Generation of Solutions of Highly Persistent Radical Cations by 4-Tolylthallium(III) Bis(trifluoroacetate) in 1,1,1,3,3,3-Hexafluoropropan-2-ol

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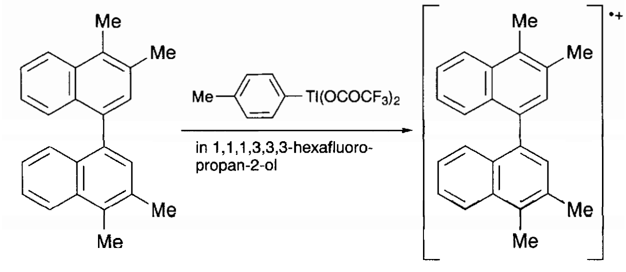
4-Tolylthallium(III) bis(trifluoroacetate) acts as a one-electron oxidant toward aromatic substrates in trifluoroacetic acid or 1,1,1,3,3,3-hexafluoropropan-2-ol, the latter solvent giving radical cation solutions of uniquely high persistency at room temperature.

Thallium(III) trifluoroacetate (Tl^{III}) in trifluoroacetic acid is a versatile one-electron oxidant for the generation of relatively stable solutions of radical cations for EPR spectral studies.[1] For hexamethylbenzene radical cation, we recently found[2] that its slow disappearance reflects its slow formation from Tl^{III} and hexamethylbenzene and that its true rate of disappearance in trifluoroacetic acid is at least 30 times higher. Moreover, the reaction between hexamethylbenzene and Tl^{III} exhibited a significant kinetic deuterium isotope effect which prompted us to suggest that an intermediate pentamethylbenzylthallium species might be the effective one-electron oxidant in the system.

To test this idea, 4-tolylthallium bis(trifluoroacetate) (TTBT) was synthesized as an easily available[3] and not too unrealistic model of the benzylthallium species above. EPR spectral examination of its properties as a one-electron oxidant showed TTBT to be capable of yielding trifluoroacetic acid solutions at 22 °C of radical cations from aromatic compounds (ArH) with $E^{\circ}(\mathrm{ArH}^{\cdot+}/\mathrm{ArH})$ at an upper limit of 1.6–1.7 V (NHE). Including compounds such as pentamethylbenzene[4] and durene,[5] which slowly and irreversibly yield persistent secondary radical cations, the upper limit extends to about 2 V. EPR spectra of such solutions were unusually free of distortion, had narrow line widths and were thus very well resolved. The radical cations prepared in this way were also significantly more long-lived than when Tl^{III} was used as the oxidant.

In themselves, these findings serve well to corroborate our proposal that an arylthallium species can act as an electron-transfer oxidant. However, the combination of TTBT with 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) as the solvent, previously used for generating radical cations with phenyliodine(III) bis(trifluoroacetate) as the oxidant,[6] introduced a wholly new dimension of radical cation stability in fluid solution. As an example, the EPR spectrum of the radical cation of 3,3′,4,4′-tetramethyl-1,1′-binaphthalene ($\mathbf{1}^{\cdot+}$) appeared with high intensity and resolution upon oxidation of **1** by TTBT in HFP at room temp. (Fig. 1). Upon storing the sample tube at room temp. in the dark, the signal decayed with $\tau_{1/2}$ = 15–20 h; a similar experiment in trifluoroacetic acid gave $\tau_{1/2}$ of $\mathbf{1}^{\cdot+}$ = 10 min, a reactivity ratio of *ca.* 10^2. Similar enhancements of $\tau_{1/2}$ were found for the radical cations of 4,4′-dimethyl- and 2,2′,4,4′-, 4,4′,5,5′- and 4,4′,6,6′-tetramethyl-1,1′-binaphthalene. 1,4,5,8-Tetramethylnaphthalene radical cation, with $\tau_{1/2}$ *ca.* 40 min when generated in TFA at 22 °C,[7] had $\tau_{1/2}$ in excess of 50 h with the TTBT–HFP reagent.



$\tau_{1/2}$ *ca.* 15 h at 22 °C

Apart from confirming that normally fairly stable radical cations were highly persistent when generated in TTBT–HFP, a few experimentally less easily accessible systems were studied. The EPR signal of the monomeric radical cation of anthracene appeared with high intensity upon treatment with TTBT in HFP and decayed with $\tau_{1/2}$ = 37 min at 22 °C. This mode of generation avoids the mono- and bis-trifluoroacetoxylation usually observed with Tl^{III} in trifluoroacetic acid.[8] Also, excellent EPR spectra were obtained from the monomeric radical cations of 1,4- and 1,5-dimethylnaphthalene, decaying with $\tau_{1/2}$ = 5 and 19 min, respectively, at 22 °C. These ions were previously generated by low-temperature methods.[9]

The radical cation of benzo-1,3-dioxole **2** was previously generated by either rapid mixing techniques[10] or a matrix method[11] at −196 °C. Attempts to generate it by Tl^{III} oxidation in trifluoroacetic acid at −11 °C or cophotolysis with DDQ at −60 °C failed owing to formation of other products with different EPR spectra. With TTBT in HFP–trifluoroacetic acid (5%) a strong signal of $\mathbf{2}^{\cdot+}$ appeared at room temp., decaying with $\tau_{1/2}$ = 2.5 h.

We also briefly explored HFP as a solvent for generation of radical cations using Tl^{III} as the oxidant. This worked well although the higher reactivity of Tl^{III} introduced complications with more reactive substrates; anthracene gave the EPR spectrum of 9-trifluoroacetoxyanthracene,[8] benzo-1,3-dioxole gave EPR spectra of various oligodehydrodimer radical cations and what presumably was the radical cation of a trifluoroacetoxylated product and 3,3′,4,4′-tetramethyl-1,1′-binaphthalene gave no spectrum at all, presumably owing to over-oxidation. On the other hand, substrates more difficult to oxidize, such as hexamethylbenzene and 4,4′-bitoluene, gave intense spectra of the monomeric radical cations. The $\tau_{1/2}$ of radical cations in Tl^{III}–HFP were generally longer than in Tl^{III}–TFA but not nearly as long as with the 4-tolylthallium(III)–HFP reagent. Thus, it appears that it is the low nucleophilicity of HFP

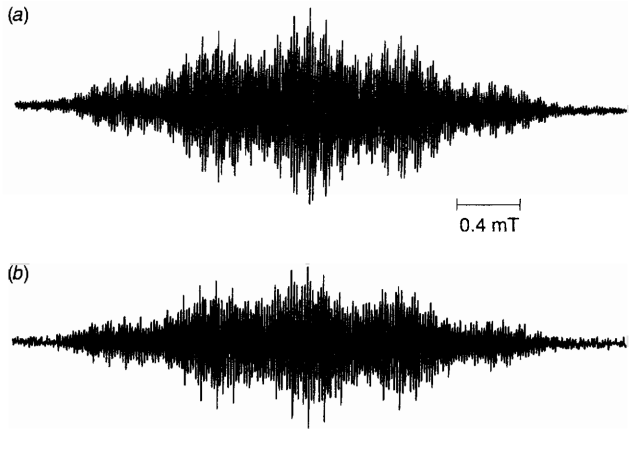


Fig. 1 EPR spectrum of a solution of 3,3′,4,4′-tetramethylnaphthalene (*ca.* 1 mmol dm^{-3}) and TTBT (*ca.* 5 mmol dm^{-3}) in HFP at 22 °C, recorded (*a*) 1 h and (*b*) 43 h after mixing. The actual ratio of the spectral intensities is *ca.* 5.

which uniquely causes the persistency of radical cations generated in this medium.

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References

1 I. H. Elson and J. K. Kochi, *J. Am. Chem. Soc.*, 1973, **95**, 5060.

2 L. Eberson, O. Persson and J. O. Svensson, *J. Chem. Soc., Chem. Commun.*, 1995, 219; L. Eberson, M. P. Hartshorn, O. Persson and J. O. Svensson, *J. Chem. Soc., Perkin Trans. 2*, 1995, in press.

3 R. M. G. Roberts, *Tetrahedron*, 1980, **36**, 3281.

4 L. Eberson and F. Radner, *Acta Chem. Scand.*, 1992, **46**, 630; W. Lau and J. K. Kochi, *J. Am. Chem. Soc.*, 1984, **106**, 7100; H. P. Fritz and R. O. Artes, *Electrochim. Acta*, 1981, **26**, 417.

5 L. Eberson, F. Radner and M. Lindgren, *Acta Chem. Scand.*, 1993, **47**, 835.

6 Y. Kita, H. Tohma, K. Hatanaka, T. Takada, S. Fujita, S. Mitoh, H. Sakurai and S. Oka, *J. Am. Chem. Soc.*, 1994, **116**, 3684; L. Eberson, M. P. Hartshorn and O. Persson, *Acta Chem. Scand.*, 1995, **49**, in press.

7 L. Eberson, J. L. Calvert, M. P. Hartshorn and W. T. Robinson, *Acta Chem. Scand.*, 1993, **47**, 1025.

8 P. D. Sullivan, E. M. Menger, A. H. Reddoch and D. H. Paskovich, *J. Phys. Chem.*, 1978, **82**, 1158.

9 A. Terahara, H. Ohya-Nishiguchi, N. Hirota and A. Oku, *J. Phys. Chem.*, 1986, **90**, 1564; H. Yoshimi and K. Kuwata, *Mol. Phys.*, 1972, **21**, 297.

10 W. T. Dixon and D. Murphy, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1823; J. Fleischhauer, S. Ma, W. Schleker, K. Gersonde, H. Twilfer and F. Dallacker, *Z. Naturforsch., Teil A*, 1982, **87**, 680.

11 D. N. R. Rao and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1985, 991.