

Triplet Aryl Cation (${}^3\text{Ar}^+$): its Photostimulated and Thermal Conversion into $\text{Ar}\cdot$ and Role as the Primary Intermediate in Matrix Photochemistry of ArN_2^+ Ions

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Photolysis at 77 K of 2,4,5-trimethoxybenzenediazonium hexafluorophosphate ($\text{ArN}_2^+\text{PF}_6^-$) yields ${}^3\text{Ar}^+$ and $\text{Ar}\cdot$ in a ratio dependent on (i) irradiation wavelength, (ii) light intensity, (iii) matrix, (iv) photolysis time, and under selected conditions, *i.e.* $\lambda_{\text{irr}} > 350$ nm, low intensity, microcrystalline matrix, short photolysis time, $[\text{}^3\text{Ar}^+]/[\text{Ar}\cdot]$ exceeds 10, implying that ${}^3\text{Ar}^+$ is the *primary* photoproduct; ${}^3\text{Ar}^+$ transforms into $\text{Ar}\cdot$ in the dark (in any matrix), and this change is accelerated under irradiation.

While a large number of organic radical reactions at cryogenic temperatures have been characterised by e.s.r. spectroscopy (consisting mostly of abstraction or addition processes),¹ and some reactions of carbenes have been examined by e.s.r. and other methods (referring mostly to cycloaddition to alkenes or insertion reactions),² very little evidence has been adduced

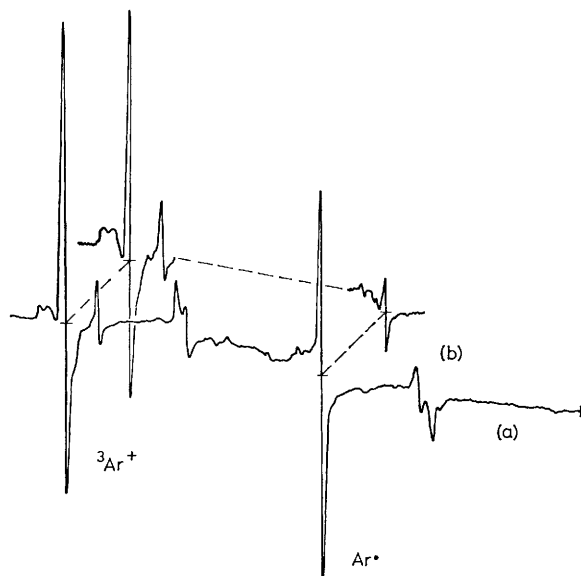
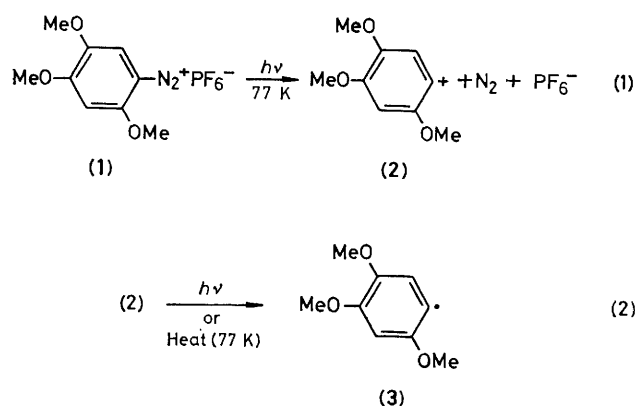


Figure 1. E.s.r. absorption (1–7 kG) obtained on photolysis (4 min) of microcrystalline (1) at 77 K: (a) u.v. irradiation using focused u.v. light from 100 W high-pressure Hg arc; (b) as (a) but using defocused (*i.e.* low intensity) source. Compare the intensities of the H_{min} (of ${}^3\text{Ar}^+$) and $\text{Ar}\cdot$ resonances.

for electron-transfer processes of paramagnetic organic species under these conditions. We report here that the triplet state aryl cation (2) generated in the photolysis of 2,4,5-trimethoxybenzenediazonium hexafluorophosphate (1), equation (1),³ is subject to one-electron reduction to the corresponding aryl radical (3) either on continued photolysis or on storage in the dark (when it occurs much more slowly), equation (2). The transformation (2) was readily monitored by X-band e.s.r. spectroscopy, when (2) and (3) are completely spectrally differentiated, Figure 1, especially by comparison of the intensities of the H_{min} component of the triplet spectrum with the absorption at $g = 2.00$. Moreover, we believe that equation (1) represents the sole primary photoprocess, (3) being produced exclusively *via* equation (2).

Large ratios of (2)/(3) are promoted by the following conditions (i) the use of visible ($\lambda \geq 350$ nm), as opposed to u.v. light; (ii) use of low irradiation intensities (of either u.v. or visible light) (this is illustrated in Figure 1); (iii) the use of 'stiff' matrices, *e.g.* microcrystals as opposed to glassy media; (iv) low (<0.05 M) concentrations of (1) in glasses; (v) (for u.v. irradiation), short photolysis times; (vi) minimal intervals between photolysis and recording. {The corollary is true, *i.e.* the use of high [(1)] in a soft matrix, yields low (2)/(3) even with visible light; after initial photolysis [(3)] increases while [(2)] remains stationary.}

More specifically, (i) focused u.v. (100 W high pressure Hg arc) and visible (200 W tungsten reading lamp) gave maximal (2)/(3) of 1.2 and 9.7, respectively (for microcrystalline powder); (ii) defocusing of the u.v. source increased (2)/(3)

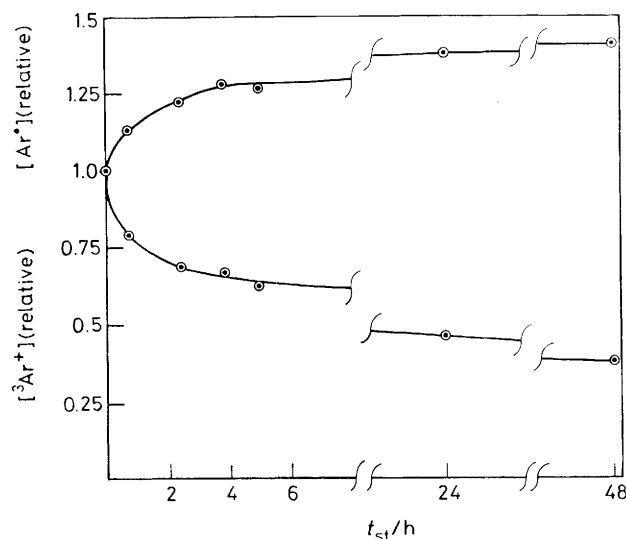


Figure 2. Post-photolysis storage time/concentration profiles of $[\text{}^3\text{Ar}^+]$ and $[\text{Ar}\cdot]$ (both of these are taken arbitrarily as 1.0 at zero storage time). Sample: (1) (0.08 M) in $\text{LiCl-H}_2\text{O-acetone}$ glass at 77 K.

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from 1.2 to 5.5 (4 min photolysis of microcrystalline powder); (iii) for 4 min photolysis, (2)/(3) is up to 5 times greater in a microcrystalline powder than in a 0.1 M solution of (1) in a 50/50 v/v mixture of LiCl (9.0 M)-H₂O and acetone, which forms a glass at 77 K (for longer photolyses the ratio of the values for (2)/(3) rises to >10²); (iv) when [(1)] is reduced below *ca.* 0.05 M in the same glass, (2)/(3) becomes too large to measure accurately, *i.e.* >20; (v) for u.v. photolysis of microcrystals, (2)/(3) falls continuously as photolysis proceeds; (vi) storage in the dark of irradiated samples, either of microcrystals or glasses, effects a slow, monotonic reduction in (2)/(3).

The last two points have been investigated in more detail. U.v. irradiation of a microcrystalline sample induces a continuous fall in (2)/(3) by up to 80% of 2 h; this figure is much greater than that achieved on simple storage of the sample in the dark (see below), and implies *photoconversion* of (2) into (3), *cf.* the reaction of photoexcited diphenylcarbene.⁴ Visible light photolysis of all types of sample caused (2)/(3) to pass through a maximum value at *t* = 10 to 60 min; this phenomenon may be associated with selective absorption of light by the three species (1)–(3) in successive layers of the sample. Individual time-profiles of [(2)] and [(3)] indicate the effect to originate in the behaviour of [(3)] which initially increases, then decreases (both relatively quickly), and then increases much more slowly (probably there are two parallel Ar•-producing pathways, of which one is exhausted after the first period). Concentration [(2)] simply increases monotonically until (1) begins to be exhausted.

The time profiles of [(2)] and [(3)] during storage in the dark are most revealing (Figure 2): these indicate unequivocally that reduction in [(2)] is compensated by increase in [(3)]. These time-profiles are virtually independent of the matrix or the previous history of the sample. The nature of the reductant in the glassy samples is unclear but in the case of microcrystalline material it must be the counter-ion, PF₆⁻. We have

also noted that while the conversion (2) → (3) proceeds with a rate of similar magnitude in glassy media, it does so only while the initial [(1)] is >0.95 M, and *not* in more dilute solution; this implies that Cl⁻ does not function as the reductant despite its high concentration in the glasses.

To summarise, the photolysis of (1) can be made to proceed nearly 100% to (2) under carefully chosen conditions. Radical (3) is then formed from (2) either under irradiation (particularly efficiently with u.v. as opposed to visible light) or in the dark, even at 77 K. This picture contrasts strongly with that established for solution photolysis of arenediazonium salts at room temperature, when *long*-wavelength light favours Ar•-derived products, and short wavelengths favour Ar⁺-dependent products.⁵ Bunnett *et al.* have suggested that the *thermal* decomposition in MeOH may proceed through a common intermediate to give Ar⁺- and Ar•-derived products.⁶

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References

- 1 T. J. Kemp, in 'Electron Spin Resonance,' ed. P. B. Ayscough, (Specialist Periodical Report), The Royal Society of Chemistry, London, 1981, vol. 6, p. 208 and preceding volumes in this series.
- 2 V. P. Senthilnathan and M. S. Platz, *J. Am. Chem. Soc.*, 1980, **102**, 7637; C.-T. Lin and P. P. Gaspar, *Tetrahedron*, 1980, **21**, 3553; R. A. Moss and M. A. Joyce, *J. Am. Chem. Soc.*, 1978, **100**, 4475; H. Tomioka, G. W. Griffin, and K. Nishiyama, *ibid.* 1979, **101**, 6009.
- 3 H. B. Ambroz and T. J. Kemp, *Chem. Soc. Rev.*, 1979, **8**, 353; *J. Chem. Soc., Perkin Trans. 2*, 1980, 768.
- 4 W. A. Gibbons and A. M. Trozzolo, *J. Am. Chem. Soc.*, 1966, **88**, 172.
- 5 H. G. O. Becker, G. Hoffman, and G. Israel, *J. Prakt. Chem.*, 1977, **318**, 1021.
- 6 T.-J. Broxton, J. F. Bunnett, and C. H. Paik, *Chem. Commun.*, 1970, 1363.