Photochemical Nitration by Tetranitromethane. Part XXXVIII.† Nitration of Tris(4-bromophenyl)amine, a Compound Corresponding to a Stable Radical Cation
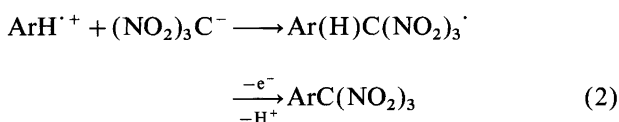
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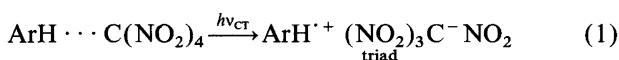
The photochemical reaction between tris(4-bromophenyl)amine (TBPA) and tetranitromethane in dichloromethane or acetonitrile gave almost exclusively the nitro-debromination product, 4-nitrophenylbis(4'-bromophenyl)amine (1). In the presence of trifluoroacetic acid, the 2-nitro-substitution product, 4-bromo-2-nitrophenylbis(4'-bromophenyl)amine (3) also appeared, together with further brominated TBPAs (4). Preparative and kinetic studies of the individual reactions involved, viz. the TBPA–NO₂, TBPA·⁺–NO₂ and TBPA·⁺–trinitromethanide ion reactions, indicated that the simple regiochemistry of the photochemical reaction is due to an addition–elimination mechanism, in which the initial attack of trinitromethanide ion occurs at the carbon *ipso* to the nitrogen function.

The photochemical excitation of the charge transfer (CT) complex between tetranitromethane and an aromatic compound (ArH) within 10 ps gives a triad, consisting of the aromatic radical cation, trinitromethanide ion and NO₂ [eqn. (1)].[1] Originally it was believed[2] that the pathways leading from the triad to final products, nitro- and trinitromethyl-substituted ArH, were controlled by the competition between eqns. (2) and (3), but later it was shown that the followup chemistry of the triad components is considerably more complicated and in fact completely different from the simple scheme of eqns. (2) and (3). In a large number of cases, such as

$$ArH \cdots C(NO_2)_4 \xrightarrow{h\nu_{CT}} \underset{\text{triad}}{ArH^{\cdot+} \ (NO_2)_3C^- \ NO_2} \quad (1)$$

$$ArH^{\cdot+} + (NO_2)_3C^- \longrightarrow Ar(H)C(NO_2)_3^{\cdot}$$

$$\xrightarrow[-H^+]{-e^-} ArC(NO_2)_3 \quad (2)$$

$$ArH^{\cdot+} + NO_2 \longrightarrow Ar(H)NO_2^+ \xrightarrow{-H^+} ArNO_2 \quad (3)$$

naphthalene,[3] dibenzofuran,[4] fluoranthene,[5] benzene,[6] methyl-[7] and dimethyl-naphthalenes,[8] polymethylbenzenes[9] and anisoles[10] the primarily formed products were *adducts* of the elements of trinitromethyl and NO₂ (or

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ONO) across the aromatic ring in 1,2- and/or 1,4-fashion, as indicated in eqn. (4). The initial step was shown to be the radical cation–trinitromethanide reaction, the ArH·⁺–NO₂ step being relatively slow.[11]

$$ArH^{\cdot+} (NO_2)_3C^- \ NO_2 \rightarrow Ar(H)(NO_2)C(NO_2)_3$$

$$+ Ar(H)(ONO)C(NO_2)_3 \quad (4)$$
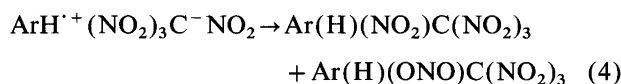
The formation of ArNO₂ and ArC(NO₂)₃ was shown to occur predominantly by elimination of nitroform and/or nitrous acid from adducts. In some cases, reaction (3) also contributed to the formation of ArNO₂, and then showed the characteristics of this reaction when realized by another reaction mechanism.[12] Also it was shown[13] that there exists a facile thermal/photochemical pathway leading from ArC(NO₂)₃ to ArNO₂ via ArCOOH [eqn. (5)] in cases where Ar has electron-donating character, such as 1-methoxy-4-naphthyl.

$$ArC(NO_2)_3 \xrightarrow{h\nu, HNO_3} ArCOOH \longrightarrow ArNO_2 \quad (5)$$
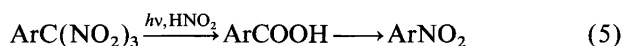
The initial attack of trinitromethanide ion upon the radical cation, forming a neutral trinitromethylcyclohexadienyl radical as the intermediate [eqn. (2), first step], is the crucial step which determines the products of recombination of the triad. As with other radical cation–nucleophile reactions,[14] reaction (2) can lead either to electron transfer (ET) or bond formation in a step which might or might not be reversible. In order to study this reaction, we have chosen a radical cation of well known

lower reactivity[15] and subjected it to a more detailed investigation. The advantage of such an approach is that the two-component reactions of the triad can be studied separately; a disadvantage is that the electron-donating substituents introduced to confer radical cation stability may strongly increase also the propensity of any adducts and/or $ArC(NO_2)_3$ formed toward decomposition.[13]

The tris(4-bromophenyl)aminium ion, TBPA$^{·+}$, is a stable radical cation which in acetonitrile and dichloromethane displays dual behaviour toward nucleophiles. Chloride, acetate and cyanide ion react with substitution at one of the 2-positions of TBPA$^{·+}$, whereas bromide and iodide ion react with ET.[15] A preliminary study[16] of the reaction between TBPA$^{·+}$ and trinitromethanide ion, compared to the TBPA$^{·+}$-NO_2 and TBPA-NO_2 reactions, indicated that it might be of the ET type. We now present a full account of this study, including the photochemistry of TBPA-tetranitromethane under various conditions. A limited study was also performed with the tris(4-chlorophenyl)aminium ion.

Results

Photochemistry of TBPA-tetranitromethane in dichloromethane or acetonitrile. The CT complex between TBPA and tetranitromethane in dichloromethane was deep brown-red. Upon irradiation with light of $\lambda > 430$ nm at room temperature, a single product was formed up to a conversion of ca. 90% (after 1 h of irradiation). It was identified as the *ipso* substitution product (1) of TBPA, which arises by nitro-debromination. Further irradiation (2 h) gave the product of bis(nitro-debromination) (2) in 18% yield at the expense of 1 (78%); after 5.5 h, 2 became the major product (72% yield, 28% of 1).
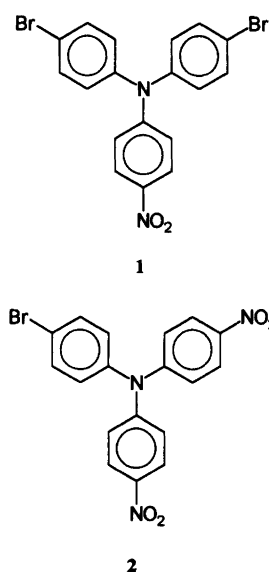

1

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Table 1 summarizes the photochemical runs with TBPA-tetranitromethane at different temperatures in dichloromethane and in acetonitrile at 20 °C. Runs conducted in the dark showed that the reaction also took place thermally, but at a much lower rate (>800 times slower).

Photochemistry of TBPA-tetranitromethane-trifluoroacetic acid in dichloromethane. In the presence of trifluoroacetic acid (0.4–0.8 mol dm^{-3}), the trinitromethanide pathway [eqn. (2)] is strongly suppressed due to protonation of trinitromethanide ion.[11] Table 2 shows the preparative outcome of photochemical runs in the presence of various concentrations of trifluoroacetic acid. In these reactions, the characteristic blue colour of the

Table 1. Products from the photolysis of TBPA-tetranitromethane[a] solutions with light of $\lambda > 430$ nm, unless otherwise stated, at various temperatures in dichloromethane and at room temperature in acetonitrile.

| Solvent[b]	Temp./°C	[TBPA]/ mmol dm^{-3}	Time/h	Conversion (%)	Yield of 1 (%)	Yield of 2 (%)
DCM	22	220	1	91	91	0
			2	96	78	18
			5.5	100	28	72
DCM	−20	110	1	69	69	0
			2	96	78	18
DCM	−50	73	0.25	12	12	0
			0.5	28	28	0
			1	55	55	0
			2	92	92	0
AN	22	9	0.5	29	29	0
			1	44	44	0
			2	75	75	0
			4	100	82	18
DCM[c]	22	220	5.5	6	6	−
			816	82	82	−
		110	216	36	36	−
AN[c]	22	9	4	0	0	0

[a] [Tetranitromethane] = 2 × [TBPA]. [b] DCM = dichloromethane, AN = acetonitrile. [c] Dark reaction.

Table 2. Products from the photolysis of TBPA–tetranitromethane[a]–trifluoroacetic acid solutions with light of λ > 430 nm in dichloromethane and at room temperature.

[TFA][b]/ mol dm^{-3}	Time/h	Conversion (%)	Yield (%) of			
			1	2	3	4
–	1	76	76	–	–	–
	2	94	84	10	–	–
0.10	4	45	14	–	21	9
	8	86	25	–	45	16
0.50	4	17	8	–	2	7
	20	100	21	–	39	30
1.00	4	57	12	–	10	35
	10	75	28	–	18	15

[a] [Tetranitromethane] = 0.22 mol dm^{-3}, [TBPA] = 0.22 mol dm^{-3}. [b] TFA, trifluoroacetic acid.

radical cation appeared immediately at the onset of irradiation. The product composition was significantly changed with the addition of trifluoroacetic acid: now the 2-nitro derivative of TBPA (3) and several brominated TBPAs (tetra- and pentabromotriphenylamines, collectively denoted 4) became appreciable products. The time to reach full conversion was much longer in the presence of TFA, typically 10–20 h.
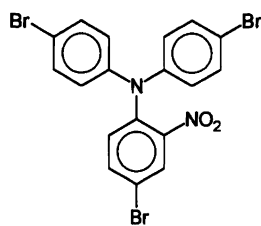

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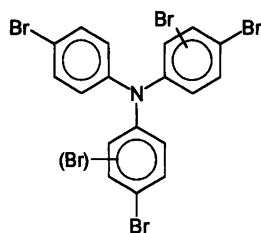
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Thermal reaction between TBPA and NO$_2$. Nitrogen dioxide is an efficient nitrating reagent for reactive ArH in dichloromethane, and the preparative outcome of this reaction was therefore examined in a range of concentrations of TBPA and NO$_2$ ([NO$_2$] is given as if all NO$_2$ + N$_2$O$_4$ was present as NO$_2$) after a reaction period of 10 min (Table 3). The products of this reaction were 1, 3 and 4 in different proportions; in one run, also the 2,2'-dinitro derivative 5 was formed in a low yield.

Thermal reaction between TBPA$^{\cdot +}$ and NO$_2$. Since TBPA$^{\cdot +}$ and NO$_2$ will co-exist in the photochemical runs

as two of the three components of the triad, control experiments were performed to determine the product distribution from this reaction after a reaction period of 1 h (Table 4). The nitro substitution products 1 and 3 predominated, but 4 was also formed at the higher reactant concentrations. In one experiment, several minor products of further nitro and/or bromo substitution were identified (5–7).
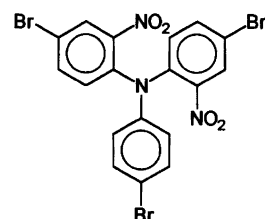
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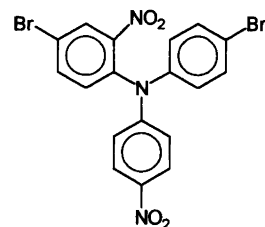
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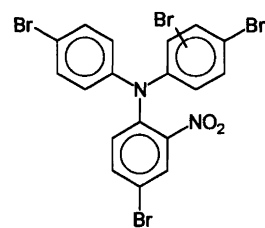
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Thermal reaction between TBPA$^{\cdot +}$ and trinitromethanide ion. Products from the second triad reaction possible, between TBPA$^{\cdot +}$ and trinitromethanide ion, are given in Table 5. The source of the nucleophile was tetrabutylammonium trinitromethanide, the solvent dichloromethane, and the reaction period 1 h. The only products detected were 1 and 3. As will be discussed below, it is assumed that the NO$_2$ groups in 1 and 3 are derived from NO$_2$ formed in the decomposition of the trinitromethyl radical.

Reactions of tris(4-chlorophenyl)amine and its radical cation. A limited product study of the reactions of tris(4-chlorophenyl)amine and its radical cation was performed in dichloromethane (Table 6). The most notable difference from the results of TBPA reactions is the decreased extent of nitro-dehalogenation in the TCPA–NO$_2$ reaction. Kinetic studies of this substrate

Table 3. Products (analyzed by chromatography and ^{1}H NMR spectroscopy) from the thermal reaction of TBPA and NO_2 at room temperature in dichloromethane, unless otherwise stated.

Time/h	[TBPA]$_0$ $=[NO_2]_0/$ mmol dm^{-3}	Yield (%) of			
		Recovered TBPA	1	3	4
0.2	20	1.5	50	17	30^a
2	10	31	36	8	25
2	2.0	31	42	4	23
2	2.0^b	35	54	10	0.6
2	100	15	44	15	26
0.5	2.0^c	7	17	66	17
0.25	100^c	–	22	62	16
0.2^d	10	30	45	10	7

^{a}(4-Bromophenyl)bis(4-bromo-2-nitrophenyl)amine (5, 2%) was also identified. ^{b}In the presence of trinitromethanide ion (2.0 mmol dm^{-3}). ^{c}In the presence of trifluoroacetic acid (0.1 mol dm^{-3}). ^{d}In acetonitrile.

Table 4. Products (analyzed by ^{1}H NMR spectroscopy) from the thermal reaction of TBPA$^{·+a}$ and NO_2 at room temperature in dichloromethane, unless otherwise stated.^{b}

Time/h	[TBPA$^{·+}$]$_0$ $=[NO_2]_0/$ mmol dm^{-3}	Yield (%) of			
		Recovered TBPA	1	3	4
1	2.8	28	15	16	9^c
0.3	2.8	46	31	19	4
0.5	0.20	76	23	<1	–
0.5	0.20	74	20	<3	–
0.5	0.20^d	26	54	<2	–^{e}
4.7^f	6.5	27	1	4	8^g

^{a}As tris(4-bromophenyl)aminium hexachloroantimonate. ^{b}Since some radical cation persisted at the end of the run, the reaction was quenched by addition of a small amount of a hindered base, 2,5-di-*tert*-butylpyridine. ^{c}Also 5 (10%), 6 (18%) and 7 (4%) were formed. ^{d}In the presence of trifluoroacetic acid (0.1 mol dm^{-3}). ^{e}Compound 2 was also identified (21%). ^{f}In acetonitrile. ^{g}Compounds 2 (31%) and 7 (2%) were also formed.

Table 5. Products (analyzed by ^{1}H NMR spectroscopy) from the thermal reaction of TBPA$^{·+a}$ and tetrabutylammonium trinitromethanide at room temperature in dichloromethane, unless otherwise stated.

Time/h	[TBPA$^{·+}$]$_0$ = [$(NO_2)_3C^-$]$_0/$ mmol dm^{-3}	Yield (%) of			
		Recovered TBPA	1	3	4
1	2.8	43	44	5	–
1	2.8	43	50	3	–
2	2.0	44	46	10	–
2	0.20	64	28	8	–
4^b	6.5	42	36	–	–

^{a}As tris(4-bromophenyl)aminium hexachloroantimonate. ^{b}In acetonitrile.

were precluded by the occurrence of a relatively rapid thermal reaction with tetranitromethane.

Kinetics of reactions of TBPA and its radical cation. An exploratory study[18] of the reaction between TBPA$^{·+}$ and trinitromethanide ion indicated that the reaction exhibited saturation behaviour in dichloromethane, in that the pseudo-first-order rate constant for disappearance of TBPA$^{·+}$ approached a limiting value of about 9 min^{-1} at 20 °C at [TBPA$^{·+}$]$_0$ = 0.162 mM and [$(NO_2)_3C^-$] > 10 mmol dm^{-3}, i.e. $\tau_{1/2}$ was of the order of 4–5 s at the plateau level. On the other hand, the same reaction in acetonitrile was slower, $k \approx 0.4$ dm^3 mol^{-1} s^{-1}, with an estimated $\tau_{1/2}$ of the order of 3–4 min at [$(NO_2)_3C^-$] = 10 mmol dm^{-3}. In 1,1,1,3,3,3-hexafluoropropan-2-ol, a solvent which strongly stabilizes anions and thus decreases their nucleophilicity,[19] the rate constant was still smaller, 7.9×10^{-4} dm^3 mol^{-1} s^{-1}.

The rate constant given above for the reaction between TBPA$^{·+}$ and trinitromethanide ion in acetonitrile was determined under conditions of second-order kinetics, the concentrations of each species being around 0.1 mmol dm^{-3}. Attempts to measure this rate constant under pseudo-first-order conditions ([TBPA$^{·+}$] =

Table 6. Products from reactions of tris(4-chlorophenyl)amine (TCPA) and its radical cation at room temperature under different conditions.

Reaction (t/h)	Yield (%) of			
	Recovered TCPA	*Ipso*-NO$_2$^{a}	2-Nitro^b	Bis-(2-nitro)^c
In dichloromethane				
TCPA + NO_2 (0.2)	33	Trace	54	–
TCPA$^{·+}$ + NO_2 (2)	27	–	16	35
TCPA$^{·+}$ + $(NO_2)_3C^-$ (2)	29	–	18	–
In acetonitrile				
TCPA + NO_2 (0.2)	32	4	60	–
TCPA$^{·+}$ + NO_2 (2)	14	–	44	31
TCPA$^{·+}$ + $(NO_2)_3C^-$ (2)	31	–	36	–

^{a}Bis(4-chlorophenyl)(4'-nitrophenyl)amine. ^{b}Bis(4-chlorophenyl)(4'-chloro-2'-nitrophenyl)amine. ^{c}(4-chlorophenyl)bis(4'-chloro-2'-nitrophenyl)amine.

0.25 mmol dm^{-3}, [(NO$_2$)$_3$C$^-$] in the 4–25 mmol range) failed, since the reaction exhibited complex kinetic behaviour, with a blend of zero- and first-order kinetics. From approximate half-life calculations, values of the 'second-order rate constant' were found to be 0.1–0.2 dm^3 mol^{-1} s^{-1}, in reasonable agreement with the value above.

Since the rate constant above was far too small to be compatible with the rather rapid consumption of TBPA$^{\cdot+}$ in the preparative photolyses of Table 1, a more direct approach resembling the actual photolysis conditions was developed. Reaction mixtures containing all three triad components, TBPA$^{\cdot+}$, (NO$_2$)$_3$C$^-$ and NO$_2$, were generated by photolysis (irradiation by light of λ > 430 nm for 5 s) of TBPA–tetranitromethane in acetonitrile, with or without extra added amounts of NO$_2$ or trinitromethanide salt. The radical cation concentration was monitored by UV spectroscopy at its 702 nm absorption maximum and its initial value was kept around 0.018 mmol dm^{-3}. The rate constant of disappearance of TBPA$^{\cdot+}$ was evaluated by second-order kinetic expressions. Table 7 shows data obtained in this way. The most notable feature of the rate constants of Table 7 is the strong increase compared to the runs in which no NO$_2$ was present (see above), from 0.2 to 3000 dm^3 mol^{-1} s^{-1}. Addition of extra NO$_2$ further increased the observed rate constant, whereas extra trinitromethanide ion decreased it somewhat.

The approach of photochemical generation of the triad described above was not feasible for reactions carried out in dichloromethane, because they were too fast. Kinetic runs for the reaction between TBPA$^{\cdot+}$ and either

or both of the triad components were performed by the stopped-flow technique, the kinetics being monitored at 728 nm (Table 8) and with rate constants evaluated according to second-order expressions. Figure 1 shows kinetic traces for the three types of run. Clearly the TBPA$^{\cdot+}$–(NO$_2$)$_3$C$^-$ reaction exhibits biphasic kinetics with a fast process during the first ca. 0.2 s (see inset;
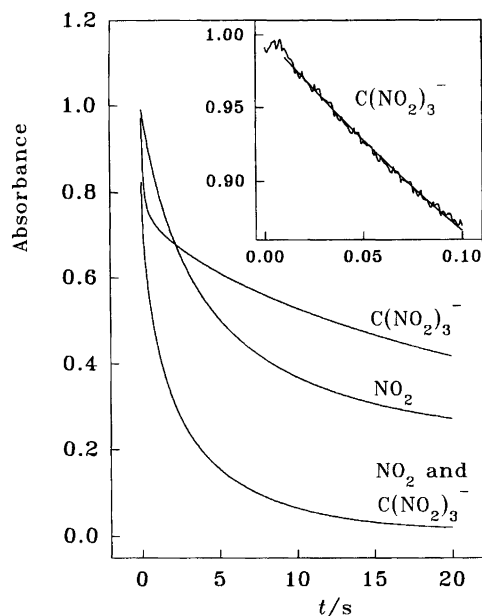

Fig. 1. Kinetic traces of the reactions listed in Table 8. The inset shows the first 0.1 s of the TBPA$^{\cdot+}$–trinitromethanide reaction.

Table 7. Kinetics of disappearance of TBPA$^{\cdot+}$ at 20 °C in acetonitrile, generated by photolysis for 5 s of a solution of TBPA (4.0 mmol dm^{-3}) and tetranitromethane by light of λ > 430 nm, with or without additives.[a]

[C(NO$_2$)$_4$]/ mmol dm^{-3}	Added [NO$_2$]/ mmol dm^{-3}	Added [$^-$C(NO$_2$)$_3$]/ mmol dm^{-3}	Abs[b]	k/dm^3 mol^{-1} s^{-1}	Rel. rate
27.3	–	–	0.465	2.6 × 10^3	0.8
109.2	–	–	0.838	4.6 × 10^3	1.5
54.6	–	–	0.66	3.1 × 10^3	1
54.6	–	0.018	0.606	1.7 × 10^3	0.5
54.6	–	0.036	0.569	9.8 × 10^2	0.3
54.6	0.012	–	0.548	2.1 × 10^4	7
54.6	0.018	–	0.479	3.4 × 10^4	11
54.6	0.028	–	0.314	7.7 × 10^4	25

[a] It was separately established that the presence of tetranitromethane did not influence the rate of the TBPA$^{\cdot+}$–trinitromethanide reaction. [b] Initial absorbance at 702 nm with a cell-path of 10 mm, converted into concentration units by multiplication by 33 000.

Table 8. Kinetics of disappearance of TBPA$^{\cdot+}$ at 20 °C in dichloromethane in the presence of one or both triad components.[a] See also Fig. 1.

Reaction	[NO$_2$]/ mmol dm^{-3}	[$^-$C(NO$_2$)$_3$]/ mmol dm^{-3}	Phase/s	k/dm^3 mol^{-1} s^{-1}	Rel. rate
TBPA$^{\cdot+}$ + NO$_2$	0.162	–	0–20	2.2 × 10^3	1
TBPA$^{\cdot+}$ + (NO$_2$)$_3$C$^-$	–	0.162	0.01–0.1	1.1 × 10^4	5
			2–20	4.4 × 10^2	0.2
TBPA$^{\cdot+}$ + (NO$_2$)$_3$C$^-$ + NO$_2$	0.162	0.162	0–20	5.2 × 10^3	2.4

[a] [TBPA$^{\cdot+}$] = 0.162 mmol dm^{-3}.

$k = 1.1 \times 10^4 \, \mathrm{dm^3 \, mol^{-1} \, s^{-1}}$), followed by a slower one ($k = 4.4 \times 10^2 \, \mathrm{dm^3 \, mol^{-1} \, s^{-1}}$), whereas the two other reactions occurred in a single phase.

The first phase (0.01–0.1 s) of the TBPA$^{\cdot +}$–(NO$_2$)$_3$C$^-$ reaction was also studied under pseudo-first-order conditions. The previous study[18] did not allow for the separate study of the initial fast reaction owing to the low time resolution of the kinetic method employed. The slope of the log–log([(NO$_2$)$_3$C$^-$]) regression line was 0.45(6) (see Fig. 2). For all runs, the rate constant of the second phase (2–50 s) was almost constant at $0.13 \, \mathrm{s^{-1}}$ (equal to $7.8 \, \mathrm{min^{-1}}$, cf. the earlier[18] value, $9 \, \mathrm{min^{-1}}$).

Spin trapping experiments in the TBPA$^{\cdot +}$–(NO$_2$)$_3$C$^-$ system. A solution of α-*N*-*tert*-butylnitrone (PBN, 6.8 mmol dm^{-3}) and tetrabutylammonium trinitromethanide (31 mmol dm^{-3}) in dichloromethane upon addition of TBPA$^{\cdot +}$ SbCl$_6^-$ gave an EPR spectrum corresponding to the trinitromethyl spin adduct of PBN ($a^N = 1.46$, $a^H = 0.50 \, \mathrm{mT}$; lit.[20] $a^N = 1.46$, $a^H = 0.44 \, \mathrm{mT}$). Separately, the ratio of the rate constants of TBPA$^{\cdot +}$ with PBN or (NO$_2$)$_3$C$^-$ was determined to be ca. 4 under these concentration conditions. At lower [PBN], ca. 1 mmol dm^{-3}, the same spin adduct signal was still detectable.

Discussion

General aspects. The initial aim of this study was to realize a clearcut case of the apparent solvent effect[2] found to operate on certain substrates in dichloromethane and acetonitrile, trinitromethyl substitution product(s) being formed in dichloromethane and nitro products in acetonitrile. Moreover, it was desirable to work with a system possessing a relatively stable radical cation of known reactivity. TBPA$^{\cdot +}$ was judged to be a suitable system, since some of its reactions with nucleophiles have been investigated[15] and moreover its stability allows for convenient kinetic studies. TCPA also appeared promising as a substrate, but its usefulness was limited by its relatively fast thermal reaction with tetranitromethane.

Three important findings with bearing on the possible pathways of product formation from ArH–tetranitromethane photolyses have emerged since the present study was initiated.[16] One was the possibility of blocking the reaction of ArH$^{\cdot +}$ and trinitromethanide ion by conducting the photolysis in the presence of 0.4–0.8 mol dm^{-3} trifluoroacetic acid.[11] In dichloromethane, it could be shown[11b] that this leads to protonation of trinitromethanide ion, yielding the non-nucleophilic nitroform. Thus the slower ArH$^{\cdot +}$–NO$_2$ reaction can compete, with coupling taking place to give the Wheland intermediate and eventually the nitro compound [eqn. (3)].

A second finding concerns trinitromethylarenes, ArC(NO$_2$)$_3$ and their mode of formation. Originally,[2] it was suggested that trinitromethylarenes were formed by
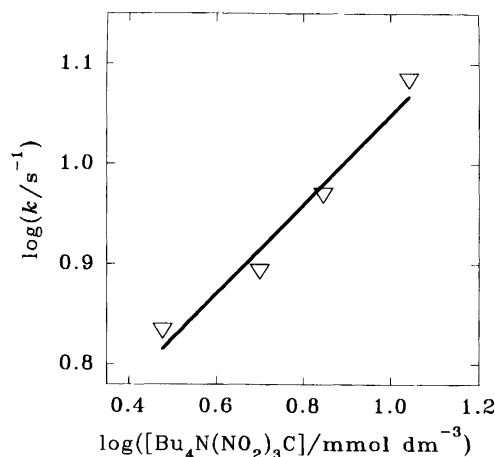

Fig. 2. Plot of log(k/s^{-1}) vs. log([Bu$_4$N(NO$_2$)$_3$C]/ mmol dm^{-3}), measured in dichloromethane at 20.2 °C. The slope of the regression line is 0.45(6).

the mechanism given in eqn. (2), a conventional oxidative substitution reaction known for a number of nucleophiles, such as cyanide, chloride and acetate ion.[14] However, later work has shown that the predominant pathway for forming trinitromethylarenes must proceed via nitro-trinitromethyl adducts [eqn. (4)] in which the nitro group is attached *ipso* to a substituent.[21] This bonding arrangement, exemplified for anisole in eqn. (6),
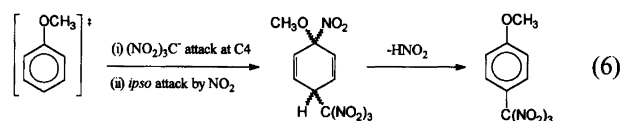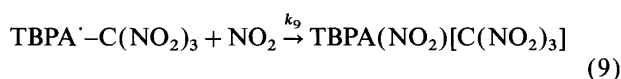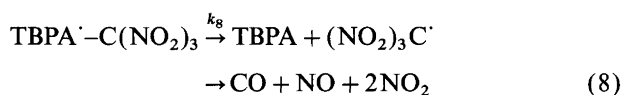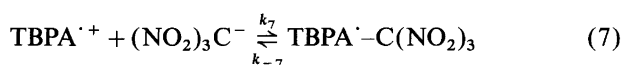

can only undergo elimination of HNO$_2$ and therefore must give a trinitromethyl substitution product. If, on the other hand, the nitro group is placed adjacent to a hydrogen atom, elimination of nitroform is more likely to take place due to the higher acidity of the CHNO$_2$ group.

Third, it has been shown[13] that ArC(NO$_2$)$_3$ containing electron-donating groups are thermally and photochemically labile and can be converted into the corresponding acid, ArCOOH, under the photolysis conditions. The acid can then be converted into ArNO$_2$ by a nitrodecarboxylation involving NO$_2$.

The possibilities listed above, combined with the complexity of the photolysis medium (it contains tetranitromethane, HNO$_2$, NO$_2$ and the strong acid nitroform, once the reaction is well underway) allows for a multitude of explanations as to how the relatively simple product mixtures are formed from the photochemical reaction. We will begin with the kinetic experiments and try to develop a mechanistic model by looking at the individual reactions leading from the triad. It should be noted that the kinetics of the TBPA$^{\cdot +}$–(NO$_2$)$_3$C$^-$ reaction was complex and hence only partly accessible for study.

A kinetic model. Earlier it was suggested[16] that the mechanism of the $TBPA^{\cdot+}-(NO_2)_3C^-$ reaction would involve the initial establishment of an equilibrium between the reactants and the neutral trinitromethyl-cyclohexadienyl radical [eqn. (7)], a common situation for radical cation–nucleophile mechanisms.[14] The latter species would then react by homolytic cleavage to TBPA and trinitromethyl radical [eqn. (8)], a highly labile species[22] which would rapidly lose NO_2 to give dinitrocarbene. Dinitrocarbene has been sought as an unstable species,[23] but no evidence for its existence has materialized, its fate being assumed to be very fast decomposition to CO, NO and NO_2. Once NO_2 has started to form according to eqn. (8), it will react with neutral trinitromethylcylohexadienyl radical to give one or several adducts [eqn. (9)].

$$TBPA^{\cdot+} + (NO_2)_3C^- \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} TBPA^{\cdot}-C(NO_2)_3 \qquad (7)$$

$$TBPA^{\cdot}-C(NO_2)_3 \overset{k_8}{\rightarrow} TBPA + (NO_2)_3C^{\cdot}$$
$$\rightarrow CO + NO + 2NO_2 \qquad (8)$$

$$TBPA^{\cdot}-C(NO_2)_3 + NO_2 \overset{k_9}{\rightarrow} TBPA(NO_2)[C(NO_2)_3] \qquad (9)$$

The kinetic scheme of eqns. (7)–(9) is fairly complex, and to begin with, eqn. (8) will be omitted from consideration. Application of the steady-state approximation to the neutral radical of eqn. (7) and (9), the observed rate constant for the second-order reaction between $TBPA345^{\cdot+}$ and $(NO_2)_3C^-$ can be expressed as in eqn. (10).

Without any NO_2 present [i.e. eqn. (9) excluded] the reaction should follow eqn. (8) and obey the kinetic expression of eqn. (11) in the beginning of the reaction.

$$k_{obs} = \frac{k_7 k_9 [NO_2]}{k_{-7} + k_9 [NO_2]} \qquad (10)$$

$$k_{obs} = \frac{k_7 + k_8}{k_{-7} + k_8} \qquad (11)$$

The mechanism of eqns. (7) and (9) for the reaction with all three triad components present is reasonably well supported by the kinetic data in dichloromethane, as shown in Fig. 1 and Table 8. The equilibrium is approached in the fast phase $(k_7 = 1.1 \times 10^4$ $dm^3 mol^{-1} s^{-1})$, and then rapid coupling between the neutral radical with NO_2 (k_9) can compete with the back reaction (k_{-7}). The strong rate dependence upon added $[NO_2]$ in the concentration range studied shows that $k_{-7} \gg k_9 [NO_2]$. The fact that the rate constant in the first phase is dependent on the square root of $[Bu_4N(NO_2)_3C]$ (Fig. 2) indicates that free trinitromethanide ion, formed by dissociation from the ion pair $Bu_4N^+(NO_2)_3C^-$, must be the kinetically active species.

Without NO_2 present from the beginning of the reaction, the first-order homolytic cleavage of $TBPA^{\cdot}-C(NO_2)_3$ becomes the slow step $(k_8$, assumed to be
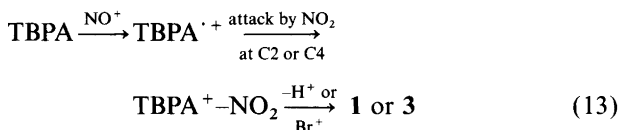
irreversible because of the rapid decay of the trinitromethyl radical), once the equilibrium has been reached. Under pseudo-first-order conditions this rate constant came out at ca. $0.13 s^{-1}$ in the $[(NO_2)_3C^-]$ range of $3–11 mmol dm^{-3}$.

The data in acetonitrile (Table 7) also support the mechanism of eqns. (7) and (9). One complicating aspect is that these data were obtained in the presence of an excess of tetranitromethane, the possible influence of which might be to act as the oxidant in eqn. (3), thus providing yet another pathway for removal of $TBPA^{\cdot}-C(NO_2)_3$. However, a control experiment showed that the presence of tetranitromethane does not influence the rate of the $TBPA^{\cdot+}-C(NO_2)_3^-$ reaction. The rate increase of this reaction from ca. $0.2 dm^3 mol^{-1} s^{-1}$ in its 'isolated' form to $3000 dm^3 mol^{-1} s^{-1}$ in the presence of NO_2 is in all probability due to the operation of eqn. (9).

Spin trapping. The spin trapping experiment seemingly indicates that trinitromethyl radical is formed from the $TBPA^{\cdot+}-(NO_2)_3C^-$ reaction and is trapped as its PBN adduct. However, this type of evidence is not as clearcut as it looks. A second mechanism for forming the spin adduct would involve oxidation of PBN by $TBPA^{\cdot+}$ to give $PBN^{\cdot+}$, capable of reacting with $(NO_2)_3C^-$ to give the same species. The latter process is a case of *inverted* spin trapping[20] and not easily distinguished from the true variety in a case such as trinitromethanide ion. The redox potentials for one-electron oxidation of PBN and $(NO_2)_3C^-$ are close, E_p being 1.74 and 1.9 V (vs. NHE), respectively, and empirically it was found that the reactions between $TBPA^{\cdot+}$ and either of the two reagents proceeded at similar rates. At the concentration levels used in the spin trapping experiment, this means that $k_{(NO_2)_3C^-}/k_{PBN}$ is ca. 4, allowing for simultaneous operation of both mechanisms. An increase in the ratio to ca. 25 still gave an EPR signal of the spin adduct, indicating that trinitromethyl radical trapping might occur. In another context,[19] the problem of trinitromethyl radical trapping has received some further evidence that the process may be feasible but difficult to distinguish from the inverted spin trapping mechanism.

Product formation. Since NO_2 is formed in the photolysis of $ArH/$tetranitromethane mixtures,[18] it is important to first establish which products are formed in the reaction between TBPA and NO_2 (Table 3). The main reaction in both acetonitrile and dichloromethane is *ipso* attack and nitrodebromination to give **1**, the bromine leaving group (believed to be Br^+; see below) appearing eventually as an almost equivalent amount of more extensively brominated TBPAs (**4**). The second mode of attack occurs at a 2-position, leading to **3**. It is likely that these two reactions proceed by an electron transfer mechanism, as demonstrated recently[17] and outlined in eqns. (12)

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and (13) for TBPA. Added trifluoroacetic acid only serves to accelerate the reaction.

$$N_2O_4 \rightleftharpoons NO^+NO_3^-$$ (12)

$$TBPA \xrightarrow{NO^+} TBPA^{\cdot +} \xrightarrow[\text{at C2 or C4}]{\text{attack by NO}_2}$$

$$TBPA^+-NO_2 \xrightarrow[Br^+]{-H^+ \text{ or}} 1 \text{ or } 3$$ (13)

The results of Table 4 on the $TBPA^{\cdot +}-NO_2$ reaction show that the same products 1, 3 and 4 are formed, except at very low reactant concentrations where the yields of 3 and 4 were significantly lower.

The reaction between $TBPA^{\cdot +}$ and trinitromethanide ion gave only the nitro products 1 and 3 and no bromination products. Previously we explained these facts by the electron transfer oxidation mechanism of eqns. (7) and (8), yielding TBPA and NO_2 which then would react according to eqns. (12) and (13); the absence of polybrominated products 4 is explicable by trinitro-methanide ion being present, a better acceptor of bromine cation than TBPA.[24] This could be shown in the reaction between TBPA and NO_2, conducted in the presence of trinitromethanide ion (Table 3).

The preparative photolysis results of Table 1 define a highly chemoselective reaction, as was found for other reactive substrates, such as 1,4-dimethoxybenzene.[2] If excessive reaction times are avoided, the only product formed in both dichloromethane and acetonitrile is the nitrodebromination product 1. Prolonged reaction times lead to the double nitrodebromination product 2, but no other products appear. When the photolysis is conducted in dichloromethane in the presence of trifluoroacetic acid, the visible effect is that the dark blue colour of the radical cation appears as soon irradiation is started, showing that the trinitromethanide reaction has been suppressed. The product distribution now assumes the characteristics of the $TBPA-NO_2$ and/or $TBPA^{\cdot +}-NO_2$ reactions, in that 3 and 4 appear at the expense of 1. The time for the reaction to reach completion increases strongly, since the fast trinitromethanide ion initiated pathway has been eliminated.

Notwithstanding some uncertain aspects in the interpretation of the kinetic data above, it is clear from the preparative reactions described that the nitro-debromination product (1) formed in the photolysis of the CT complex of TBPA with tetranitromethane arises by initial attack of trinitromethanide on $TBPA^{\cdot +}$, and that the nitro group enters the substrate by radical coupling of NO_2 with the delocalized carbon radical [eqn. (14)] ipso to a bromine substituent. Decomposition of this adduct with expulsion of $BrC(NO_2)_3$ would yield the observed exclusive aromatic product of short-term reaction. The formation of $BrC(NO_2)_3$ could unfortunately not be confirmed, due to its ready decomposition during the reaction and the analytical problems involved.
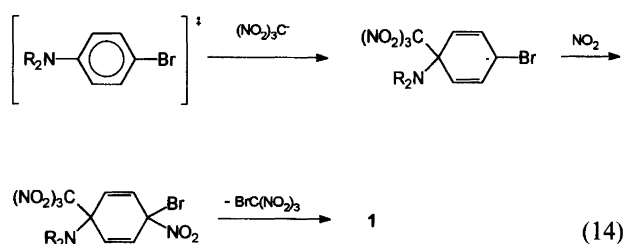

$$(14)$$

Table 9 summarizes some diagnostic indices of the various types of TBPA reactions studied here. The photochemical reaction in nominally neutral medium emerges as being by far the most chemoselective one. The absence of polybrominated products 4 is now hardly explicable in terms of capture of the bromine cation from the mechanism of eqns. (12) and (13), since the trinitromethanide ion is consumed by reaction with $TBPA^{\cdot +}$; only with trifluoroacetic acid present is there evidence for the NO_2 mediated reaction (13). We therefore favour the addition-elimination mechanism [eqn. (14)] as the origin of substitution product 1 from the photolysis of TBPA–tetranitromethane.

Experimental

Materials. Tetranitromethane (Aldrich), 2,6-di-tert-butylpyridine (Merck), pentane (Merck, p.a.) and acetonitrile (Merck, UVASOL) were used as received and tris(4-bromophenyl)aminium hexachloroantimonate (Aldrich) was washed several times with anhydrous diethyl ether and dried in vacuo immediately before use.[15] Dichloromethane (Merck, SupraSolv) was dried over 4 Å molecular sieves and tris(4-bromophenyl)amine (Janssen, 98%) was recrystallised from heptane. Solutions of nitrogen dioxide in dichloromethane and acetonitrile were prepared as previously described.[25]

Instruments. NMR spectra were recorded by a Varian XL 200 or 300 spectrometer. Stopped-flow measurements were performed at 20.0 °C, using either the spectrometer SF-3L (cell path 2 mm) and control unit SF-3C with IS-2 software, version 2.3b6, from HI-TECH, Salisbury, UK, or the Rapid Kinetics Spectrometer Accessory (model RX.1000, cell path 2 or 10 mm) from Applied Photophysics, Leatherhead, UK. UV/VIS spectra were recorded by an HP 8452A diode-array spectrophotometer equipped with the HP 89532A and HP 89532K software. Mass spectra were recorded by a Jeol JMS SX-102 instrument. EPR spectra were recorded by the Upgrade Version ESP 3220–200SH of a Bruker ER-200D instrument.

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.[26]

Table 9. Diagnostic product ratios (**1:3** and **1:4**) from various reactions of TBPA or its radical cation.

Reaction	Ratio **1:3**	Ratio **1:4**
TBPA–C(NO$_2$)$_4$-hv in dichloromethane	>50	>50
TBPA–C(NO$_2$)$_4$-hv in dichloromethane–TFA	1.2	0.34
TBPA–C(NO$_2$)$_4$-hv in acetonitrile	>50	>50
TBPA–NO$_2$ in dichloromethane	3.1	1.7
TBPA$^{·+}$–NO$_2$ in dichloromethane	1.6	8
TBPA$^{·+}$–(NO$_2$)$_3$C$^-$ in dichloromethane	13	>50
TBPA$^{·+}$–(NO$_2$)$_3$C$^-$ in acetonitrile	>50	>50

General procedure for the photonitration of TBPA with tetranitromethane without or with TFA. A solution of TBPA (concentration, see Tables 1 and 2) and tetranitromethane and, in the appropriate cases, TFA in dichloromethane (at 22, −20, or −50 °C) or acetonitrile (22 °C) was irradiated with filtered light ($\lambda_{cut-off}$= 435 nm). Aliquots were withdrawn from the reaction mixture at appropriate time intervals, the volatile material removed under reduced pressure at ≤0 °C, and the product composition determined by NMR spectral analysis (Tables 1 and 2).

Product studies. General procedure. To a stirred solution of TBPA in dichloromethane in a round bottomed flask, the nitrating agent was added dropwise and the flask was sealed with a stopper. In the case of tetrabutylammonium trinitromethanide, the salt was dissolved in a small volume of dichloromethane before the addition and in the case of nitrogen dioxide, the appropriate amount of the stock solution was diluted to a larger volume. When tris(4-bromophenyl)aminium hexachloroantimonate was used, the solution was placed in an ultrasonic bath for 4 min to facilitate the dissolution prior to the addition of the nitrating agent. In reactions with trifluoroacetic acid present, the acid was added to the reaction mixture before addition of the nitrating agent. For concentrations and reaction times, see Tables 3–5. After the reaction time had elapsed, the solvent was evaporated and the product distribution was determined by ^{1}H NMR spectroscopy, in some cases preceded by flash chromatography on a silica column eluted with pentane–dichloromethane. Control experiments were performed to check the agreement between product distributions determined by NMR spectral analysis of the crude product mixture and distributions based on products separated by chromatography. The average difference was found to be ±3%.

Synthesis of tetrabutylammonium trinitromethanide. Potassium trinitromethanide was prepared according to a literature procedure.[27] An ion-exchange reaction was performed with equal amounts of the potassium salt and tetrabutylammonium hydrogensulfate dissolved in a two-phase system containing equal volumes of distilled water and dichloromethane. After vigorous mixing, the phases were separated and the aqueous phase extracted with two portions of dichloromethane. The combined organic

phases were dried and evaporated and the crude product was recrystallised from methanol:water, 70:30, and dried in vacuum, yield: 60%.

4-Nitrophenyl-bis(4′-bromophenyl)amine (**1**). ^{1}H NMR (300 MHz, CDCl$_3$): 8.06 (d, $J_{H3,H2}$, $J_{H5,H6}$=9.1 Hz, H3, H5), 7.47 (d, $J_{H3′,H2′}$, $J_{H5′,H6′}$ =8.6 Hz, H3′, H5′), 7.02 (d, $J_{H2′,H3′}$, $J_{H6′,H5′}$=8.6 Hz, H2′, H6′), 6.95 (d, $J_{H2,H3}$, $J_{H6,H5}$=9.1 Hz, H2, H6). ^{13}C NMR (300 MHz, CDCl$_3$): 152.6 (C1), 144.5 (C1′), 141.1 (C4), 133.2 (C3′, C5′), 127.7 (C2′, C6′), 125.6 (C3, C5), 119.3 (C2, C6), 118.9 (C4′). MS (GLC inlet, EI, 70 eV), m/z (rel. intensity): 450 (54), 448 (100), 446 (52), 418 (23), 402 (8), 241 (39).

2-Nitro-4-bromophenyl-bis(4′-bromophenyl)amine (**3**). ^{1}H NMR (300 MHz, CDCl$_3$): 7.94 (d, $J_{H3,H5}$=2.3 Hz, H3), 7.60 (dd, $J_{H5,H6}$=8.7 Hz, $J_{H5,H3}$=2.3 Hz, H5), 7.35 (d, $J_{H3′,H2′}$, $J_{H5′,H6′}$=8.9 Hz, H3′, H5′), 7.13 (d, $J_{H6,H5}$= 8.7 Hz, H6), 6.84 (d, $J_{H2′,H3′}$, $J_{H6′,H5′}$ =8.9 Hz, H2′, H6′). ^{13}C NMR (300 MHz, CDCl$_3$): 145.7 (C1), 144.7 (C1′), 139.2 (C2), 136.9 (C5), 132.7 (C3′, C5′), 131.0 (C6), 129.0 (C3), 124.7 (C2′, C6′), 117.3 (C4), 117.1 (C4′). MS (Direct inlet, EI, 70 eV), m/z (rel. intensity): 530 (34), 528 (97), 526 (100), 524 (33), 403 (23), 401 (47), 399 (24), 241 (39).

2,4-Dibromophenyl-bis(4′-bromophenyl)amine (part of **4**). ^{1}H NMR (300 MHz, CDCl$_3$): 7.78 (d, $J_{H3,H5}$=2.2 Hz, H3), 7.44 (dd, $J_{H5,H6}$=8.5 Hz, $J_{H5,H3}$=2.2 Hz, H5), 7.32 (d, $J_{H3′,H2′}$, $J_{H5′,H6′}$=8.9 Hz, H3′, H5′), 7.06 (d, $J_{H6,H5}$= 8.5 Hz, H6), 6.80 (d, $J_{H2′,H3′}$, $J_{H6′,H5′}$=8.9 Hz, H2′ H6′). MS (GLC inlet, EI, 70 eV), m/z (rel. intensity): 565 (22), 563 (76), 561 (100), 559 (79), 557 (21), 403 (38), 401 (79), 399 (41), 241 (53).

Pentabromotriphenylamine (part of **4**). MS (GLC inlet, EI, 70 eV), m/z (rel. intensity): 645 (8), 643 (46), 641 (97), 639 (100), 637 (53), 635 (11), 483 (24), 481 (73), 479 (75), 477 (24), 319 (32).

Kinetic experiments. These were made on freshly prepared solutions, the precautions previously suggested[15] being observed. The experiments of Table 7 were performed by irradiating the solution of the premixed components in acetonitrile in the cuvette for 5 s. A rigidly mounted fiber-optical lamp (type EK-1 from Euromex, Arnhem, Holland) with a controllable light output was employed,

and the light was passed through a filter with cutoff at 430 nm. The cuvette was then transferred to the spectrometer and the kinetics monitored at 702 nm.

There is a report[28] that alkali metal trinitromethanides may undergo thermal decomposition in aprotic solvents with formation of nitrite ion and dinitrocarbene, the latter being capable of reacting with cyclohexene to give a derivative of isoxazoline-N-oxide. Since the presence of even small amounts of nitrite ion might be suspected to be responsible for the fast phase of the reaction between TBPA$^{\cdot +}$ and trinitromethanide ion, we checked this aspect in two ways. The percentage reaction of the fast phase (Fig. 1) was independent of $[Bu_4N(NO_2)_3C]$ in the range 3–13 mM, and a solution of $Bu_4N(NO_2)_3C$ in dichloromethane or acetonitrile was completely stable over several hours at 22 °C in the presence of cyclohexene, as monitored by UV spectroscopy.

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