

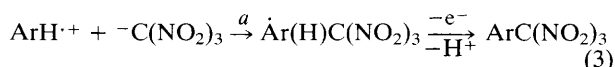
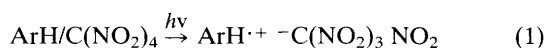
Electron-transfer Oxidation of Trinitromethanide Ion by Radical Cations

Lennart Ebersson,* Finn Radner and Jan Olof Svensson

MAX Chemistry, Chemical Center, University of Lund, PO Box 124, S-221 00 Lund, Sweden

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 assumed¹ to occur *via* excitation of a charge-transfer complex between the two components, giving directly a triad consisting of ArH^{·+}, trinitromethanide and nitrogen dioxide [eqn. (1)]. The products, either ArNO₂ or ArC(NO₂)₃, are then viewed as being formed by reaction between ArH^{·+} and either NO₂ [eqn. (2)] or trinitromethanide [eqn. (3)].



However, there is strong evidence that nitro/trinitromethyl adducts play an important role in these reactions,²⁻⁴ 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,^{5,6} and the rules governing the choice between these routes are not yet known.

Tris(4-bromophenyl)aminium (TBPA^{·+}) is a stable radical cation⁷ which displays such dual reactivity, in that chloride, acetate and cyanide ion react with substitution at one of the 2-positions of TBPA^{·+}, whereas bromide and iodide ion react with ET.^{8,9} We have shown² that the kinetics of the reaction between TBPA^{·+} and C(NO₂)₃ exhibits saturation behaviour in dichloromethane already at [(NO₂)₃C⁻] ≈ 5 mmol dm⁻³ (pseudo-first-order rate constant ≈ 9 min⁻¹). Such kinetics would be expected of what is generally termed the complexation mechanism of radical cation/nucleophile interaction;⁵ here a first, reversible step is assumed to give a

complex which is then transformed irreversibly into products, as shown for ArH^{·+} and C(NO₂)₃ in eqn. (4).



We now have isolated the products of the reaction between TBPA^{·+} and C(NO₂)₃, 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 nitrodehalogenation product, 4-nitrophenyl-bis(4-bromophenyl)amine (Table 1). Tris(4-chlorophenyl)aminium (TCPA^{·+}) 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^{·+} gave only the nitrodehalogenation product and TCPA^{·+} only the 2-nitro product.

This unexpected finding is presumably due to ET within the complex of eqn. (4) instead of further 1e⁻ 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 NO₂ and dinitrocarbene. Previous attempts¹⁰ to generate and trap the latter species were not successful, presumably because of its facile decomposition to CO, NO and NO₂. Thus, trinitromethanide ion, with an estimated E°(X[·]/X⁻) of 1.5 V in acetonitrile,² falls in line with the ET reactivity of bromide and iodide ion, E°(X[·]/X⁻) = 1.7 and 1.2 V, respectively.¹¹

If the nitro products were formed by NO₂ 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 NO₂ in dichloromethane gave 46% *ipso* substitution product and 15% 2-nitro product, whereas TCPA and NO₂ 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) ^d	<i>ipso</i> ^a	2-Nitro ^b	Bis(2-nitro) ^c
In dichloromethane					
TBPA ^{·+} + C(NO ₂) ₃ (1)	34	—	39	3	—
TBPA + NO ₂ (0.2)	7	27	46	15	2
TBPA ^{·+} + NO ₂ (1)	22	8	13	13	8 ^c
TCPA ^{·+} + C(NO ₂) ₃ (2)	29	—	—	18	—
TCPA + NO ₂ (0.2)	33	—	Trace	54	—
TCPA ^{·+} + NO ₂ (2)	27	—	—	16	35
In acetonitrile					
TBPA ^{·+} + C(NO ₂) ₃ (4)	42	—	36	—	—
TBPA + NO ₂ (0.2)	7	30	45	10	—
TBPA ^{·+} + NO ₂ (4.7)	27	8	1	4	31 ^f
TCPA ^{·+} + C(NO ₂) ₃ (8)	31	—	—	36	—
TCPA + NO ₂ (0.2)	32	—	4	60	—
TCPA ^{·+} + NO ₂ (1.6)	14	—	—	44	31

^a 4-Nitrophenyl-bis(4-X-phenyl)amine (X = Br, Cl). ^b 2-Nitro-4-X-phenyl-bis(4-X-phenyl)amine (X = Br, Cl). ^c 4-X-phenyl-bis(2-nitro-4-X-phenyl)amine (X = Br, Cl). ^d Tetra- and penta-bromotriphenylamine. ^e In addition, a dibromo-dinitro (15%) and a tetrabromo-nitro (4%) derivative of triphenylamine were formed. ^f 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/NO₂, 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^{•+}/-C(NO₂)₃ reaction, presumably because of trinitromethanide functioning as a superior acceptor of bromine atom (or bromine) in competition with TBPA.¹²

Another reaction which must be considered is the reaction between radical cation still present and NO₂ which has built up during the run.¹³ 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 NO₂ probably does not contribute to the formation of nitro products from the radical cation/(NO₂)₃C⁻ reaction.

We have also obtained evidence for the formation of the trinitromethyl radical from TBPA^{•+} and -C(NO₂)₃ by spin trapping experiments.¹⁴ Thus, a solution of α-phenyl-*N*-*tert*-butylnitron (PBN, 6.8 mmol dm⁻³) and tetrabutylammonium trinitromethanide (31 mmol dm⁻³) in dichloromethane upon addition of TBPA^{•+} SbCl₆⁻ gave an ESR signal corresponding to the trinitromethyl spin adduct of PBN (earlier¹⁴ found to have $a^N = 1.46$ and $a^H = 0.48$ 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(NO₂)₃ are both oxidized by TBPA^{•+} with similar rate constants, and kinetic runs established separately that the spin trapping experiment described above was performed with $k_{(\text{NO}_2)_3\text{C}^-}/k_{\text{PBN}} \approx 4$ (k = the pseudo-first-order rate constant) for reaction with TBPA^{•+}. Thus, PBN^{•+} is formed to some extent in this experiment. By analogy with TPBA^{•+}, 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⁻³ 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.

These findings put the scheme of eqns. (1)–(3) in a wholly different perspective. The complexation mechanism, applied to ArH^{•+} and -C(NO₂)₃, can give a complex that will either

react with ET and regenerate ArH and form a second equivalent of NO₂, or be trapped by NO₂ 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 NO₂. We also believe that the missing source of NO₂ alluded to in previous work² has now been identified.

We thank the Swedish Natural Science Research Council, the KNUT and Alice Wallenberg Foundation and the Crafoord Foundation for financial support.

Received, 3rd April 1992; Com. 2/01761J

References

- 1 J. K. Kochi, *Acc. Chem. Res.*, 1992, **25**, 39.
- 2 L. Ebersson and F. Radner, *J. Am. Chem. Soc.*, 1991, **113**, 5825.
- 3 L. Ebersson, M. P. Hartshorn, F. Radner and W. T. Robinson, *J. Chem. Soc., Chem. Commun.*, 1992, 566.
- 4 L. Ebersson, M. P. Hartshorn, F. Radner, M. Merchán and B. O. Roos, *Acta Chem. Scand.*, 1993, **47**, in the press.
- 5 O. Hammerich and V. D. Parker, *Adv. Phys. Org. Chem.*, 1984, **20**, 55.
- 6 A. J. Bard, A. Ledwith and H. J. Shine, *Adv. Phys. Org. Chem.*, 1976, **13**, 155.
- 7 See, e.g., S. Dapperheld, E. Steckhan, K.-H. Grosse Brinkhaus and T. Esch, *Chem. Ber.*, 1991, **124**, 2557 and references cited therein.
- 8 L. Ebersson and B. Larsson, *Acta Chem. Scand., Ser. B*, 1986, **40**, 210.
- 9 L. Ebersson and B. Larsson, *Acta Chem. Scand., Ser. B*, 1987, **41**, 367.
- 10 U. Schöllkopf and P. Markus, *Liebigs Ann. Chem.*, 1971, **753**, 143.
- 11 L. Ebersson, *Adv. Phys. Org. Chem.*, 1982, **18**, 79.
- 12 E. Schmidt, R. Schumacher and H. Kuhlmann, *Ber. Dtsch. Chem. Ges.*, 1921, **54**, 1483.
- 13 V. E. Titov, as quoted in A. S. Morkovnik, *Russ. Chem. Rev. (Engl. Transl.)*, 1988, **57**, 144 (ref. 68).
- 14 L. V. Okhlobystina, V. A. Tyurikov, B. I. Shapiro, Ya. K. Syrkin and A. A. Frainzil'berg, *Bull. Acad. Sci. USSR, Ser. Chem. (Engl. transl.)*, 1975, 2323.