack upon (naphthalene)$^{\bullet +}$, followed by reaction between the naphthalenyl radical and NO_2, attack occurring *via* either nitrogen or oxygen. The selectivity of the latter step, coupling between two neutral radicals, is expected to be low.

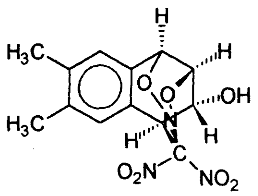


Scheme 1

The formation of a small amount of 1- and 2-nitronaphthalene can, in principle, be explained as a result of elimination of nitroform from the adducts taking place during the photolytic run. However, since the proportion of nitro isomers was higher at lower temperatures, where elimination is expected to be less favoured, it was concluded that 1- and 2-nitronaphthalene were partially and even predominantly formed by coupling between (naphthalene)$^{\bullet +}$ and NO_2. The high 1-/2-nitronaphthalene isomer ratios observed at low conversion in runs at low temperature agreed with this suggestion. Finally, it was noticed that adduct **4** is a logical precursor of the 1-trinitromethyl substitution product, for example, by acid-catalysed elimination of nitrous acid. 1-Trinitromethylnaphthalene was not detected as such, but decomposed upon GLC of the crude reaction mixture to give 1-naphthonitrile.

Further experimentation with other substrates[3a,3c–3l] was completely in line with the general features of Scheme 1. In particular, X-ray crystallographic evidence was obtained for the formation of intramolecular cycloadducts in several cases, among them **5**,[3l] clearly a cycloadduct formed from a primary hydroxy–trinitromethyl adduct. Also, it was established with 4-chloroanisole as the substrate[3f] that adducts of this type indeed can undergo acid-catalysed elimination to give trinitromethyl substitution products.

The preparative naphthalene results described above were reproduced in their main features by Kim, Bockman and Kochi,[1e] but interpreted differently on the basis of kinetic studies. The mechanism of Scheme 1 was inverted with respect to the sequence of the chemical follow-up reactions, the initial step now being assumed to be the (naphthalene)$^{\bullet +}$–NO_2 reaction. The resulting Wheland intermediate would then form adducts by reaction with trinitromethanide ion, in our opinion a less likely possibility in view of the high acidity of the Wheland intermediate favouring proton loss instead.



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It was shown early on that the photochemical step very rapidly (< 3 ps) gives the triad consisting of the aromatic radical cation ($ArH^{\bullet +}$), trinitromethanide ion and nitrogen dioxide [eqn. (1)] from which products develop.[5] The

$$\underset{\text{CT complex}}{ArH\cdots C(NO_2)_4} \xrightarrow[< 3\ \text{ps}]{h\nu_{CT}} \underset{\text{triad}}{ArH^{\bullet +}(NO_2)_3C^{-}NO_2} \qquad (1)$$

mechanistic problem at hand is defined as follows: is the initial chemical step attack of the nucleophilic trinitromethanide ion at positions of high charge density in the radical cation [eqn. (2), rate constant k_2] or is it the coupling of NO_2 with positions of high spin density [eqn. (3), rate constant k_3]?

$$ArH^{\bullet +} + (NO_2)_3C^{-} \xrightarrow{k_2} Ar(H)C(NO_2)_3^{\bullet} \qquad (2)$$

$$ArH^{\bullet +} + NO_2 \xrightarrow{k_2} Ar(H)NO_2{}^{+} \qquad (3)$$

The consequences of the very fast removal of one of the tetranitromethane-derived components of the triad might be susceptible to direct experimental observation. We have reported[6] in preliminary form that protonation of trinitromethanide ion by an added protic acid is such a process. Irradiation of ArH–tetranitromethane at -60 °C in dichloromethane produced no EPR signal from the radical cation in cases of reactive or moderately reactive $ArH^{\bullet +}$, whereas irradiation of a solution containing additionally 0.4 mol dm^{-3} trifluoroacetic acid (TFA) produced a signal from $ArH^{\bullet +}$ in all cases except the most reactive systems, such as naphthalene$^{\bullet +}$. Similar observations were made on acetonitrile solutions of some systems when a stronger acid, methanesulfonic acid, was used. This was taken as evidence that the added acid protonates trinitromethanide ion, giving the much less nucleophilic trinitromethane, thus allowing the significant operation of the $ArH^{\bullet +}$–NO_2 pathway. Two mechanistic features are immediately obvious from this phenomenology, namely (*i*) that trinitromethanide ion must be more reactive than NO_2 in the unperturbed triad ($k_2 > k_3$; the irradiated solution is EPR-silent), and (*ii*) the reaction between $ArH^{\bullet +}$ and NO_2 must be relatively slow since the EPR signal of $ArH^{\bullet +}$ builds up when the trinitromethanide ion is removed by protonation. As a corollary, the preparative outcome of the naphthalene–tetranitromethane reaction at -20 °C in dichloromethane could be switched from a ratio of adducts/nitronaphthalenes of 7.2 with no TFA added to a ratio of 0.054 with 1.5 mol dm^{-3} TFA present. The 1-/2-nitronaphthalene ratio in the latter case was > 50, in excellent agreement with the ratio obtained[7] by coupling between presynthesized naphthalene radical cation salt and NO_2.

This paper is a detailed account of the study referred to above, and describes further experimentation based on the same idea. It is concluded that the main features of the photochemical reaction between tetranitromethane and aromatics are now understood.

Results

Protonation of Trinitromethanide Ion in Dichloromethane or Acetonitrile

In order to determine the approximate equilibrium constant of eqn. (4), a solution of tetrabutylammonium trinitromethanide

$$(NO_2)_3C^- + HA \overset{K_4}{\rightleftharpoons} (NO_2)_3CH + A^- \qquad (4)$$

$$A = CF_3COO \text{ or } CH_3SO_3$$

in dichloromethane was titrated with aliquots of TFA, dissolved in dichloromethane, and the process monitored by UV spectrophotometry at 348 nm, the wavelength of the absorbance maximum of trinitromethanide ion. However, K_4 could not be calculated from the concentrations obtained in this way, presumably due to the fact that the effect of the homoconjugation equilibrium of trifluoroacetate ion has been neglected.[8] This should be pronounced in a non-basic solvent like dichloromethane. From eqn. (4) the following apparent values of the equilibrium constant ('K_4') were calculated from five data points in the region of 40–60% neutralization: 0.18, 0.22, 0.28, 0.33, 0.35, in increasing order of neutralization. Further values calculated on both sides of this region showed that 'K_4' increases with the degree of neutralization of trinitromethanide ion. The value of 'K_4' at 50% neutralization was taken as a measure of the relative strengths of the two acids. For the purpose at hand, we note that the effect of added TFA is sufficiently high to allow for efficient suppression of $[(NO_2)_3C^-]$ in the concentration range in which it is formed during photolysis.

In acetonitrile, 'K_4' was determined for TFA in the same way which gave a value of 0.020 at 50% neutralization. Again, 'K_4' increased with the degree of neutralization of trinitromethanide ion. Since we wanted the proton-donating power of the acid to be approximately the same as in the TFA–dichloromethane system, methanesulfonic acid was tried instead. A value of 'K_4' = 0.6 was obtained, resembling more closely the conditions in the TFA–dichloromethane system.

Nucleophilicity of the Trinitromethanide Ion

Since no quantitative measure of the nucleophilicity of trinitromethanide ion is available, we measured the $n(CH_3I)$ value[9] by recording spectrophotometrically the rate of disappearance of $[(NO_2)_3C^-]$ in methanol at 25 °C in the presence of a large excess of methyl iodide at four concentrations in the region of 1.8–3.5 mol dm^{-3}. The reaction was reversible with an equilibrium constant of $8(3) \times 10^{-5}$ and the kinetics had to be calculated according to the rate expression for a second-order equilibrium process,[10] resulting in a forward rate constant of $1.1(2) \times 10^{-4}$ dm^3 mol^{-1} s^{-1} and a backward rate constant of 1.5(2) dm^3 mol^{-1} s^{-1}. Thus $n(CH_3I)$ is $\log (1.1 \times 10^{-4}/1.3 \times 10^{-7}) = 2.9$, slightly above that of fluoride ion (2.7) and a bit below that of acetate ion (4.3).[9]

An EPR-based Method for Determining the Relative Reactivity of Trinitromethanide Ion and Nitrogen Dioxide

Preliminary experimentation by low-temperature EPR spectroscopy, aimed at the possible detection of paramagnetic intermediates from the photochemistry of ArH–tetranitromethane CT complexes, revealed that most systems were EPR-silent at −60 °C, a convenient temperature for work in dichloromethane considering the solubility and phase problems involved. Even irradiation times of up to 60 min in combination with spectral accumulation during the whole irradiation period failed to give any indication of paramagnetic species, except for systems corresponding to long-lived radical cations, like that of tris(4-bromophenyl)amine. However, in all cases, except for the most reactive radical cations, the presence of 0.4 mol dm^{-3} TFA caused an immediate build-up of an EPR signal which could be assigned to $ArH^{\bullet+}$ or $(ArH)_2^{\bullet+}$. This phenomenon showed that removal of trinitromethanide ion by protonation allowed the accumulation of the aromatic radical cation, immediately suggesting that the k_3 step [eqn. (3)] must be slower than the k_2 step [eqn. (2)], provided the former reaction is irreversible and followed by fast proton loss. These requirements are certainly met, since in eqn. (3) we are dealing with the Wheland intermediate of aromatic nitration.[11]

The photochemical experiments were run in a highly standardized way (see the Experimental section) with (*i*) a solution of ArH–tetranitromethane, (*ii*) a solution of ArH–tetranitromethane–TFA and (*iii*) a solution of ArH–TFA, the latter a precaution to exclude the possibility that photooxidation of ArH in the presence of TFA might be responsible for the appearance of the EPR signal of the radical cation.[12] These solutions will be referred to in the following as solution I, II or III. Irradiation was performed with focussed light from a 50 W high-pressure Hg lamp (Bruker ER 202), passed through a filter with cutoff at < 435 nm. Solutions I and II were coloured, varying between faintly yellow and red, due to formation of the CT complex between ArH and tetranitromethane.[5] The solvent in general was dichloromethane, but acetonitrile was used in some cases. Each solution was irradiated for 6 min, 30 or 100 spectra being accumulated during this period. The signal intensities were determined as absolute values of half the peak-to-peak amplitude of the most prominent peak, and tests (see below and in the Experimental section) showed that these were reproducible to within ±30%, fully adequate for the purpose at hand. This procedure is less reliable when signals of different line widths are compared (*e.g.*, a resolved spectrum *vs.* a broad singlet), but this situation was encountered only in the case of 1-methoxynaphthalene for solution I/II comparisons. Since peak-to-peak amplitudes are inversely proportional to the square of the peak-to-peak width, the 1-methoxynaphthalene ξ values would actually come out larger if this effect is taken into account.

In cases where no literature EPR data of a particular radical cation were available, the appropriate EPR spectrum was recorded under solution III conditions, with the provision that a small amount of 2,3-dichloro-4,5-dicyanobenzoquinone (DDQ) was added. Depending on the ease of oxidation of ArH, the radical cation is formed thermally[12,13] or photochemically,[14] generally giving a well-resolved spectrum.

Fig. 1 shows a set of EPR spectra obtained for solutions I–III of one substrate, 1,2-dimethylnaphthalene, which was singled out for a more detailed study (see below).

Application of EPR Spectral Analysis to the Competitive Reactions of Trinitromethanide Ion and Nitrogen Dioxide with Radical Cations

Table 1 shows the aromatic substrates used, listed approximately in order of decreasing $E°(ArH^{\bullet+}/ArH)$, together with the EPR spectra intensities measured for solutions I–III, as described above, and the ratio of intensities (denoted ξ) between those of the solutions II and I. Fig. 2 shows log ξ (shaded bars) in a bar chart for all systems studied at −60 °C, in the same

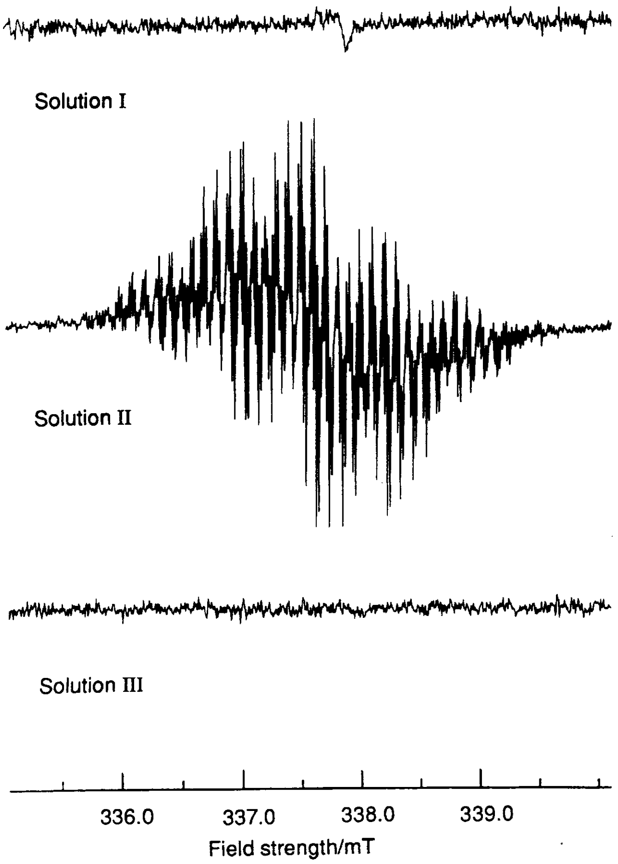

Fig. 1 EPR spectra of solutions I–III of the 1,2-dimethylnaphthalene system at −60 °C

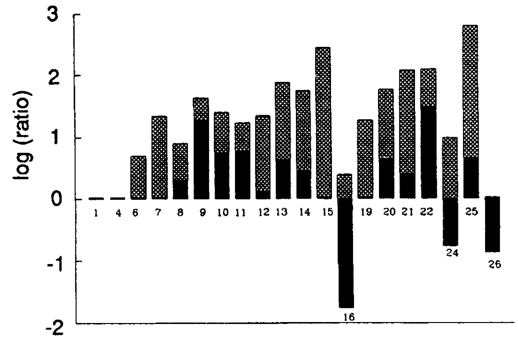

Fig. 2 Bar chart of the logarithms of the ratio between the EPR intensities of solutions II and I (log ξ, shaded bars) and solution III and I (black bars, placed over the shaded ones), determined at −60 °C (Table 1). A log (ratio) of '0' is represented by 0.02 in order to be visible and the substrates are from left to right (entry of Table 1): naphthalene (1), 1-methylnaphthalene (4), 1,4- (6), 1,2- (7), 1,8- (8) and 2,3-dimethylnaphthalene (9), acenaphthene (10), fluoranthene (11), 1,2,5,8- (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-diphenyl-anthracene (21), pyrene (22), tris(4-bromophenyl)amine (24), 9,10-dimethylanthracene (25) and 1-methoxynaphthalene (26).

order as in Table 1. Also the logarithms of the ratios between the intensities of solutions III and I (black bars, superimposed on the shaded ones) are shown for comparison. Two extreme situations are easily recognized: one where the high reactivity of the radical cation under both solutions II and I conditions gives $\xi \approx 1$, as exemplified by naphthalene$^{\bullet +}$ and 1-methylnaphthalene$^{\bullet +}$ (entries 1 and 4), and one where low reactivity of the radical cation makes it appear to be almost equally unreactive under both sets of conditions, as typified by (dibenzo-1,4-dioxin)$^{\bullet +}$ (entry 16), a fairly unreactive radical cation. The stability is also reflected under solution III conditions. It is for radical cations of intermediate reactivity that one finds the high ξ values; an implication is that one and the same substrate can be induced to exhibit any behaviour by suitable choice of temperature (see Table 1, entries 26–28 for 1-methoxynaphthalene).

Systems with ξ around 1 at −60 °C were studied at lower temperature(s) where the radical cation reactivity is lower. The behaviour of naphthalene was unaffected even at −80 °C, whereas 1-methylnaphthalene gave a high ξ at −70 °C. At the other extreme, the 2,5-di-*tert*-butyl-1,4-dimethoxybenzene radical cation exhibited very low reactivity[15] which permitted its study even at +20 °C.

Experiments were also performed with acetonitrile as the solvent, as shown in Table 2. Here the method could be applied only to systems with rather unreactive radical cations, such as 9,10-dimethylanthracene, 9,10-diphenylanthracene, 1,4,5,8-tetramethylnaphthalene, 1,4-dimethoxybenzene and dibenzo-1,4-dioxin. One obvious reason for this behaviour is that these reactions had to be run at a higher temperature, −40 °C, because of the physical properties of acetonitrile. The stronger acid, methanesulfonic acid, was used to protonate trinitromethanide ion (see above). In addition, the relatively high nucleophilicity of acetonitrile[16] must exert a levelling effect in systems with high radical cation reactivity.

In all cases where irradiation led to the build-up of a significant radical cation concentration, the stability of the radical cation was checked after discontinuation of irradiation. Under solution I conditions (both trinitromethanide ion and NO_2 present), the radical cation inevitably disappeared within < 10 s, whereas under solution II conditions (only NO_2 present) the time dependency of the decay was sometimes monitored in cases of relatively stable radical cations.

Descriptions of the behaviour of the individual systems are given below. The identification of the radical cations mostly rests on comparison with simulated spectra using published EPR parameters. This was, however, not always an unambiguous method. The EPR spectra from solution II were sometimes poorly resolved, and identification then was less certain. For radical cations with no EPR parameters published, identification was ascertained by independent generation under conditions resembling those of solution II (DDQ treatment; see above).

Naphthalene and 1-Methylnaphthalene

At −60 °C, both systems exhibited a ξ of about 1, and lowering the temperature to −80 °C made no difference for naphthalene, whereas 1-methylnaphthalene–tetranitromethane–TFA at −70 °C gave a well-resolved EPR spectrum of (1-methylnaphthalene)$_2^{\bullet +}$, identical with the published spectrum[17] obtained for a dichloromethane solution at < −80 °C and satisfactorily simulated by their parameters for the dimer radical cation.

1,4-Dimethylnaphthalene

Irradiation of solution II at −60 °C gave a broad, unresolved signal with $\Delta H_{pp} \sim 1.0$ mT and some indication of further fine structure. Solution III required irradiation by UV light to give a resolved spectrum which could be simulated by published EPR parameters of (1,4-dimethylnaphthalene)$_2^{\bullet +}$ but not by those of the monomeric radical cation.[17] Use of a large linewidth in the simulation provided an unresolved peak of $\Delta H_{pp} \sim 1.0$ mT.

1,2-Dimethylnaphthalene, a more detailed study

Since irradiation of solution II of this system gave a well resolved EPR spectrum (Fig. 1), it was chosen for a closer study

Table 1 EPR spectral intensities after irradiation of ArH–tetranitromethane solutions in dichloromethane without and with TFA present. Irradiation time 6 min (during which 30 or 100 spectra were accumulated), $\lambda > 435$ nm, [ArH] = 20–40 mmol dm^{-3}, [$C(NO_2)_4$] = 0.8 mol dm^{-3}, [TFA] = 0.4 mol dm^{-3}, $T = 213$ K, unless otherwise stated in the table or text

		EPR spectral intensity			
Entry No.	ArH	With TNM[a] (solution I)	With TNM[a] and TFA[b] (solution II)	With TFA[b] (solution III)	Ratio ξ
1	Naphthalene	< 2	< 2[c]	< 2	1
2	Naphthalene (at −70 °C)	< 2	< 2	< 2	1
3	Naphthalene (at −80 °C)	< 2	< 2	< 2	1
4	1-Methylnaphthalene	< 2	< 2	< 2	1
5	1-Methylnaphthalene (at −70 °C)	< 2	117	< 2	> 58
6	1,4-Dimethylnaphthalene	< 2	10	< 1.5	> 5
7	1,2-Dimethylnaphthalene	< 2.5	54	< 2	> 22
8	1,8-Diemthylnaphthalene	< 2	16	4	> 8
9	2,3-Dimethylnaphthalene	< 2	87	38	> 43
10	Acenaphthene	< 2	50	11	> 25
11	Fluoranthene	< 2	34	12	> 17
12	1,3,5,8-Tetramethylnaphthalene	< 2	44	2.6	> 22
13	1,4,6,7-Tetramethylnaphthalene	< 0.7	52	3	> 74
14	1,4,5,8-Tetramethylnaphthalene	< 1.8	100	5	> 55
15	1,4-Dimethoxybenzene	< 2	540	< 2	> 270
16	Dibenzo-1,4-dioxin	2300	5450	40	2.4
17	Dibenzo-1,4-dioxin (at −40 °C)	1180	2250	20	1.9
18	Dibenzo-1,4-dioxin (at −20 °C)	62	463	20	7.5
19	Anthracene	< 2	37	< 2	> 18
20	9-Phenylanthracene	< 1.8	100	8	> 56
21	9,10-Diphenylanthracene	2.6	300	6.5	115
22	Pyrene	15	1800	440	120
23	Perylene (−70 °C)	8	230	25	106
24	Tris(4-bromophenyl)amine	19	181	3.2	9.5
25	9,10-Dimethylanthracene	< 1	600	4.6	> 600
26	1-Methoxynaphthalene	600	610	78	*ca.* 1[d]
27	1-Methoxynaphthalene (at −50 °C)	19	2450	40	129
28	1-Methoxynaphthalene (at −40 °C)	10	570	5	57
29	2,5-Di-*tert*-butyl-1,4-dimethoxybenzene (at +20 °C)[e]	40	400	—	10

[a] TNM = tetranitromethane. [b] [TFA] = 0.4 mol dm^{-3}. [c] At [TFA] = 1 mol dm^{-3}, the naphthalene radical cation concentration was above the noise level (intensity *ca.* 3.5). [d] This is a minimum value, since intensities were obtained from signals of differing linewidth. [e] At [TFA] = 0.1 mol dm^{-3}.

Table 2 EPR spectral intensities after irradiation of ArH–tetranitromethane solutions in acetonitrile without and with methanesulfonic acid present. Irradiation time 6 min (during which period 100 spectra were accumulated), $\lambda > 435$ nm, [ArH] = 20–40 mmol dm^{-3}, [$C(NO_2)_4$] = 0.8 mol dm^{-3}, [CH_3SO_3H] = 0.4 mol dm^{-3}, $T = 233$ K, unless otherwise stated in the table or text

		EPR spectral intensity		
Entry No.	ArH	With $C(NO_2)_4$ (solution I)	With $C(NO_2)_4$ and CH_3SO_3H (solution II)	Ratio ξ
1	1,2-Dimethylnaphthalene	< 2	< 2	1
2	1,4,5,8-Tetramethylnaphthalene	< 2	7	> 3.5
3	1,4-Dimethoxybenzene	7	23	3.3
4	Dibenzo-1,4-dioxin	2700	3830	1.4
5	Dibenzo-1,4-dioxin (at −20 °C)	170	1170	7.0
6	9-Phenylanthracene	< 2	< 2	1
7	9,10-Diphenylanthracene	3	19	6.3
8	9,10-Dimethylanthracene	< 2	41	20

of some features of interest. The method worked equally well at −40, −50 and −60 °C, the ξ values being > 73, > 70 and > 22, respectively. The EPR spectrum could be simulated reasonably well by the published EPR parameters[17] of (1,2-dimethylnaphthalene)$_2{}^{\bullet +}$, provided two modifications in the hfsc ($a^{2\text{-CH}_3} = 0.098$ instead of 0.106 mT, $a^{6\text{-H}} = 0.075$ instead of 0.083 mT) were introduced. For comparison, a DDQ–*hv* generated EPR spectrum of similar resolution as in Fig. 1 is shown in Fig. 3.

If the equilibrium of eqn. (4) governs the concentration of trinitromethanide ion, and ArH$^{\bullet +}$ disappears predominantly by reaction with this species, one would expect that d[ArH$^{\bullet +}$]/dt should depend on [$(NO_2)_3C^-$], generated at approximately constant rate by the constant light flux, according to eqn. (5). Combination of eqn. (5) with eqn. (4) then leads to a dependence on [CF_3COOH] as shown in eqn. (6) (C_1 and C_2 are constants).

$$d[ArH^{\bullet +}]/dt = C_1 - k_2[(NO_2)_3C^-] \qquad (5)$$

$$d[ArH^{\bullet +}]/dt = C_2 + k_2[CF_3COOH] \qquad (6)$$

Thus at any given time [ArH$^{\bullet +}$] = $C_3 + k'_2$[CF_3COOH], where C_3 is a constant (C_2t) and $k'_2 = k_2t$.

We first checked the reproducibility of the absolute intensities of the EPR spectra obtained under solution II conditions. From

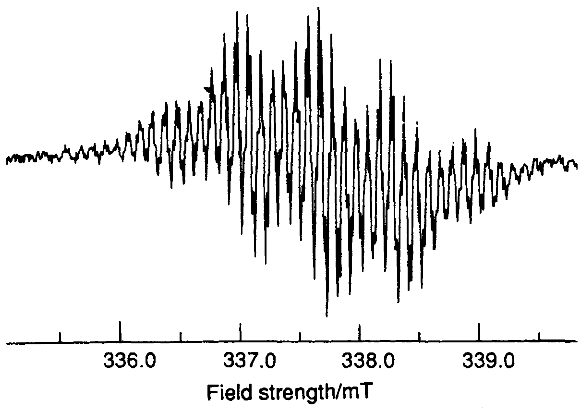

Fig. 3 EPR spectrum of (1,2-dimethylnaphthalene)$_2^{\bullet +}$ in dichloromethane–TFA (0.4 mol dm^{-3}) at −60 °C in the presence of DDQ and after 2 min of UV irradiation

five identical experiments the absolute intensities (in arbitrary units) of the most prominent peak were 196, 267, 190, 206 and 306, corresponding to a maximum deviation of 30% in the average value. Fig. 4 shows the variation of the EPR signal intensity with [CF_3COOH]. The data exhibit appreciable scatter in the region of high [TFA], and an attempt to fit the data to a mathematical model involving four disposable parameters and based on eqns. (4) and (6) was only semiquantitatively significant. The solid line of Fig. 4 represents the calculated behaviour of the model, with K_4 = 1.0 ± 0.5, [$(NO_2)_3C^-$]$_0$ at constant light flux = −120 ± 130 mmol dm^{-3}, C_2 = 13 ± 20 mmol dm^{-3} s^{-1} and d (a scaling parameter) = (5 ± 3) × 10^{-3}.

The irradiation of solution II built up a significant [1,2-$Me_2Naph^{\bullet +}$] which decayed at a measurable rate after the light had been turned off. At −50 and −60 °C, the rates could be monitored by the automation routine of the EPR instrument and were evaluated according to first-order kinetic behaviour with rate constants 0.31 and 0.22 min^{-1}, respectively.

1,8-Dimethylnaphthalene

Irradiation of solution II at −60 °C gave a moderately well resolved spectrum of (1,8-dimethylnaphthalene)$^{\bullet +}$, simulated by published EPR parameters[17] for the monomeric radical cation. Solution III upon irradiation with UV light gave an identical spectrum using identical spectral parameters; at lower modulation amplitude further fine-structure appeared.

2,3-Dimethylnaphthalene

Irradiation of solution II at −60 °C gave a broad, unresolved signal with ΔH_{pp} ~ 0.8 mT and some indication of further fine structure. Solution III gave a similarly broad, low-intensity signal with ΔH_{pp} ~ 0.5 mT.

Acenaphthene

Irradiation of solution II at −60 °C gave a broad, unresolved signal with ΔH_{pp} ~ 2.8 mT and no indication of further fine structure. Irradiation of solution III with UV light gave a moderately well resolved signal, simulated by the published EPR parameters for the dimer radical cation.[17]

Fluoranthene

Irradiation of solution II at −60 °C gave a broad, unresolved signal with ΔH_{pp} ~ 2.0 mT and no indication of further fine structure. Irradiation of solution III–DDQ at −40 °C (at −60 °C precipitation of solid radical cation salt occurred to some extent, as indicated by the appearance of an intense narrow singlet in the middle of the spectrum) gave a resolved EPR spectrum of > 60 lines with a width of ~ 1.9 mT. Since monomeric (fluoranthene)$^{\bullet +}$ would generate maximally 32 lines, this spectrum is presumably derived from (fluoranthene)$_2^{\bullet +}$. To the best of our knowledge, no isotropic EPR spectrum of fluoranthene radical cation has been published.[18]

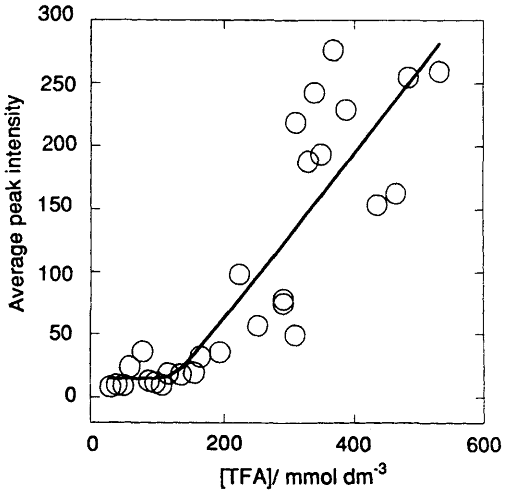

Fig. 4 Plot of average EPR peak intensity (30 spectra accumulated) *vs.* [TFA] from the photolysis of solutions of 1,2-dimethylnaphthalene (0.07 mol dm^{-3}), tetranitromethane (0.8 mol dm^{-3}) and TFA. The curve represents the best fit of the four-parameter equation described in the text.

1,3,5,8-Tetramethylnaphthalene

Irradiation of solution II at −60 °C gave a moderately well resolved spectrum of ~ 50 lines with a 0.075 mT spacing. Further fine structure was visible in spectra run at low modulation amplitude, and a fully resolved spectrum was obtained by DDQ oxidation[17] of 1,3,5,8-tetramethylnaphthalene at − 15 °C; its main features were the same as those of the spectrum from solution II. To the best of our knowledge, no isotropic EPR spectrum of 1,3,5,8-tetramethylnaphthalene radical cation has been published.

1,4,6,7-Tetramethylnaphthalene

Irradiation of solution II produced a resolved spectrum of (1,4,6,7-tetramethylnaphthalene)$^{\bullet +}$, identical with that obtained from DDQ treatment of solution III at − 15 °C and well simulated by published parameters for the monomeric radical cation.[17]

1,4,5,8-Tetramethylnaphthalene

Irradiation of solution II at − 60 °C produced a fully resolved spectrum of (1,4,5,8-tetramethylnaphthalene)$^{\bullet +}$, identical with that obtained from DDQ treatment of solution III at − 15 °C and simulated by published parameters for the monomeric radical cation.[17] The behaviour of this system has already been studied[3d] at −20 °C, and was virtually identical. The system was also run in acetonitrile at −40 °C with methanesulfonic acid as the proton donor, solution II providing a fully resolved spectrum of (1,4,5,8-tetramethylnaphthalene)$^{\bullet +}$.

1,4-Dimethoxybenzene

Irradiation of solution II at −60 °C produced a resolved spectrum of (1,4-dimethoxybenzene)$^{\bullet +}$, which was best simulated by the published parameters[19] for the *cis* conformer of the radical cation.

Dibenzo-1,4-dioxin

This compound has a rather stable radical cation with a simple and easily identifiable EPR spectrum (quintet[20] with a^H to the four α hydrogens = 0.21 mT). Accordingly, the radical cation was detectable with a well-resolved spectrum under solution I conditions at temperatures up to at least −20 °C, which provides a reason for the relatively low ξ values. The radical cation concentration built up in solution II during the irradiation period decayed with a first-order rate constant of 1.8(1) min^{-1} at −40 °C. In acetonitrile, the corresponding rate constant was 1.5(2) min^{-1}.

9-Phenylanthracene

Irradiation of solution II gave a broad signal ($\Delta H_{pp} \sim 0.8$ mT) with evidence of further fine structure (about twenty peaks visible). The EPR spectrum of solution III (irradiation with light of $h\nu > 430$ nm) gave a weak, somewhat better resolved spectrum which matched the one from solution II in all essential details. Simulation with published parameters of the monomeric radical cation[21] duplicated both spectra with a suitable choice of linewidth. In acetonitrile at −40 °C, no EPR spectrum was obtained from any of solutions I–III (methanesulfonic acid as proton donor), attesting to the high reactivity of (9-phenylanthracene)$^{\bullet +}$ in acetonitrile.[22]

9,10-Diphenylanthracene

With this system, we enter a domain where the kinetic stability of the radical cation is such that an EPR spectrum of low intensity could be obtained even from solution I at −60 °C. A slightly more intense spectrum was seen at −70 °C. Both these spectra matched the EPR spectra from solutions II and III, which were well simulated by the EPR spectral parameters of this well-known radical cation in monomeric form.[21]

At −40 °C in acetonitrile, solution I (saturated in 9,10-diphenylanthracene) showed an indication of the EPR spectrum of (9,10-diphenylanthracene)$^{\bullet +}$ whereas solution II (with methanesulfonic acid as the proton donor) gave a well-resolved spectrum.

Pyrene

Solution I gave a weak unresolved signal with $\Delta H_{pp} \sim 0.7$ mT, which became much more intense in solution II ($\Delta H_{pp} = 0.13$ mT). At low [pyrene], DDQ treatment of solution III gave a resolved signal which was simulated by known EPR parameters of the dimeric radical cation.[21]

Perylene

The perylene experiments were run at low [perylene] (~5 mmol dm^{-3}) in order to avoid precipitation of the radical cation. The EPR spectrum of solution I at −70 °C was weak but clearly showed the middle five lines of the major nonet of (perylene)$^{\bullet +}$. Solution II gave a better resolved spectrum of (perylene)$^{\bullet +}$ well reproducible by published EPR spectral parameters for the monomeric radical cation.[21]

Tris(4-bromophenyl)amine (TBPA)

At −60 °C, it was found that the normally unresolved signal of TBPA$^{\bullet +}$ from an authentic sample of its hexachloroantimonate was split into a triplet ($a^N = 1.05$ mT), a phenomenon discernible already around −20 °C. The ξ value was rather low, mostly because of the low reactivity of the radical cation under solution I conditions.

9,10-Dimethylanthracene

Irradiation of solution II (with a substrate concentration of about 5 mmol dm^{-3}) gave an intense, well resolved spectrum of (9,10-dimethylanthracene)$^{\bullet +}$ which was well reproduced by published EPR parameters for the monomeric radical cation.[21] The same was true for experiments in acetonitrile at −40 °C with methanesulfonic acid as the proton donor.

1-Methoxynaphthalene

Irradiation of solution I gave a strong, moderately well resolved signal (*ca.* 45 lines with spacing ≈ 0.032 mT) with a width of *ca.* 1.5 mT. Recording the spectrum with lower modulation amplitude gave a well-resolved spectrum. Under solution II conditions, an unresolved signal with $\Delta H_{pp} = 0.75$ mT was obtained, and its intensity was about the same as under solution I conditions. A well-resolved spectrum, identical with that from solution I, was obtained under solution III–DDQ conditions. The identity of the spectrum from 1-methoxynaphthalene is not entirely clear. It may actually originate from the dehydro dimer, 4,4′-dimethoxy-1,1′-binaphthalene, as suggested[23a] for the radical cation obtained by Tl^{III} oxidation of 1-methoxynaphthalene in TFA at room temperature.

2,5-Di-*tert*-butyl-1,4-dimethoxybenzene

This compound has a very stable radical cation,[15] and experiments with solutions I–III could be run at room temperature. Solution I showed a weak but identifiable spectrum of the radical cation, whereas solution II gave a partly resolved spectrum (seven broad lines due to splitting by the six CH_3O hydrogens). Full resolution of all lines was obtained by DDQ treatment of solution III, in agreement with a simulated spectrum based on published parameters[15] and an additional, small hfsc of 0.013 mT to 18 *tert*-butyl hydrogens.

Other Systems

Substrates with even lower $E^\circ(\mathrm{ArH}^{\bullet +}/\mathrm{ArH})$ than those in Table 1, as for example tris(4-tolyl)amine with $E^\circ(\mathrm{ArH}^{\bullet +}/\mathrm{ArH}) = 1.0$ V *vs.* NHE (normal hydrogen electrode), were tried, but here the interperetation was complicated by the *thermal* reaction between ArH and tetranitromethane which becomes feasible in this potential region. $E^\circ[(NO_2)_4C/(NO_2)_4C^{\bullet -}]$ has earlier been approximately determined[2] to be *ca.* 0.4 V *vs.* NHE, so this type of reaction is predicted to occur with tris(4-tolyl)amine.

Dibenzofuran, with a redox reactivity similar to that of naphthalene,[3e] was photolysed under solution I and II conditions down to −80 °C but no sign of radical cation production was seen.

A different approach would be to photolyse a mixture of tetranitromethane and an aromatic spin trap, such as α-phenyl-*N*-*t*-butylnitrone (PBN),* in order to arrest the reaction at the stage of the neutral radical formed in eqn. (2) (equal to the spin adduct) and/or detect the carbonyl aminoxyl radical [PhCON(O$^\bullet$)Bu^t] known[23b] to result from reaction of PBN and NO_2. This spin-trapping experiment has already been published,[24] using 'UV light' for irradiation, and showed that the trinitromethyl spin adduct was formed, possessing a characteristically large coupling to the hydrogen atom ($a^H = 0.37$–0.47 mT, depending on the solvent) and $a^N = 1.41$–1.47 mT.

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* IUPAC-recommended name: *N*-benzylidene-*tert*-butylamine *N*-oxide.

The same spin adduct was also detected under conditions of 'inverted spin trapping', where in all probability the radical cation of the spin trap is formed initially and then reacts with a nucleophile.[25]

A solution of PBN–tetranitromethane in dichloromethane was orange-red in colour, presumably due to the formation of a CT complex by analogy with all other substrates studied. Irradiation of this solution with filtered light (cut-off < 435 nm) at −60 °C produced an intense signal of the trinitromethyl spin adduct (a^N = 1.45 mT, a^H = 0.41 mT, lit.,[25a] 1.46, 0.44 mT). Addition of TFA (0 8 mol dm^{-3}) to the coloured solution of PBN and tetranitromethane removed the colour, and irradiation with filtered or unfiltered light failed to produce any EPR signal. Under solution III conditions, no signal was seen, but addition of DDQ followed by irradiation at −60 °C induced the formation of a weak EPR signal (quintet of spacing 0.052 mT).

It has recently been shown[26] that some arylolefins, *e.g.*, stilbene, undergo nitro/trinitromethyl adduct formation upon photolysis of the arylalkene–tetranitromethane CT complex, and it was suggested that a first chemical step equivalent to eqn. (3), attack of nitrogen dioxide upon an olefinic carbon in the radical cation, would take place after the photochemical step. Since there is no compelling reason why olefins should differ from ArH in this respect, we applied the EPR method described above to a few simple arylalkenes, *viz.*, styrene, anethole (4-methoxypropenylbenzene), (*E*)-stilbene and (*E*)-α-methylstilbene. However, even at −70 °C there was too small a distinction between solution I and II behaviour for any decisive results to be obtainable. Thus the corresponding radical cations must be of the highly reactive type. We also tried the sterically congested 1,1-di-*tert*-butylethylene as the substrate, but here the absence of any CT complex made photoexcitation impossible.[25d] However, 1,1-dimesitylethylene showed the expected behaviour, a ξ value of > 8 being obtained at −70 °C. More highly arylated alkenes, like triphenylethylene and tetraphenylethylene at −60 °C gave ξ = 25 and 2, respectively. The reason for the low ξ value in the latter case again was traced to the low reactivity of the radical cation;[27] at −30 °C, ξ was higher, 4.2.

Preparative Experiments

As a corollary of the analytical data described above, preparative experiments were carried out with some substrates. Table 3 and Fig. 5 show how the relative product distribution from the photolysis of naphthalene–tetranitromethane changes with [TFA] in dichloromethane at −20 °C. Without TFA, nitro–trinitromethyl adducts dominated, as found before,[3b] whereas an increase in [TFA] up to 2 mol dm^{-3} gradually diminished the adduct yield, increased the yield of 1- and 2-nitronaphthalene and diminished the degree of conversion. This behaviour is easily understood in terms of removal of trinitromethanide ion by protonation, thus reducing the extent of reaction according to eqn. (2), and increasing the proportion of the reaction taking place *via* eqn. (3). Since the latter reaction is the slower one, a decrease in conversion with increasing [TFA] is to be expected. The 1-/2-nitronaphthalene ratio increases with increasing [TFA], eventually reaching a value of 50–60, in perfect agreement with the ratio found from the coupling of presynthesized naphthalene radical cation salt and NO_2.[7] Finally, one notes that the adduct proportion does not reduce to zero level but instead levels out at about 16% between 1 and 2 mol dm^{-3} TFA. This indicates that some part of the reaction goes through a state, most likely a contact ion pair,[5] where the trinitromethanide ion can react with $ArH^{•+}$ rapidly enough to avoid being protonated.

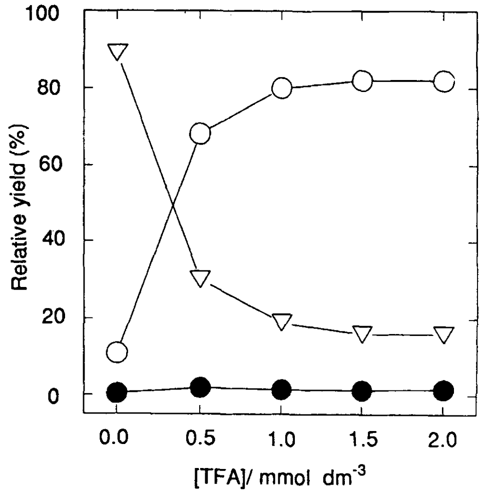

Fig. 5 Dependence of the yields of 1-nitronaphthalene (○), 2-nitronaphthalene (●) and adducts (▽) as a function of [TFA] from the photolysis of naphthalene (0.4 mol dm^{-3}), tetranitromethane (0.8 mol dm^{-3}) and TFA in dichloromethane at −20 °C

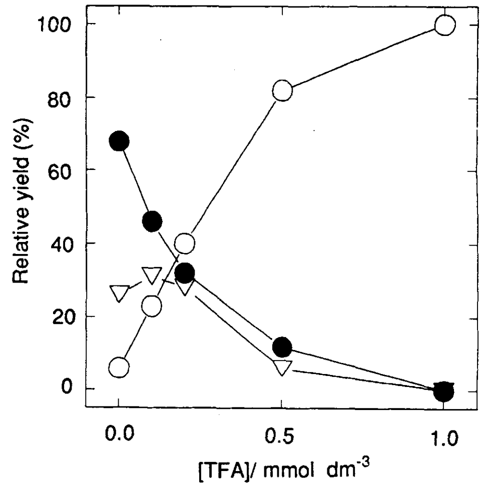

Fig. 6 Dependence of the yields of 2-nitro-1,4-dimethylnaphthalene (○), adducts (●) and 1-methyl-4-nitromethylnaphthalene (▽) as a function of [TFA] from the photolysis of 1,4-dimethylnaphthalene (0.4 mol dm^{-3}), tetranitromethane (0.8 mol dm^{-3}) and TFA in dichloromethane at −20 °C

The radical cation of 1,4-dimethylnaphthalene is expected to be less reactive than that of naphthalene and therefore the 1,4-dimethylnaphthalene–tetranitromethane system was selected for a comparison. The outcome of a series of photolyses of this system (dichloromethane, −20 °C) in the presence of varying [TFA] is shown in Table 4 and Fig. 6. The same trend as for naphthalene is evident; the yields of adducts and the side-chain substitution product, dependent on the presence of trinitromethanide ion for their formation,[3a] decreased to zero with increasing [TFA], whereas the yield of the 2-nitro compound increased to 100% and the conversion decreased. Thus it seems that one can drive the reaction almost to 100% radical cation–NO_2 coupling at [TFA] = 1 mol dm^{-3}. The reaction between presynthesized 1,4-dimethylnaphthalene radical cation salt and NO_2 is known to give exclusively 2-nitro-1,4-dimethylnaphthalene.[7b]

For 1-methylnaphthalene and 1,8-dimethylnaphthalene similar experiments were performed at −20 °C but at only one [TFA] (0.2 mol dm^{-3}). The changes in the adducts/$ArNO_2$ ratio were from 8.5 to 0.39 (1-methylnaphthalene) and 1.1 to < 0.1 (1,8-dimethylnaphthalene). Similarly, the same ratio changed for the 1,4,5,8-tetramethylnaphthalene reaction from 0.7 to

Table 3 Product yields from preparative photolyses of solutions of naphthalene (0.4 mol dm^{-3}), tetranitromethane (0.8 mol dm^{-3}) and TFA in various concentrations in dichloromethane at −20 °C, irradiation time 8 h

	Relative yield (%) of				
TFA/mol dm^{-3}	1-Nitronaphthalene	2-Nitronaphthalene	Σ adducts	1-/2-nitro isomer ratio	Conversion (%)
0	11	0.4	89	28	69
0.5	68	1.9	30	36	57
1.0	80	1.5	19	53	50
1.5	82	1.3	16	63	40
2.0	82	1.6	16	51	37

Table 4 Product yields from preparative photolyses of solutions of 1,4-dimethylnaphthalene (0.4 mol dm^{-3}), tetranitromethane (0.8 mol dm^{-3}) and TFA in various concentrations in dichloromethane at −20 °C, irradiation time 2 h

	Relative yield (%) of					
TFA/mol dm^{-3}	2-Nitro-1,4-Me$_2$-naphthalene	*cis*-1,4-adduct	*trans*-adduct	Σ Adducts	Side-chain nitro product	Conversion (%)
0	6	10	58	68	26	59
0.1	23	8	38	46	31	60
0.2	40	8	24	32	28	43
0.5	82	0	12	12	6	32
1.0	100	0	0	0	0	16

<0.04 (at [TFA] = 0.4 mol dm^{-3}). In the latter reaction, the reaction became impractically slow at higher [TFA] and thus could not be further investigated.

Discussion

Nucleophilicity and Basicity of the Trinitromethanide Ion

The nucleophilicity of trinitromethanide ion, as measured by $n(CH_3I) = 2.9$, places it among the moderately strong nucleophiles, between fluoride (2.7) and acetate ion (4.3).[9] This value is in qualitative accordance with the reactivity of trinitromethanide ion in a number of nucleophilic processes in protic media.[28] Since $n(CH_3I)$ is measured in methanol, one might anticipate higher absolute reactivity in dipolar aprotic media, such as the ones employed here.

The relative log ('K_4') values, as calculated from the titration experiments and referenced to trinitromethane, can be summarized as follows (values in parentheses obtained from pK determinations in the literature),[29] the values in dichloromethane being approximated by those obtained in acetone and nitromethane:

	ΔpK (CH$_3$CN)	ΔpK ('CH$_2$Cl$_2$')
Trinitromethane	0.0 (0.0)	0.0 (0.0)
Methanesulfonic acid	−0.2 (−2.7*h*)	— (−1.0)
Trifluoroacetic acid	−1.7 (−5.4*h*)	−0.6 (−6.3*h*, −2.1)

The large discrepancy between our *apparent* ΔpK values and the published ones is explained by the fact that the latter ones have been corrected for the effect of homoconjugation,[9] denoted *h* above. As seen for the TFA values in 'CH$_2$Cl$_2$' (actually in nitromethane), the apparent pK is 4.2 powers of the ten lower when no correction for homoconjugation is made. However, we deem this problem to be of little relevance for the present study, since the main purpose was to establish that TFA and methanesulfonic acid in reasonable concentrations will protonate trinitromethanide ion in the solvents used.

Relative Reactivity of Trinitromethanide Ion and NO$_2$ with Radical Cations

The EPR method described above originates from attempts to detect paramagnetic species from the photolysis of ArH–tetranitromethane further along the reaction pathway than the triad of eqn. (1), primarily by observing the neutral trinitromethylcyclohexadienyl radical of eqn. (2). Similar photochemical experiments have been performed[30] on solid samples of ArH-tetranitromethane at 77 K and the formation of paramagnetic species monitored by a combination of UV–VIS and EPR spectroscopy. It was concluded that the paramagnetic species observed at 77 K were the radical cations which disappeared upon warming. It should be noted that trinitromethyl radical has been generated by γ irradiation of tetranitromethane in ethanol at 77 K and detected by EPR spectroscopy (a 1:3:6:7:6:3:1 septet with an hfsc of 0.35 mT).[31] This spectrum could not be detected after photolysis of tetranitromethane at 77 K.

Neutral trinitromethylcyclohexadienyl radicals were not observed in our study, except for the special case of substituting ArH for PBN. This spin trap can be photo-oxidized to give its radical cation which however is too unstable for EPR spectral observation[25c] even at temperatures as low as −80 °C. Thus, photolysis of the coloured PBN–tetranitromethane CT complex at −60 °C gives highly reactive PBN$^{\bullet+}$ which has the option of reacting either with trinitromethanide ion to give the spin adduct, analogous to the neutral radical of eqn. (2), or with NO$_2$ to give a diamagnetic species.

However, the method of blocking one of the triad reactions by protonation is a much more versatile one. The forced disappearance of the trinitromethanide ion is clearly indicated by the appearance of the EPR signal of the radical cation, in most cases identifiable by comparison with known data. Table 1 and Fig. 2 demonstrate the range of possible behaviour: from systems with low ξ due to very high reactivity of the radical cations against *both* trinitromethanide ion and NO$_2$, through systems with high ξ at intermediate radical cation reactivity where the radical cation reacts slowly with NO$_2$, to systems with low ξ due to low radical cation reactivity toward *both* trinitromethanide ion and NO$_2$. For one and the same compound, this spectrum of

Table 5 Adduct/nitro substitution product ratios from the photolysis of ArH–tetranitromethane in dichloromethane at −20 °C, unless otherwise stated, and changes in this ratio with addition of TFA

	No TFA added			TFA added	
	Yield (%) of				
Substrate	Adducts	$ArNO_2$	Ratio	Ratio	Reference
Benzene	7.7	2.8	2.8		3(*i*)
Toluene	47	27	1.7	0[a]	3(*m*)
tert-Butylbenzene	14	9	1.6		3(*m*)
Anisole	1	22	0.05		3(*m*)
Dibenzofuran	50	4.5	11	0[b]	3(*e*), 32
Fluoranthene	18	82	0.22		3(*c*)
Naphthalene	89	11	8.1	0.19[c]	This work
1-Methylnaphthalene	80	9.4	8.5	0.39[d]	This work, 3(*k*)
1,4-Dimethylnaphthalene	68	6	11	0[e]	This work
1,4-Dimethylnaphthalene at 23 °C	34	57	0.6	0[e]	This work, 1(*g*)
1,2-Dimethylnaphthalene	92	8	12		3(*h*)
1,8-Dimethylnaphthalene	33	31	1.1	< 0.1[d]	This work, 3(*j*)
2,3-Dimethylnaphthalene	31	69	0.45		3(*l*)
1,4,5,8-Tetramethylnaphthalene	24	35	0.7	< 0.04[f]	This work, 3(*d*)

[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}.

reactivities can be duplicated by simply changing the temperature (see 1-methoxynaphthalene, entries 26–28, Table 1).

Preparative Implications

In order to assess the possible implications of the TFA effect in ArH–tetranitromethane photochemistry for synthetic purposes, Table 5 summarizes data for all systems where information on the adduct/$ArNO_2$ distribution is available. We have also included preliminary data[3m] on the adduct/$ArNO_2$ ratio for three monocyclic systems (toluene, *tert*-butylbenzene, anisole) deemed to be important in order to show that photoaddition of tetranitromethane can break the conjugation even in benzene and its derivatives. Available data on the TFA effect are also included.

The effect of adding a protic acid, such as TFA, to the photolysis of ArH–tetranitromethane, is expected to decrease the importance of the adduct pathway and thus by default favour the coupling between $ArH^{\bullet+}$ and NO_2. As seen from Tables 3 and 4 and Figs. 5 and 6 this prediction is fully confirmed. It also appears that a small proportion of the reaction of a highly reactive radical cation like (naphthalene)$^{\bullet+}$ proceeds *via* an intermediate whose reaction according to eqn. (2) is too fast for protonation to intervene. Most likely, this intermediate is the contact ion pair. For the less reactive (1,4-dimethylnaphthalene)$^{\bullet+}$ no such levelling out is observed; the triad components have time to diffuse apart, trinitromethanide ion becoming protonated before any follow-up reactions take place, and the adduct pathway is completely blocked.

It should be noted that the photolysis of ArH–tetranitromethane–TFA in principle offers a convenient way of carrying out the most regioselective method for nitration of the currently existing ones. This has been shown earlier[7b] in a comparison of the following reactions: (*i*) coupling between presynthesized radical cation salt and NO_2, (*ii*) nitration by NO_2 in dichloromethane and (*iii*) nitration *via* nitronium ion, where the first-mentioned was the most regioselective one. Photolysis of ArH–tetranitromethane–TFA generates the same intermediates as in (*i*), but in an experimentally much simpler way. Reaction (*ii*)—in essence an aprotic version of nitrous acid catalysed nitration,[33] the crucial product-forming step of which is the coupling between $ArH^{\bullet+}$ and NO_2[34]—can compete but is presumably accompanied by some nitronium ion induced nitration of lower regioselectivity.[7]

It has been suggested[35] that nitration of aromatics on catalytic solid supports, like clays or zeolites, might take place *via* $ArH^{\bullet+}$–NO_2 coupling, the aromatic radical cation being formed at the surface or in the cavities of the solid. There is ample EPR spectral evidence for such a proposal.[36] This mechanism would for example be expected to increase the *para*-selectivity for nitration of alkylbenzenes. Indeed, this effect was found, although it was numerically—but not economically!—small. Thus the *o*/*m*/*p* distribution for nitration of toluene changed from 63/3/34 under homogeneous conditions to 43/2/55 ('claycop') or 32/1/67 (mordenite) under heterogeneously catalysed conditions. It is too early to say whether photolysis of toluene–tetranitromethane–TFA might improve further on these distributions; a published experiment[1f] gave an *o*/*m*/*p* distribution of 32/31/37 in acetonitrile at 23 °C. However, in the light of the findings reported and discussed above, it should be possible to direct the reaction toward an increased proportion of $ArH^{\bullet+}$–NO_2 coupling at lower temperatures in dichloromethane.

Mechanism of the Photonitration of Aromatics: Some Conclusions

It has been shown extensively (see Table 5) that the photolysis of aromatic hydrocarbons with tetranitromethane leads to adducts of the nitro- and/or nitrito-trinitromethyl variety. It has now been shown that the adduct pathway, initiated by attack of trinitromethanide ion upon $ArH^{\bullet+}$ [eqn. (2)], can be partially or completely blocked by running the photolysis in the presence of a protic acid, such as TFA. This finding establishes eqn. (2) as the initial chemical step after the photochemical step. By inference, it has also been shown that $ArH^{\bullet+}$–NO_2 coupling [eqn. (3)] is a relatively slow reaction compared with reaction (2). Thus most of the phenomena associated with photonitration of aromatics by tetranitromethane are now understandable. It can also be concluded that isomer distributions obtained from the photolysis of ArH–tetranitromethane cannot be used in support of an electron transfer mechanism for thermal nitration by NO_2^+.[5]

A few problems of tetranitromethane photonitration remain, though. Methoxy-substituted aromatics in most cases appear to give nitro and/or trinitromethyl substitution products directly, although adducts have been detected in some cases (4-methylanisole[1c] and 4-haloanisoles[1c] and, with full quantitative documentation, 4-chloroanisole).[3f] As shown above, the methoxy compounds studied respond to our EPR method in the same way as do the adduct-forming substrates, and therefore should react according to eqn. (2). The resulting adducts must then be much less thermally stable than those obtained from hydrocarbons. Another group of problematic substrates is the methylbenzenes where the high acidities of the corresponding radical cations open a third pathway, proton abstraction from the radical cation by trinitromethanide ion. We are currently addressing these problems.

Experimental

Materials

Most chemicals and other materials were either of commercial origin or available from earlier studies and have been described there.[2,3,25d] Dibenzo-1,4-dioxin,[37] 2,5-di-*tert*-butyl-1,4-dimethoxybenzene[38] and 1,1-dimesitylethylene[39] were synthesized according to literature recipes.

WARNING. While we did not experience any incidents in working with tetranitromethane, it should be noted that its mixtures with hydrocarbons are detonative within certain concentration limits and that due care should be taken in handling mixtures of tetranitromethane and organic compounds.[40]

Reactions with EPR Spectral Monitoring

Photolyses were performed in the photolysis cavity of the Upgrade Version ESP 3220-200SH of a Bruker ER-200D spectrometer. The light source was the 50 W high-pressure Hg lamp from Bruker (ER 202) and the filter was from Schott, Germany (cut-off at < 430 nm).

The reactions were performed in the following way. The substrate was weighed into a vial and solvent (700 μl) added. After addition of tetranitromethane (80 μl) and/or TFA (20 μl), the solution was transferred to the EPR sample tube and bubbled with a stream of argon for 2 min. The tube was stoppered and allowed to reach thermal equilibrium in the cavity. The lamp was then switched on and allowed to run for 1 min, before the accumulation of spectra was initiated. Thirty or 100 spectra (irradiation time *ca.* 6 min) were accumulated, and the intensity determined as the absolute intensity of the most prominent line in the spectrum, divided by the number of spectra. Great care was taken that each set of solutions I–III was run under identical conditions of spectrometer settings, lamp position, sample tube position and temperature. Frequent duplications showed that the intensities, and particularly the ratios between then, were sufficiently reproducible (maximally ± 30%) for the purpose at hand (see also the main text for a test series with 1,2-dimethylnaphthalene).

Preparative Reactions

These were run as described before,[2a,b] care being taken that the work-up procedure was carried out at a temperature ≤ 0 °C. Analysis was performed by NMR spectroscopy. Isomer distributions were determined by NMR spectral analysis in order to avoid the error source inherent in the presence of thermally labile adducts in GLC analysis.[3a,b]

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