

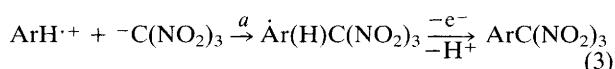
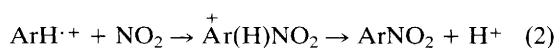
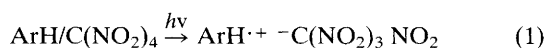
## Electron-transfer Oxidation of Trinitromethanide Ion by Radical Cations

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The reaction between tris(4-X-phenyl)aminium ions (X = Br, Cl) and trinitromethanide ion in dichloromethane or acetonitrile takes place by one-electron transfer, eventually leading to nitro derivatives of the triarylamines.

The photolysis of an aromatic compound (ArH) by tetranitromethane is assumed<sup>1</sup> to occur *via* excitation of a charge-transfer complex between the two components, giving directly a triad consisting of ArH<sup>•+</sup>, trinitromethanide and nitrogen dioxide [eqn. (1)]. The products, either ArNO<sub>2</sub> or ArC(NO<sub>2</sub>)<sub>3</sub>, are then viewed as being formed by reaction between ArH<sup>•+</sup> and either NO<sub>2</sub> [eqn. (2)] or trinitromethanide [eqn. (3)].



However, there is strong evidence that nitro/trinitromethyl adducts play an important role in these reactions,<sup>2-4</sup> and consequently, the scheme of eqns. (1)–(3) should be viewed as a hypothesis to be tested. We have focused on step *a* of eqn. (3), since it is not self-evident that this reaction should result in C–C bond formation. Radical cations are known to react either by electron transfer (ET) or bond formation,<sup>5,6</sup> and the rules governing the choice between these routes are not yet known.

Tris(4-bromophenyl)aminium (TBPA<sup>•+</sup>) is a stable radical cation<sup>7</sup> which displays such dual reactivity, in that chloride, acetate and cyanide ion react with substitution at one of the 2-positions of TBPA<sup>•+</sup>, whereas bromide and iodide ion react with ET.<sup>8,9</sup> We have shown<sup>2</sup> that the kinetics of the reaction between TBPA<sup>•+</sup> and C(NO<sub>2</sub>)<sub>3</sub> exhibits saturation behaviour in dichloromethane already at [(NO<sub>2</sub>)<sub>3</sub>C<sup>−</sup>] ≈ 5 mmol dm<sup>−3</sup> (pseudo-first-order rate constant ≈ 9 min<sup>−1</sup>). Such kinetics would be expected of what is generally termed the complexation mechanism of radical cation/nucleophile interaction;<sup>5</sup> here a first, reversible step is assumed to give a

complex which is then transformed irreversibly into products, as shown for ArH<sup>•+</sup> and C(NO<sub>2</sub>)<sub>3</sub> in eqn. (4).



We now have isolated the products of the reaction between TBPA<sup>•+</sup> and C(NO<sub>2</sub>)<sub>3</sub>, anticipating that mainly trinitromethylated derivatives of TBPA would be formed [eqn. (3)]. To our surprise, reaction of equimolar amounts of the two components in dichloromethane gave 34% TBPA, 3% of 2-nitro-TBPA and 39% of the nitrodecomposition product, 4-nitrophenyl-bis(4-bromophenyl)amine (Table 1). Tris(4-chlorophenyl)aminium (TCPA<sup>•+</sup>) behaved similarly, except that no *ipso* substitution product was formed. In acetonitrile, the difference between the two radical cations became even more distinct in that TBPA<sup>•+</sup> gave only the nitrodecomposition product and TCPA<sup>•+</sup> only the 2-nitro product.

This unexpected finding is presumably due to ET within the complex of eqn. (4) instead of further 1e<sup>−</sup> oxidation and bond formation. This would give the neutral amine and the trinitromethyl radical, which can either give nitroform by H-atom abstraction from the solvent or decompose to give NO<sub>2</sub> and dinitrocarbene. Previous attempts<sup>10</sup> to generate and trap the latter species were not successful, presumably because of its facile decomposition to CO, NO and NO<sub>2</sub>. Thus, trinitromethanide ion, with an estimated E°(X<sup>•</sup>/X<sup>−</sup>) of 1.5 V in acetonitrile,<sup>2</sup> falls in line with the ET reactivity of bromide and iodide ion, E°(X<sup>•</sup>/X<sup>−</sup>) = 1.7 and 1.2 V, respectively.<sup>11</sup>

If the nitro products were formed by NO<sub>2</sub> nitration of the neutral amine one would expect a similar product pattern from this reaction. Table 1 shows that in essence this was confirmed; TBPA and NO<sub>2</sub> in dichloromethane gave 46% *ipso* substitution product and 15% 2-nitro product, whereas TCPA and NO<sub>2</sub> gave 54% 2-nitro product and trace amounts

**Table 1** Nitration reactions of tris(4-bromophenyl)amine(aminium) and tris(4-chlorophenyl)amine(aminium) and their parent compounds; T = 20 °C

Reaction (t/h)	Triarylamine (%)		Nitro product (%)		
	Starting material	With extra halogen(s) <sup>d</sup>	<i>ipso</i> <sup>a</sup>	2-Nitro <sup>b</sup>	Bis(2-nitro) <sup>c</sup>
In dichloromethane					
TBPA <sup>•+</sup> + C(NO <sub>2</sub> ) <sub>3</sub> (1)	34	—	39	3	—
TBPA + NO <sub>2</sub> (0.2)	7	27	46	15	2
TBPA <sup>•+</sup> + NO <sub>2</sub> (1)	22	8	13	13	8 <sup>e</sup>
TCPA <sup>•+</sup> + C(NO <sub>2</sub> ) <sub>3</sub> (2)	29	—	—	18	—
TCPA + NO <sub>2</sub> (0.2)	33	—	Trace	54	—
TCPA <sup>•+</sup> + NO <sub>2</sub> (2)	27	—	—	16	35
In acetonitrile					
TBPA <sup>•+</sup> + C(NO <sub>2</sub> ) <sub>3</sub> (4)	42	—	36	—	—
TBPA + NO <sub>2</sub> (0.2)	7	30	45	10	—
TBPA <sup>•+</sup> + NO <sub>2</sub> (4.7)	27	8	1	4	31 <sup>f</sup>
TCPA <sup>•+</sup> + C(NO <sub>2</sub> ) <sub>3</sub> (8)	31	—	—	36	—
TCPA + NO <sub>2</sub> (0.2)	32	—	4	60	—
TCPA <sup>•+</sup> + NO <sub>2</sub> (1.6)	14	—	—	44	31

<sup>a</sup> 4-Nitrophenyl-bis(4-X-phenyl)amine (X = Br, Cl). <sup>b</sup> 2-Nitro-4-X-phenyl-bis(4-X-phenyl)amine (X = Br, Cl). <sup>c</sup> 4-X-phenyl-bis(2-nitro-4-X-phenyl)amine (X = Br, Cl). <sup>d</sup> Tetra- and penta-bromotriphenylamine. <sup>e</sup> In addition, a dibromo-dinitro (15%) and a tetrabromo-nitro (4%) derivative of triphenylamine were formed. <sup>f</sup> In addition, a tetrabromo-nitro derivative (2%) of triphenylamine was formed.

of *ipso* product. A similar difference was found in acetonitrile (Table 1). In the case of TBPA/NO<sub>2</sub>, there were also products formed by further bromination of TBPA (≈30%), a consequence of the leaving group in the *ipso*-substitution process being bromine atom. This reaction mode was not seen in the TBPA<sup>•+</sup>/C(NO<sub>2</sub>)<sub>3</sub> reaction, presumably because of trinitromethanide functioning as a superior acceptor of bromine atom (or bromine) in competition with TBPA.<sup>12</sup>

Another reaction which must be considered is the reaction between radical cation still present and NO<sub>2</sub> which has built up during the run.<sup>13</sup> These reactions, run separately, were relatively slow for both radical cations and gave partly different products, particularly dinitro derivatives. Thus, the coupling between radical cation and NO<sub>2</sub> probably does not contribute to the formation of nitro products from the radical cation/(NO<sub>2</sub>)<sub>3</sub>C<sup>-</sup> reaction.

We have also obtained evidence for the formation of the trinitromethyl radical from TBPA<sup>•+</sup> and C(NO<sub>2</sub>)<sub>3</sub> by spin trapping experiments.<sup>14</sup> Thus, a solution of α-phenyl-*N*-tert-butyl nitron (PBN, 6.8 mmol dm<sup>-3</sup>) and tetrabutylammonium trinitromethanide (31 mmol dm<sup>-3</sup>) in dichloromethane upon addition of TBPA<sup>•+</sup> SbCl<sub>6</sub><sup>-</sup> gave an ESR signal corresponding to the trinitromethyl spin adduct of PBN (earlier<sup>14</sup> found to have *a*<sup>N</sup> = 1.46 and *a*<sup>H</sup> = 0.48 mT in acetonitrile; we found 1.46 and 0.50 mT in acetonitrile and 1.46 and 0.44 mT in dichloromethane, respectively).

PBN and C(NO<sub>2</sub>)<sub>3</sub> are both oxidized by TBPA<sup>•+</sup> with similar rate constants, and kinetic runs established separately that the spin trapping experiment described above was performed with *k*<sub>(NO<sub>2</sub>)<sub>3</sub>C<sup>-</sup>}/*k*<sub>PBN</sub> ≈ 4 (*k* = the pseudo-first-order rate constant) for reaction with TBPA<sup>•+</sup>. Thus, PBN<sup>•+</sup> is formed to some extent in this experiment. By analogy with TPBA<sup>•+</sup>, this radical cation should undergo electron transfer from trinitromethanide, thus avoiding bond formation which would be another pathway to the spin adduct. Increase of the rate ratio to ≈25 (when [PBN] was only ≈1 mmol dm<sup>-3</sup> and its trapping efficiency considerably impaired) still produced a weak ESR signal of the spin adduct. Thus, trinitromethyl radical in all probability must be the spin-adduct generating species.</sub>

These findings put the scheme of eqns. (1)–(3) in a wholly different perspective. The complexation mechanism, applied to ArH<sup>•+</sup> and C(NO<sub>2</sub>)<sub>3</sub>, can give a complex that will either

react with ET and regenerate ArH and form a second equivalent of NO<sub>2</sub>, or be trapped by NO<sub>2</sub> from the triad to give an adduct; the latter gives rise to substitution product(s) by elimination of mainly nitroform but also nitrous acid in some cases. Thus, our hypothesis has further strengthened the idea that the nitration chemistry following the initial photochemical event of eqn. (1) is essentially one of adduct formation/elimination and/or nitration by NO<sub>2</sub>. We also believe that the missing source of NO<sub>2</sub> alluded to in previous work<sup>2</sup> has now been identified.

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