

Competitive Reactions of Trinitromethanide Ion and Nitrogen Dioxide with Radical Cations

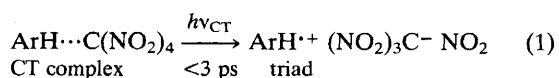
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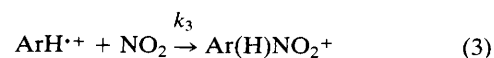
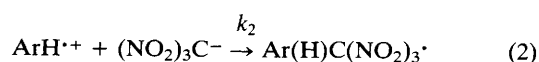
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From the species generated by photoexcitation of ArH–tetranitromethane charge transfer complexes, ArH^{•+}, trinitromethanide ion and nitrogen dioxide, the reaction between ArH^{•+} and trinitromethanide has been shown to be significantly faster than that between ArH^{•+} and nitrogen dioxide.

The photochemical activation of the charge transfer (CT) complex between an aromatic compound (ArH) and tetranitromethane leads within 3 ps to a triad consisting of ArH^{•+}, nitrogen dioxide and trinitromethanide ion [eqn. (1)].¹ These



species then combine to form primarily nitro–trinitromethyl and/or nitrito–trinitromethyl adducts which can undergo various thermal reactions during photolysis and/or workup.² One mechanistic problem concerns the nature of the first chemical step: is it reaction between ArH^{•+} and trinitromethanide ion² or nitrogen dioxide^{3,4} [eqn. (2) or (3)]? Is there a



solvent effect, such that the ArH^{•+}–trinitromethanide reaction is favoured in a less polar solvent, *e.g.* dichloromethane, whereas the ArH^{•+}–NO₂ reaction would occur predominantly in a polar medium, such as acetonitrile?¹

One way of approaching this problem is to study the effect on the lifetime of ArH^{•+} of removing one of the ‘inorganic’ triad components as soon as it is formed. For example, this can be achieved by adding a protic acid which can protonate

trinitromethanide ion and thus completely suppress or drastically decrease its reactivity towards $\text{ArH}^{\cdot+}$. With radical cations of suitable reactivity, it might then be possible to answer the problems posed above.

Trifluoroacetic acid (TFA) in dichloromethane was found to be *ca.* 0.5 pK unit weaker than nitroform, whereas in acetonitrile the difference was *ca.* 1.7 pK units. This means that at a $[(\text{NO}_2)_3\text{C}^-]_0$ of 0.1 mmol dm^{-3} , it takes $[\text{TFA}] = 1 \text{ mmol dm}^{-3}$ to suppress $[(\text{NO}_2)_3\text{C}^-]$ to $<0.001 \text{ mmol dm}^{-3}$ in dichloromethane, whereas the same effect is reached in acetonitrile only at $[\text{TFA}] = 16 \text{ mmol dm}^{-3}$. Thus, at least in dichloromethane TFA was judged to be a suitable protic acid for the purpose at hand.

Solutions of ArH (20–40 mmol dm^{-3}) and tetranitromethane (0.8 mol dm^{-3}) in dichloromethane were photolysed with filtered light ($\lambda > 435 \text{ nm}$) in an EPR cavity at -60°C for a fixed period of time. The aromatic substrates used, listed approximately in order of decreasing $E^\circ(\text{ArH}^{\cdot+}-\text{ArH})$ in Table 1, ranged from those corresponding to very reactive radical cations (like naphthalene and 1-methylnaphthalene) to those corresponding to radical cations of high stability [tris(4-bromophenyl)amine]. Only for the least reactive radical cations, those of perylene, 9,10-diphenylanthracene and tris(4-bromophenyl)amine, was any radical cation EPR signal visible above noise level, whereas in the remaining cases the intensity (indicated as $<$) corresponded to the noise level.

When TFA (0.4 mol dm^{-3}) was present in solutions of the same composition as above, photolysis under identical conditions produced EPR signals of the radical cations ranging from relatively weak to very strong ones in all cases except naphthalene and 1-methylnaphthalene (Table 1). For naphthalene a low radical cation concentration was detectable at $[\text{TFA}] = 1 \text{ mol dm}^{-3}$. The signals were many times stronger than for solutions containing no TFA; in view of the photooxidizing properties of TFA⁵ check experiments were performed also with only TFA present, resulting in weak EPR signals in cases of relatively stable $\text{ArH}^{\cdot+}$.

Similar experiments were performed in acetonitrile, although its physical and chemical properties necessitated the use of a stronger protic acid (methanesulfonic acid) and a higher temperature (-40°C). As examples, three of the substrates of Table 1 gave the following radical cation

Table 1 EPR spectral intensities (absolute) after irradiation of ArH -tetranitromethane solutions in dichloromethane without and with TFA present^a

ArH	EPR spectral intensity		
	With $\text{C}(\text{NO}_2)_4$	With $\text{C}(\text{NO}_2)_4$ and TFA ^b	Ratio
Naphthalene	<2	$<2^c (<2)$	1
1-Methylnaphthalene	<2	$<2 (<2)$	1
1,4-Dimethylnaphthalene	<2	10 (<1.5)	>5
1,2-Dimethylnaphthalene	<2.5	54 (<2)	>22
1,8-Dimethylnaphthalene	<2	16 (4)	>8
1,4,6,7-Tetramethylnaphthalene	<0.7	52 (4)	>74
1,4,5,8-Tetramethylnaphthalene	<1.8	100 (5)	>55
1,3,5,8-Tetramethylnaphthalene	<2	44 (2.6)	>22
1,4-Dimethoxybenzene	<2	540 (<2)	>270
9-Phenylanthracene	<1.8	100 (8)	>56
9,10-Diphenylanthracene	2.6	300 (6.5)	115
Perylene	8	230 (25)	106
Tris(4-bromophenyl)amine	19	181 (3.2)	9.5
9,10-Dimethylanthracene	<1	600 (4.6)	>600

^a Irradiation time 6 min (during which 100 spectra were accumulated), $\lambda > 435 \text{ nm}$, $[\text{ArH}] = 20\text{--}40 \text{ mmol dm}^{-3}$, $[\text{C}(\text{NO}_2)_4] = 0.8 \text{ mol dm}^{-3}$, $[\text{TFA}] = 0.4 \text{ mol dm}^{-3}$, $T = 213 \text{ K}$. ^b The number within parentheses refers to an identical check experiment with only TFA (0.4 mol dm^{-3}) added. ^c At $[\text{TFA}] = 1 \text{ mol dm}^{-3}$, the naphthalene radical cation concentration was above noise level (intensity *ca.* 3.5).

concentration enhancements in acetonitrile in the presence of both tetranitromethane and methanesulfonic acid relative to when only tetranitromethane was present: 9,10-dimethylanthracene (>20), 9,10-diphenylanthracene (5.6) and 1,4,5,8-tetramethylanthracene (>3.5). For 9-phenylanthracene, no radical cation signal was detected under any of these conditions; both this fact and the relatively small enhancement factors in acetonitrile are presumably due to the nucleophilic properties of this solvent.

We interpret the results in dichloromethane in the following way. Among the components of the triad, trinitromethanide ion is much more reactive towards $\text{ArH}^{\cdot+}$ than nitrogen dioxide [$k_2 \gg k_3$, assuming that reaction (3) is irreversible and followed by fast proton loss from all the substrates]. Thus only unreactive radical cations, such as [perylene] $^{\cdot+}$, [9,10-diphenylanthracene] $^{\cdot+}$ and [tris(4-bromophenyl)amine] $^{\cdot+}$, can be generated in a concentration above the noise level in the presence of trinitromethanide ion. With TFA added, the trinitromethanide ion is protonated rapidly and the radical cation concentration in all cases but two will grow since the radical cation is much less reactive toward nitrogen dioxide. (Naphthalene) $^{\cdot+}$ and (1-methylnaphthalene) $^{\cdot+}$ are reactive enough towards NO_2 to be undetectable under the conditions employed for the other substrates, even in the presence of 0.4 mol dm^{-3} TFA. In acetonitrile, the same effect is found, but owing to the levelling effect of this solvent it is detectable only for less reactive radical cations with the method used here.

As a corollary, the preparative photolysis of naphthalene-tetranitromethane was performed in dichloromethane at -20°C under the same conditions as reported before,^{2b} except that TFA was present in a 1.5 mol dm^{-3} concentration. After 8 h of photolysis, the yields of adducts and 1-nitronaphthalene were 2 and 37%, respectively, drastically different from the run without added TFA,^{2b} 47 and 6.5%, a change by a factor of >130 . Since the adducts were found to be stable towards acid at room temperature,^{2b} the change must originate from almost complete removal of trinitromethanide ion from reaction with the radical cation by protonation. The yield of 2-nitronaphthalene was *ca.* 0.7%, thus putting the ratio of 1-/2- isomer at >50 . Similar experimental consequences of TFA addition have been seen in earlier studies.^{1e,4,6}

In conclusion, for a range of moderately reactive to stable radical cations it has been shown that the radical cation is much more reactive toward trinitromethanide ion than nitrogen dioxide in dichloromethane or acetonitrile. This reactivity order is presumably valid generally.

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