1,1,1,3,3,3-Hexafluoropropan-2-ol as a solvent for the generation of highly persistent radical cations

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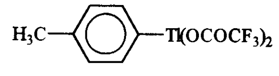
1,1,1,3,3,3-Hexafluoropropan-2-ol (HFP) has been found to be a superior solvent for the generation of radical cations, in many cases increasing their half-lives by a factor of 10^2 compared with those pertaining to trifluoroacetic acid. This study has mainly used 4-tolylthallium(III) bis(trifluoroacetate) and thallium(III) tris(trifluoroacetate) as oxidants, but DDQ could also be employed in the presence of 5% trifluoroacetic acid. Photochemical oxidation by mercury(II) bis(trifluoroacetate) also worked well. Thus room temperature recording of high quality EPR spectra of radical cations previously accessible only by flow or low-temperature procedures has become feasible.

As pointed out by Davies,[1] there is no single method equivalent to the alkali-metal route to radical anions, by which stable solutions of radical cations can be generated for EPR spectral study. Radical cations are electron-deficient, often highly reactive species which can undergo a variety of further transformations in the presence of nucleophiles and/or bases.[2] Current methods of generation often involve low-temperature procedures in acidic media, sometimes in combination with rapid mixing techniques, irradiation or anodic oxidation. Thus the development of new combinations of milder reagents and less nucleophilic solvents is desirable.

Thallium(III) trifluoroacetate (to be denoted Tl^{III} throughout this paper) in trifluoroacetic acid is probably the best general oxidant–solvent system so far introduced,[3] although thermal or photochemical oxidation by 2,3-dichloro-4,5-dicyanobenzoquinone (DDQ) in trifluoroacetic acid has emerged as a strong competitor.[4] We found[5] that phenyliodine(III) bis(trifluoroacetate) (denoted PhI^{III}) in trifluoroacetic acid can be a useful alternative to Tl^{III} in many cases, but not all. A case where PhI^{III} did not seem to work in spite of the fact that other compounds, with much higher $E°(ArH^{•+}/ArH)$, underwent facile oxidation to radical cations, was hexamethylbenzene. However, a more detailed study[6] of the mechanism of oxidation of hexamethylbenzene (HMB) by Tl^{III} showed that the strangely slow decay of $HMB^{•+}$, as monitored by the disappearance of its EPR signal, was actually dependent on its *slow rate of formation* from HMB and Tl^{III}. In itself, $HMB^{•+}$ is a very reactive species in trifluoroacetic acid, as indeed found in the first studies of its reactivity.[7] Similar behaviour—slow decay due to slow rate of formation—was exhibited by the radical cation of 4,4′-bitoluene,[8] showing that this type of kinetic behaviour is not limited to substrates without free nuclear positions.

Since the slow step in the formation of $HMB^{•+}$ from HMB and Tl^{III} showed a significant kinetic substrate deuterium isotope effect, we tentatively suggested that a thalliation step involving a pentamethylbenzylthallium(III) intermediate might qualify as the slow step. The organothallium(III) intermediate would then act as the ET oxidant toward the substrate. To test this hypothesis, 4-tolylthallium(III) bis(trifluoroacetate)[9] (**1**, to be denoted tolyl-Tl^{III} in the following) was used as a not too unrealistic model of a benzylthallium(III) derivative, and indeed was shown to be a good ET oxidant toward moderately reactive and reactive substrates in trifluoroacetic acid.[10]



1 (tolyl-Tl^{III})

The investigation[11] which prompted our study of PhI^{III} as an oxidant for the generation of radical cations, used 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) as a solvent for EPR monitoring of putative radical cation intermediates in the oxidative azidation of aromatic ethers. We found HFP to be an excellent solvent for PhI^{III} generation of radical cations, approximately equivalent to trifluoroacetic acid with respect to the persistence of the radical cations. However, when the use of HFP was extended to thallium(III)-based oxidants, such as Tl^{III} and tolyl-Tl^{III}, an entirely new dimension of radical cation persistence was encountered, observation times increasing by factors of up to 10^2 or more. This allowed for easy recording at room temperature, of EPR spectra almost free from distortion and with unprecedented high resolution that otherwise are difficult to access. In what follows, we document the scope and limitations of HFP as a solvent for EPR spectral observation of radical cations.

Results

Oxidation by tolyl-Tl^{III} in trifluoroacetic acid

The $1e^-$ oxidizing power of tolyl-Tl^{III} in trifluoroacetic acid was first briefly investigated in order to find the upper limit for EPR-detectable production of radical cations. As seen from Table 1, tolyl-Tl^{III} just barely gave a detectable radical cation concentration from 4,4′-bitoluene and ($^2H_{14}$)-4,4′-bitoluene ($E° = 1.69$ V) and hexaethylbenzene (1.63 V). For substrates with lower $E°$, radical cation formation was efficient and gave rise to intense EPR spectra which persisted for periods of about the same duration as is normal for trifluoroacetic acid. In special cases, where the initially formed radical cation is known to be transformed into much more persistent species by further reactions,[12] the upper $E°$ limit for oxidation increased. Thus durene (1.87 V) slowly gave a strong EPR signal from 1,2,4,5,6,8-hexamethylanthracene radical cation, signifying that oxidation takes place, but that the initially formed radical cation undergoes further transformation.

However, the interpretation of experiments, in which the oxidation reaction was slow but still gave detectable concentrations of radical cations, might possibly be complicated by

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Table 1 Oxidation of aromatic substrates (ArH) by 4-tolyl-Tl^{III} bis(trifluoroacetate) in trifluoroacetic acid (TFA) at room temperature

ArH	$E°(ArH^{\bullet +}/ArH)$/V *vs.* Ag/AgCl	Spectrum recorded (ref. to previous work)	Strength of EPR signal
1,3,5-Tri-*tert*-butylbenzene	2.05	None	
Durene	1.87	(1,2,4,5,6,8-Hexamethylanthracene)$^{\bullet +}$ [12(*b*)]	Strong after > 12 h in the dark
Pentamethylbenzene	1.79	1,2,3,4,5,6,7,8-Octamethylanthracene$^{\bullet +}$ [12(*a*)]	Strong after > 3 h in the dark
($^2H_{14}$)-4,4′-Bitoluene	1.69	$ArH^{\bullet +}$	Weak
4,4′-Bitoluene	1.69	$ArH^{\bullet +}$ (32)	Weak
Hexaethylbenzene	1.63	$ArH^{\bullet +}$ (62)	Weak
1,2-Dimethylnaphthalene	1.60	$(Ar–Ar)^{\bullet +}$ [43(*c*)]	Strong
2,2′,4,4′-Tetramethyl-1,1′-binaphthalene	1.55	$ArH^{\bullet +}$ [43(*c*)]	Strong
1,3-Benzodioxole	1.50	$Ar–Ar^{\bullet +}$ (25)	Strong
2,2′-Dimethoxy-5,5′-di-*tert*-butylbiphenyl	1.47	$ArH^{\bullet +}$ (5)	Strong
Anthracene	1.41	$ArH^{\bullet +}$ (39)	Weak
3,3′,4,4′-Tetramethyl-1,1′-binaphthalene	1.40	$ArH^{\bullet +}$ [43(*c*)]	Strong

Table 2 Oxidation of aromatic substrates (ArH) by 4-tolyl-Tl^{III} bis(trifluoroacetate) in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) at room temperature

ArH	$E°(ArH^{\bullet +}/ArH)$/ *vs.* Ag/AgCl	Spectrum recorded (ref. to previous work)	Strength of EPR signal
4,4′-Bitoluene	1.69	None	
4-*tert*-Butylanisole	1.67	None	
1,5-Dimethylnaphthalene	1.67	None	
1,4-Dimethylnaphthalene	1.63	None	
2,3-Dihydro-1,4-benzodioxine	1.58	$ArH^{\bullet +}$	Weak
9,10-Diphenylphenanthrene	1.57	None	
9,10-Diphenylphenanthrene 5% TFA added	1.57	$ArH^{\bullet +}$	Weak
2,2′,4,4′-Tetramethyl-1,1′-binaphthalene	1.55	$ArH^{\bullet +}$ [43(*c*)]	Strong
1,4-Benzodioxole + 5% TFA	1.50	$ArH^{\bullet +}$ (25)	Strong
1,2-Dimethoxybenzene	1.49	$ArH^{\bullet +}$ (25)	Weak
1,2-Dimethoxybenzene 5% TFA added	1.49	$ArH^{\bullet +}$ (25)	Medium
4,4′-Dimethyl-1,1′-binaphthalene	1.49	$ArH^{\bullet +}$	Very weak
4,4′-Dimethyl-1,1′-binaphthalene 5% TFA added	1.49	$ArH^{\bullet +}$ [43(*c*)]	Weak
2,2′-Dimethoxy-5,5′-di-*tert*-butylbiphenyl	1.47	$ArH^{\bullet +}$ (5)	Strong
1-Methoxynaphthalene	1.47	$(Ar–Ar)^{\bullet +}$ [43(*b*)]	Strong
2,2′-Bithiophene	1.45	$ArH^{\bullet +}$	Weak
Dibenzo-1,4-dioxine	1.41	$ArH^{\bullet +}$ (25)	Strong
Anthracene	1.41	$ArH^{\bullet +}$ (39)	Strong
3,3′,4,4′-Tetramethyl-1,1′-binaphthalene	1.40	$ArH^{\bullet +}$ [43(*c*)]	Very strong
4,4′,6,6′-Tetramethyl-1,1′-binaphthalene	1.40	$ArH^{\bullet +}$ [43(*c*)]	Strong
4,4′,5,5′-Tetramethyl-1,1′-binaphthalene	1.38	$ArH^{\bullet +}$ [43(*c*)]	Strong
Dibenzo[*a*,*c*]triphenylene	1.33	$ArH^{\bullet +}$ (39)	Strong
Tetraphenylethylene	1.32	$ArH^{\bullet +}$ (39)	Strong
Thianthrene	1.32	$ArH^{\bullet +}$ (15)	Strong
5-Methoxy-1,3-benzodioxole	1.17	Some $ArH^{\bullet +}$ (25); mostly 5,5′-$ArAr^{\bullet +}$, see the text	Strong

tolyl-Tl^{III} being involved in a process reforming the stronger oxidant, Tl^{III}, *via* equilibrium (1).[13] Even if the effect of this

$$\text{tolyl-Tl}^{III} + CF_3COOH \rightleftharpoons C_6H_5CH_3 + Tl^{III}(OCOCF_3) \quad (1)$$

equilibrium has been experimentally verified only at elevated temperatures (heating tolyl-Tl^{III} in trifluoroacetic acid at 73 °C for prolonged periods),[14] it is necessary to check this possibility. Since equilibrium (1) cannot be established in HFP, this solvent was used instead for tolyl-Tl^{III} oxidation and was eventually found to be an exceptionally good medium for radical cation generation (see below).

Oxidation by tolyl-Tl^{III} in HFP

The oxidizing power of tolyl-Tl^{III} in HFP is illustrated in Table 2 where a series of ArH have been reacted with tolyl-Tl^{III} at room temperature and the EPR activity of the solution monitored. The borderline for reactive substrates was found to be around 1.6 V, slightly lower than in trifluoroacetic acid. Weak signals could be strengthened by performing the reaction in the presence of 5% trifluoroacetic acid, as exemplified by 9,10-diphenylphenanthrene, 1,3-benzodioxole, 1,2-dimethoxybenzene and 4,4′-dimethyl-1,1′-binaphthalene. In general, radical cations were much more persistent in HFP than in trifluoroacetic acid, as shown by the comparison of radical cation half-lives in the two solvents made in Table 3. Except for cases in the borderline region, EPR spectra were intense and almost free of distortion, had narrow linewidths and were thus very well resolved. An example is given in Fig. 1, where the EPR spectrum of 3,3′,4,4′-tetramethyl-1,1′-binaphthalene (**2**) is shown 1 and 46 h

Table 3 Comparison between persistences of $ArH^{\cdot +}$ of radical cations, generated by tolyl-Tl^{III} in HFP or trifluoroacetic acid at room temperature

Radical cation from	$\tau_{\frac{1}{2}}$/h in HFP	$\tau_{\frac{1}{2}}$/h in TFA	Ratio HFP: TFA
2,2′,4,4′-Tetramethyl-1,1′-binaphthalene	16	≈0.1	≈160
1,3-Benzodioxole (5% TFA)	2.5	0.017	147
Anthracene	0.61	0.017	36
3,3′,4,4′-Tetramethyl-1,1′-binaphthalene	15.3	0.17	90
4,4′,6,6′-Tetramethyl-1,1′-binaphthalene	≈5	≈0.05	≈100
4,4′,5,5′-Tetramethyl-1,1′-binaphthalene	≈5	≈0.05	≈100
Biphenylene	> 100	3.5	> 29
1,4,5,8-Tetramethylnaphthalene	28	0.67	42
1,2,4,5-Tetrahydroxybenzene, diacetonide	141	18	8

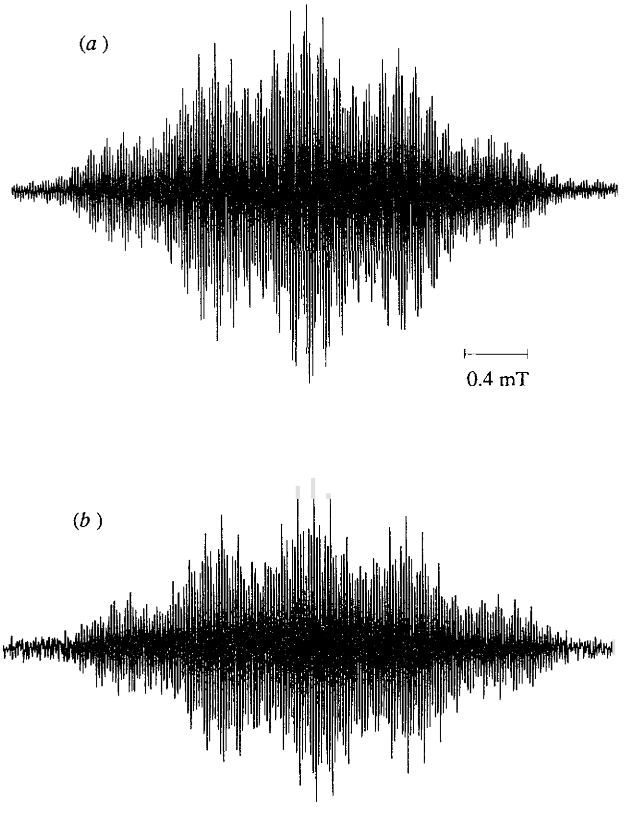
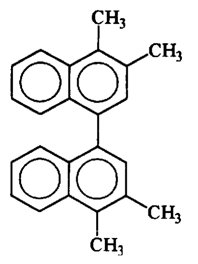


Fig. 1 EPR spectrum of a solution of 3,3′,4,4′-tetramethylnaphthalene (≈1 mmol dm^{-3}) and tolyl-Tl^{III} (≈5 mmol dm^{-3}) in HFP at 22 °C, recorded (*a*) 1 h and (*b*) 46 h after mixing. The actual ratio of the spectral intensities is *ca.* 5.

after mixing, the sample being kept in the dark at 22 °C between recordings. Similar increases in persistence were found for a number of other 1,1′-binaphthalenes. A large number of other substrates with $E°(ArH^{\cdot +}/ArH) < 1.4$ V (for a list, see the Experimental section) were oxidized by tolyl-Tl^{III} in HFP and confirmed the general picture of uniquely high radical cation persistence and exceptionally good resolution of their EPR spectra. As an example, the coupling constant to the 1,4,5,8-hydrogens of thianthrene radical cation could be obtained ($a^{1,4,5,8\text{-H}} = 0.012$, lit.,[15] 0.0135 mT). Also notice that the anthracene radical cation persisted as such, and was not transformed into 9-trifluoroacetoxyanthracene radical cation, as is the case when Tl^{III} is the oxidant (see below). Only in the oxidation of 5-methoxy-1,3-benzodioxole (**3**) was a complication encountered (see below), namely the formation of the dimer (**4**).



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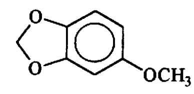

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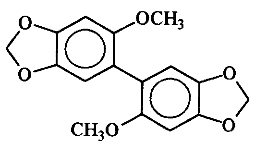

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However, the upper limit of $E°(ArH^{\cdot +}/ArH) \approx 1.6$ V for oxidation by tolyl-Tl^{III} is a serious limitation for testing the scope and limitations of HFP as a solvent for radical cations. At this limit, the corresponding radical cations are not reactive enough to bring out fully the advantages of the gain in stabilization. Therefore, other, stronger oxidants were tested in order to generate more reactive radical cations for convenient EPR observation at room temperature.

Oxidation by Tl^{III} in HFP

As expected, the use of Tl^{III} as the oxidant increased significantly the borderline potential between reactive and unreactive substrates while still allowing for much longer observation periods of the radical cations. The results of Table 4 place the borderline somewhere around 2.0 V, thus allowing for room temperature observation of a number of radical cations which previously either required rapid mixing techniques or low-temperature generation. For sterically crowded radical cations, the limit can be extended about 0.1 V upwards. However, the higher reactivity of Tl^{III} also caused side-reactions of anticipated types; trifluoroacetoxylation occurred with anthracene,[16] 1,3-benzodioxole underwent dimerization and ring opening (see below), 9,10-diphenylphenanthrene gave the radical cation of the cyclized product,[17] dibenzo[*a*,*c*]-triphenylene, and an easily oxidizable compound like 3,3′,4,4′-tetramethyl-1,1′-binaphthalene plainly underwent over-oxidation, no radical cation activity being recorded. Tetraphenylethylene underwent double cyclization to give dibenzo[*a*,*c*]-triphenylene radical cation; note that tolyl-Tl^{III} oxidized tetraphenylethylene to its radical cation and that 9,10-diphenylphenanthrene was not oxidized by tolyl-Tl^{III} alone but required the addition of 5% TFA.

Oxidation by 2,3-dichloro-4,5-dicyanobenzoquinone (DDQ) in HFP

DDQ in trifluoroacetic acid acts thermally as an oxidant for $E°(ArH^{\cdot +}/ArH)$ up to around 1.6 V. UV irradiation permits oxidation of even less-reactive substrates. A test with 3,3′,4,4′-tetramethyl-1,1′-binaphthalene as the substrate in HFP showed that a weak EPR spectrum of the radical cation could be recorded after addition of DDQ. Irradiation by UV light destroyed the radical cation spectrum and replaced it with the spectrum of $DDQ^{\cdot -}$ [$a^{N}(2) = 0.058$ mT; lit.,[18] 0.058 mT). It is obvious that the protonating ability of HFP (pK = 9.3)[19] is not sufficient to protonate this radical anion, and that a stronger acid must be present for this purpose. The addition of 5% trifluoroacetic acid increased the intensity of the EPR spectrum by a factor of 20–30, but its stability was low compared with the

Table 4 Oxidation of aromatic substrates (ArH) by $\mathrm{Tl^{III}}$ tris(trifluoroacetate) in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) at room temperature

ArH	$E^\circ(\mathrm{ArH}^{\cdot+}/\mathrm{ArH})$/V *vs.* Ag/AgCl	Spectrum recorded (ref. to previous work)	Strength of EPR signal ($\tau_{\frac{1}{2}}$/h)
1,4-Di-*tert*-butylbenzene	2.07	$\mathrm{Ar}^{\cdot+}$ (63)	Strong
1,3,5-Tri-*tert*-butylbenzene	2.05	$\mathrm{ArH}^{\cdot+}$ (63)	Strong
Triphenylene, tetraphenylene	≈2.0	None	
4,4′-Difluorobiphenyl	—	$\mathrm{ArH}^{\cdot+}$ (32)	Medium
4-Fluoroanisole	1.87	$\mathrm{ArH}^{\cdot+}$ (25)	Strong
4-Methoxytoluene	1.86	$\mathrm{ArH}^{\cdot+}$ (25); see the text	Medium
Triptycene	1.82	$\mathrm{ArH}^{\cdot+}$ (23)	Weak (≈0.03)
Biphenyl	1.8	$\mathrm{ArH}^{\cdot+}$ (31)	Weak
4-Chloroanisole	1.76	$\mathrm{ArH}^{\cdot+}$	Medium
4,4′-Bitoluene	1.69	$\mathrm{ArH}^{\cdot+}$ (32)	Strong (1.1)
4,4′-Di($^2\mathrm{H}_3$)methylbiphenyl	1.69	$\mathrm{ArH}^{\cdot+}$	Strong (11.5)
4,4′-Di-*tert*-butylbiphenyl	1.69	$\mathrm{ArH}^{\cdot+}$ (33)	Strong
1,5-Dimethylnaphthalene	1.67	$\mathrm{ArH}^{\cdot+}$ (37)	Strong
4-*tert*-Butylanisole	1.67	$\mathrm{Ar{-}Ar}^{\cdot+}$ (5)	Weak
Hexamethylbenzene	1.66	$\mathrm{ArH}^{\cdot+}$ (6)	Strong (0.06)
1,1′-Binaphthalene	1.66	$\mathrm{ArH}^{\cdot+}$	Strong
Hexaethylbenzene	1.63	$\mathrm{ArH}^{\cdot+}$ (62)	Strong
1,4-Dimethylnaphthalene	1.63	$\mathrm{ArH}^{\cdot+}$ (37)	Strong (0.1)
3,3′,4,4′-Tetramethylbiphenyl	1.57	$\mathrm{ArH}^{\cdot+}$ (33)	Strong
9,10-Diphenylphenanthrene	1.57	(Dibenzo[*a*,*c*]triphenylene)$^{\cdot+}$ (39)	Strong
Phenanthrene	1.54	$\mathrm{ArH}^{\cdot+}$	Medium
1,3-Benzodioxole	1.50	(*i*) $\mathrm{ArH}^{\cdot+}$ (*ii*) radical cation of singly ring-opened **5**; see the text	Strong (0.025)
Pentamethylanisole	1.48	$\mathrm{ArH}^{\cdot+}$	Strong
3,3′,4,4′,5,5′-Hexamethylbiphenyl	1.47	$\mathrm{ArH}^{\cdot+}$ (32)	Strong (0.1)
2,2′-Dimethoxy-5,5′-dimethylbiphenyl	1.46	$\mathrm{ArH}^{\cdot+}$	Strong
Anthracene	1.41	9-Ar-$\mathrm{OCOCF_3}^{\cdot+}$ (16)	Strong
3,3′,4,4′-Tetramethyl-1,1-binaphthalene	1.40	None	Over-oxidation
Tetraphenylethylene	1.32	(Dibenzo[*a*,*c*]triphenylene)$^{\cdot+}$ (39)	Strong

Table 5 Oxidation of aromatic substrates (ArH) by $\mathrm{Hg^{II}}$ tris(trifluoroacetate)–UV light in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) at room temperature

ArH	$E^\circ(\mathrm{ArH}^{\cdot+}/\mathrm{ArH})$/V *vs.* Ag/AgCl	Spectrum recorded (ref. to previous work)	Strength of EPR signal
Pentamethylbenzyl acetate	—	$\mathrm{ArH}^{\cdot+}$ (6)	Weak
Pentamethylbenzyl trifluoroacetate	1.68	$\mathrm{ArH}^{\cdot+}$ (6)	Weak
Pentamethylbenzyl alcohol	—	$\mathrm{ArH}^{\cdot+}$ (6)	Medium
Triphenylene	2.0	$\mathrm{ArH}^{\cdot+}$ (23)	Weak
4-*tert*-Butylanisole	1.67	2-Ar-$\mathrm{HgOCOCF_3}^{\cdot+}$	Strong
Tetraphenylene	2.0	$\mathrm{ArH}^{\cdot+}$ (24)	Medium

tolyl-$\mathrm{Tl^{III}}$ reagent, the half-life being of the order of 0.5 h instead of 15.3 h (Table 3).

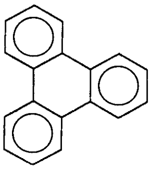
4,4′-Bitoluene was used to probe the upper limit of $E^\circ(\mathrm{ArH}^{\cdot+}/\mathrm{ArH})$. In HFP–trifluoroacetic acid (5%) the EPR spectrum was very weak, but a stronger signal was obtained by UV irradiation. The spectrum disappeared within < 10 s upon discontinuation of irradiation. Thus DDQ does not seem to offer any advantage, except for its lower toxicity, over tolyl-$\mathrm{Tl^{III}}$ or $\mathrm{Tl^{III}}$ and was not further investigated.

Oxidation by irradiation in the presence of mercury(II) trifluoroacetate

Mercury(II) trifluoroacetate (to be denoted $\mathrm{Hg^{II}}$ in the following) is a weak oxidant in thermal reactions. Irradiation of its charge-transfer complex with UV light at low temperatures is an excellent method for the generation of radical cations of low persistence,[20] although sometimes mercuriation is a complicating process.[21] In the present context, it was of interest to try the $\mathrm{Hg^{II}}/h\nu$ method in HFP to see whether highly reactive radical cations could be generated in photostationary concentrations large enough for EPR detection at room temperature. A few examples are listed in Table 5.

Triphenylene (**5**) and tetraphenylene (**6**) did not show any sign of EPR activity upon oxidation by $\mathrm{Tl^{III}}$ in HFP (Table 4). Irradiation of triphenylene with $\mathrm{Hg^{II}}$ in HFP at 22 °C gave a broad singlet with clear indications of couplings; a forward and back Fourier transformation removed the broad background signal and showed the expected pattern of a septet of septets, a^{H2} (6 H) = 0.352 and a^{H1} (6 H) = 0.092 mT. Previous recordings were made in $\mathrm{SbCl_5}$–dichloromethane at −91 °C (unresolved spectrum of ~30 lines)[22] and $\mathrm{Hg^{II}}$–$h\nu$–trifluoroacetic acid at −13.0 °C;[23] in the latter case, the spectrum of the dimer radical cation, $(\mathrm{triphenylene})_2^{\cdot+}$, was found [$a^{\mathrm{H1}}$ (12 H) = 0.0915 and a^{H2} (12 H) = 0.0588 mT].

It should be noted that the set of a^{H} reported above for $(\mathrm{triphenylene})^{\cdot+}$ is not consistent with the rule that these coupling constants should be approximately double those of $(\mathrm{triphenylene})_2^{\cdot+}$, nor is the ratio between the coupling constants similar to that obtained for the radical anion (3.8 *vs.* 1.5).



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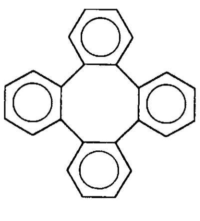

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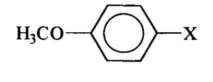
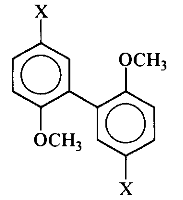
Tetraphenylene upon irradiation with $\mathrm{Hg^{II}}$ in HFP at 22 °C gave a nonet with spacing 0.130 mT with no further splitting detectable [lit.,[24] a^{H1} (8 H) < 0.001 and a^{H2} (8 H) = 0.134 mT; the radical cation was generated by $\mathrm{Hg^{II}}$–$h\nu$–trifluoroacetic acid at −13 °C].

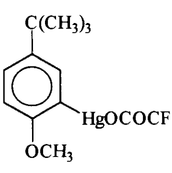
4-*tert*-Butylanisole (**7a**) upon oxidation by $\mathrm{Tl^{III}}$ was converted into the radical cation of its dimer, 2,2'-dimethoxy-5,5'-di-*tert*-butylbiphenyl (**8a**); the EPR spectrum was weak (Table 4). Attempted oxidation by tolyl-Tl^{III} failed (Table 2). Oxidation by Hg^{II}–*hν* gave a mercuriated radical cation, most likely that of 2-trifluoroacetoxymercurio-4-*tert*-butylanisole (**9**) [a^{OMe} (3 H) = 0.390, a^{Hg} = 4.38, a^{H3} (1 H) = 0.0, a^{Bu^t} = 0.071, a^{H5} = 0.090 mT].



7a (X = *t*-C_4H_9)
7b (X = CH_3)
7c (X = F)
7d (X = Cl)



8a (X = *t*-C_4H_9)
8b (X = CH_3)



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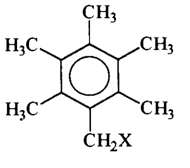


10a (X = $OCOCH_3$)
10b (X = $OCOCF_3$)
10c (X = OH)

Pentamethylbenzyl acetate, trifluoroacetate and alcohol (**10a**, **10b** and **10c**) by the Hg^{II}–*hν* method all gave nearly identical 13-line spectra[6] with spacing 0.990, 0.987 and 0.993 mT, respectively. Only for the alcohol was the spectrum intense enough to allow for resolution of the lines into an octet of spacing 0.011 mT.

Comparison between oxidation in HFP and other media in some case studies

In this section we describe a number of cases where the advantages of HFP are clearly seen in relation to previously used procedures. Many other substrates were tried (see the Experimental section) and in general well resolved spectra were obtained.

A large number of alkoxy- and dialkoxy-benzenes have previously been oxidized by Ce^{IV} in strong sulfuric acid in a flow system and EPR spectra of the radical cations recorded.[25] Low-temperature techniques have also been used.[26] It was noticed that many of the spectra from anisole derivatives were badly resolved owing to a poor signal to noise ratio. In HFP, 4-methoxytoluene (**7b**) upon oxidation by Tl^{III} at 22 °C gave a well resolved EPR spectrum of its radical cation [Fig. 2(*a*)], somewhat contaminated in the central part by the spectrum of its dimer radical cation, [2,2'-dimethoxy-5,5'-dimethylbiphenyl]$^{\cdot+}$ (**8b**$^{\cdot+}$). The spectrum of **7b**$^{\cdot+}$ was reasonably well simulated by the published[25a] parameters [a^{OMe} (3 H) = 0.435, a^{H2} (1 H) = 0.435, a^{H3} = 0.080, a^{Me} (3 H) = 1.51, a^{H5} (1 H) = 0.020, a^{H6} (1 H) = 0.35 mT]. The EPR signal of **7b**$^{\cdot+}$ decayed within an hour and left behind a weak signal from the dimer radical cation **8b**$^{\cdot+}$ [Fig. 2(*b*)]. A spectrum of the authentic dimer radical cation **8b**$^{\cdot+}$ is shown in Fig. 2(*c*). (α,α,α-$^2H_3$)-4-Methoxytoluene in the same way gave an EPR spectrum which was simulated by the same parameters as for **7b**$^{\cdot+}$, except for a^{Me} being 1.51/6.51 = 0.232 (I = 1).

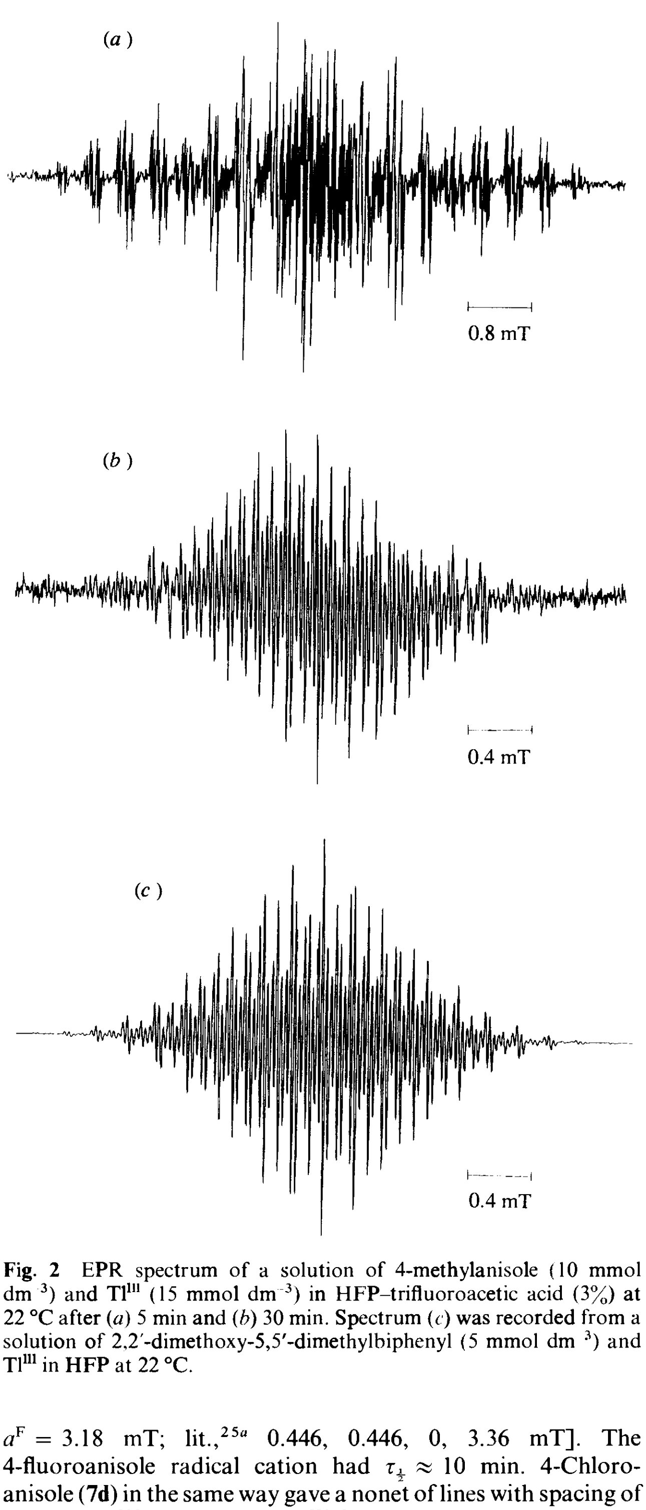


Fig. 2 EPR spectrum of a solution of 4-methylanisole (10 mmol dm^{-3}) and Tl^{III} (15 mmol dm^{-3}) in HFP–trifluoroacetic acid (3%) at 22 °C after (*a*) 5 min and (*b*) 30 min. Spectrum (*c*) was recorded from a solution of 2,2'-dimethoxy-5,5'-dimethylbiphenyl (5 mmol dm^{-3}) and Tl^{III} in HFP at 22 °C.

4-Fluoroanisole (**7c**) was oxidized in the same way, giving an EPR spectrum with hfs constants almost identical with the published ones [a^{OMe} (3 H) = 0.45, a^{H2} (2 H) = 0.45, a^{H3} = 0.0, a^F = 3.18 mT; lit.,[25a] 0.446, 0.446, 0, 3.36 mT]. The 4-fluoroanisole radical cation had $\tau_{\frac{1}{2}} \approx 10$ min. 4-Chloroanisole (**7d**) in the same way gave a nonet of lines with spacing of 0.41 mT [a^{OMe} (3 H) = 0.82, $a^{H2,6}$ (2 H) = 0.41] each of which had a fine-structure corresponding to coupling with one chlorine [a^{35Cl} = 0.033 mT (I = 3/2)] and one hydrogen (a^{H5} = 0.100 mT). The coupling to ^{37}Cl was not detectable. Finally, pentamethylanisole upon oxidation by Tl^{III} generated a strong signal of the corresponding radical cation [a^{OMe} (3 H) = 0.378, $a^{2\text{-}CH_3}$ (6 H) = 0.396, $a^{3\text{-}CH_3}$ (6 H) = 0.070, $a^{4\text{-}CH_3}$ (3 H) = 1.32 mT].

1,3-Benzodioxole (**11**) was found to be rather a sensitive compound under oxidizing conditions. Thus irradiation of 1,3-benzodioxole in dichloromethane–trifluoroacetic acid (5%) in the presence of electron acceptors (DDQ, tetranitromethane) at −60 °C failed to give the EPR spectrum of the radical cation. Other, more complicated spectra of what was presumably a

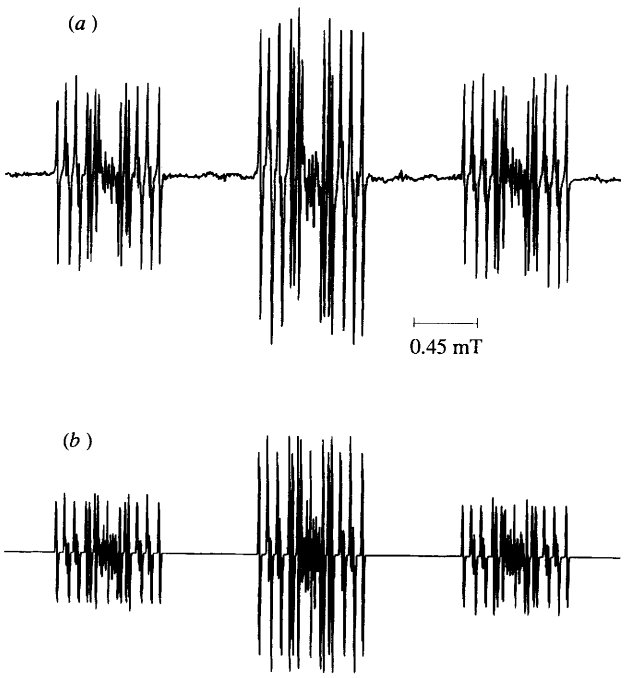
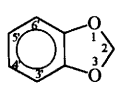


Fig. 3 (*a*) EPR spectrum of a solution of 1,3-benzodioxole (5 mmol dm^{-3}) and Tl$^{\mathrm{III}}$ (15 mmol dm^{-3}) in HFP at 22 °C, recorded after 30 min. (*b*) Simulated Lorentzian spectrum, using hfs coupling constants given in the text and a linewidth of 0.005 mT.

mixture of several radical cations, were detected. Oxidation of 1,3-benzodioxole by tolyl-Tl$^{\mathrm{III}}$ in trifluoroacetic acid at 22 °C gave the EPR spectrum of what was identified as the 5,5′-dimer **12** [a^{H2} (4 H) = 0.65, $a^{\mathrm{H3'}}$ (2 H) = 0.034, $a^{\mathrm{H5'}}$ = 0.381, $\alpha^{\mathrm{H6'}}$ = 0.0 mT; 5,5′-connected bi(1,3-benzodioxoles) are known to have methylene group hfs constants around 0.6 mT].[27] Only by oxidation under the mildest possible conditions, tolyl-Tl$^{\mathrm{III}}$ in HFP–trifluoroacetic acid (5%) at 22 °C, was the spectrum [a^{H2} (2 H) = 2.15, $a^{\mathrm{H3'}}$ (2 H) = 0.040, $a^{\mathrm{H5'}}$ (2 H) = 0.49 mT; lit.,[25] a^{H2} (2 H) = 2.19, $a^{\mathrm{H3'}}$ (2 H) = 0.040, $a^{\mathrm{H5'}}$ (2 H) = 0.49 mT] of the radical cation (**11**$^{\bullet+}$) obtained. This signal decayed with $\tau_{\frac{1}{2}}$ = 2.6 h.



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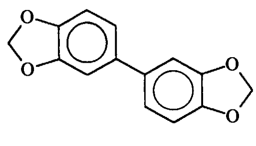

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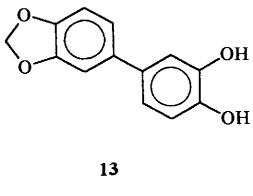

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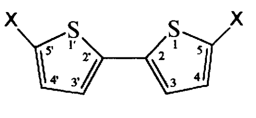
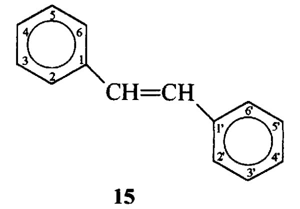
Oxidation of 1,3-benzodioxole by Tl$^{\mathrm{III}}$ in HFP again gave its radical cation which under these conditions decayed with $\tau_{\frac{1}{2}}$ = 1.5 min, being converted into a new species with the EPR spectrum shown in Fig. 3(*a*). This spectrum could be simulated [Fig. 3(*b*)] by the hfs constants 1.48 (2 H), 0.284, 0.245, 0.086, 0.073, 0.061, 0.0066 and 0.0051 mT (1 H of each). It appears likely that this species corresponds to a singly ring-opened dimer (**13**). This radical cation had $\tau_{\frac{1}{2}} \approx$ 1 h. The 5-methoxy derivative of 1,3-benzodioxole (**3**) even by oxidation by tolyl-Tl$^{\mathrm{III}}$ gave the dimer (**4**) spectrum [$a^{\mathrm{CH_2}}$ (4 H) = 0.518, a^{OMe} (6 H) = 0.137, $a^{\mathrm{H3',3''}}$ (2 H) = 0.105, $a^{\mathrm{H6',6''}}$ (2 H) = 0.076 mT; lit.,[27] $a^{\mathrm{CH_2}}$ (4 H) = 0.546, a^{OMe} (6 H) = 0.140, $a^{\mathrm{H6,6'}}$ (4 H) = 0.033 mT], attesting to the well-known, high propensity for 1,2,4-trialkoxybenzenes to undergo dimerization.[28]

The 2,2′-bithiophene radical cation (**14a**$^{\bullet+}$) is a reactive species, prone to undergo dimerization to quaterthienyl in trifluoroacetic acid.[29] Its EPR spectrum was previously[30] recorded by low-temperature oxidation (irradiation in the presence of Hg$^{\mathrm{II}}$ trifluoroacetate) of 2,2′-bithiophene in dichloromethane–trifluoroacetic acid. In HFP, tolyl-Tl$^{\mathrm{III}}$ oxidation of 2,2′-bithiophene gave a weak spectrum of a radical cation [$a^{\mathrm{H5,5'}}$ (2 H) 0.77, $a^{\mathrm{H4,4'}}$ (2 H) 0.027, $a^{\mathrm{H3,3'}}$ (2 H) 0.385 mT; lit.,[30] $a^{\mathrm{H5,5'}}$ (2 H) 0.327, $a^{\mathrm{H4,4'}}$ (2 H) 0.222, $a^{\mathrm{H3,3'}}$ (2 H) 0.106 mT]. These values differ widely. A consideration of the hfs constants of a number of radical cations of 5,5′-dialkyl-2,2′-bithiophenes (**14b**$^{\bullet+}$) indicated that $a^{\mathrm{H3,3'}}$ is generally *ca.* 0.4 mT and $a^{\mathrm{H4,4'}}$ in the range 0.07–0.1 mT. The hfs constant of methyl groups in the 5,5′-positions was around 0.9 mT,[29] compatible with the value found for $a^{\mathrm{H5,5'}}$, 0.77 mT. The theoretically calculated[30] hfs constants, $a^{\mathrm{H5,5'}}$ 0.60, $a^{\mathrm{H4,4'}}$ 0.019 and $a^{\mathrm{H3,3'}}$ 0.432 mT, agree reasonably well with the values found here.



14a (X = H)
14b (X = alkyl)



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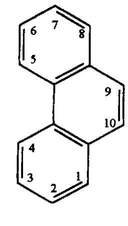

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Biphenyl upon oxidation with HFP–Tl$^{\mathrm{III}}$ at 22 °C gave a weak spectrum of the same appearance as that published by Davies *et al.*[31] and with almost identical hfs constants [a^{H2} (2 H) = 0.316, a^{H3} (2 H) = 0.053, a^{H4} (1 H) = 0.63 mT; lit.,[31] a^{H2} (2 H) = 0.315, a^{H3} (2 H) = 0.051, a^{H4} (1 H) = 0.63 mT]. 4,4′-Bitoluene, also in fully deuteriated form or with the methyl groups deuteriated, in HFP-Tl$^{\mathrm{III}}$ at 22 °C gave persistent solutions of its radical cation ($\tau_{\frac{1}{2}} \approx$ 1 h) with a very strong and well resolved EPR spectrum [a^{Me} (6 H) = 0.875, a^{H2} (4 H) = 0.266, a^{H3} (4 H) = 0.013 mT; lit.,[32] a^{Me} (6 H) = 0.88, a^{H2} (4 H) = 0.265, a^{H3} (4 H) = 0.008 mT]. This radical cation was previously prepared by XeF$_2$ oxidation[32] of 4,4′-bitoluene or toluene in dichloromethane at −70 °C or by Tl$^{\mathrm{III}}$ oxidation in trifluoroacetic acid at −16 °C.[3] Tl$^{\mathrm{III}}$ oxidation of 4,4′-di-*tert*-butylbiphenyl in HFP gave a highly persistent radical cation with a fully resolved EPR spectrum [$\tau_{\frac{1}{2}} \approx$ 25 h; a^{H2} (4 H) = 0.265, a^{H3} (4 H) = 0.0095, $a^{\mathrm{Bu^t}}$ (18 H) = 0.039 mT; lit.,[33] a^{H2} (2 H) = 0.267, $a^{\mathrm{Bu^t}}$ (18 H) = 0.039 mT], previously generated by SbCl$_5$ oxidation[33] of 4,4′-di-*tert*-butylbiphenyl in dichloromethane at −70 °C or by Co$^{\mathrm{III}}$ trifluoroacetate oxidation of *tert*-butylbenzene in dichloromethane–trifluoroacetic acid at −30 °C.[34] Another biphenyl derivative previously studied by XeF$_2$ oxidation at low temperature, 3,3′,4,4′,5,5′-hexamethylbiphenyl, gave a fully resolved EPR spectrum in HFP–Tl$^{\mathrm{III}}$ at 22 °C [$a^{\mathrm{4\text{-}Me}}$ (6 H) = 0.876, $a^{\mathrm{3\text{-}Me}}$ (12 H) = 0.013, a^{H2}

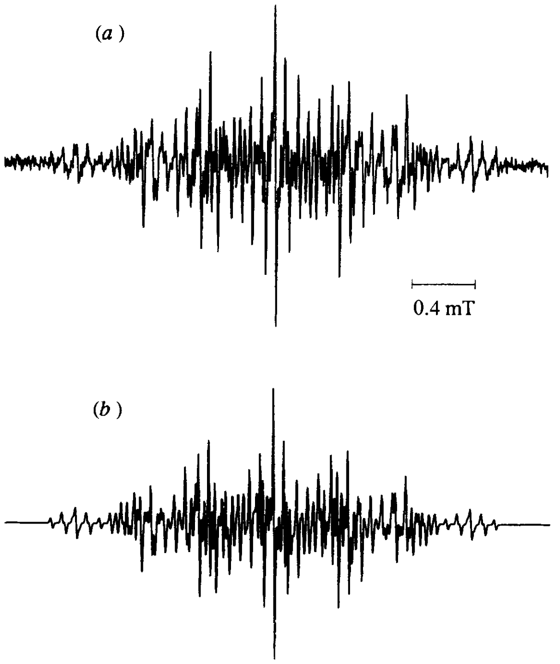


Fig. 4 (*a*) EPR spectrum of a solution of phenanthrene (5 mmol dm^{-3}) and Tl$^{\mathrm{III}}$ (15 mmol dm^{-3}) in HFP at 22 °C. (*b*) Simulated Lorentzian spectrum, using hfs coupling constants given in the text and a linewidth of 0.02 mT.

(4 H) = 0.250 mT; lit.,[32] $a^{\text{4-Me}}$ (6 H) = 0.877, a^{H2} (4 H) = 0.243 mT]. This radical cation had $\tau_{\frac{1}{2}} = 0.1$ h. Finally, 4,4′-difluorobiphenyl was oxidized by Tl$^{\mathrm{III}}$ in HFP at 22 °C and gave its radical cation [a^{F} (2 F) = 2.00, a^{H2} (4 H) = 0.276 mT, a^{H3} (4 H) unresolved; lit.,[32] a^{F} (2 F) = 1.93, a^{H2} (4 H) = 0.273 mT, a^{H3} (4 H) < 0.005 mT].

The radical cations of (*E*)-stilbene (**15**) and phenanthrene (**16**) were previously[35] generated by irradiation of the substrate in trifluoroacetic acid in the presence of Hg$^{\mathrm{II}}$ trifluoroacetate at −7 to 15 °C. We obtained an almost identical spectrum from the treatment of (*E*)-stilbene by Tl$^{\mathrm{III}}$ in HFP at 22 °C [$a^{\text{H-olefinic}}$ (2 H) 0.457, $a^{\mathrm{H4,4'}}$ (2 H) 0.457, $a^{\mathrm{H2,2',6,6'}}$ (4 H) 0.232, $a^{\mathrm{H3,3',5,5'}}$ (4 H) 0.070 mT; lit.,[35] $a^{\text{H-olefinic}}$ (2 H) 0.453, $a^{\mathrm{H4,4'}}$ (2 H) 0.453, $a^{\mathrm{H2,2',6,6'}}$ (4 H) 0.278, $a^{\mathrm{H3,3',5,5'}}$ (4 H) 0.0715 mT] but not from phenanthrene. The reason for the discrepancy was traced to the fact that commercial phenanthrene contains 1–2% anthracene which is enriched by recrystallization from ethanol. Any attempt to record a radical cation EPR spectrum from this material resulted in the appearance of the thermodynamically more stable radical cation of (anthracene)$^{\bullet +}$ For complete removal of anthracene, oxidation of the phenanthrene sample by a deficit of chromic acid in HOAc was necessary.[36] With the purified sample, the spectrum of Fig. 4(*a*) was recorded in HFP at 22 °C, using Tl$^{\mathrm{III}}$ as the oxidant. A simulated spectrum with the hfs constants $a^{\mathrm{H1,8}}$ (2 H) 0.422, $a^{\mathrm{H2,7}}$ (2 H) 0.086, $a^{\mathrm{H3,6}}$ (2 H) 0.383, $a^{\mathrm{H4,5}}$ (2 H) 0.070 and $a^{\mathrm{H9,10}}$ (2 H) 0.489 mT is shown in Fig. 4(*b*). These hfs constants are in good agreement with the theoretically calculated ones.[35]

Triptycene upon oxidation by Tl$^{\mathrm{III}}$ in HFP gave a solution of its radical cation which persisted long enough (8–10 min) for a resolved EPR spectrum to be recorded [a^{H1} (6 H) = 0.018, a^{H2} (6 H) = 0.226, $a^{\text{bridgehead-H}}$ (2 H) = 0.0095 mT; lit.,[23] a^{H1} (6 H) = 0.0175, a^{H2} (6 H) = 0.228, $a^{\text{bridgehead-H}}$ (2 H) = 0.0071 mT].

The radical cations of 1,4- and 1,5-dimethylnaphthalene (**17** and **18**) were obtained in HFP at 22 °C, using Tl$^{\mathrm{III}}$ as the oxidant but not with the tolyl-Tl$^{\mathrm{III}}$ reagent, and had half-lives of 5–10 min. The strong and well-resolved EPR spectra corresponded to those of the monomeric radical cations.[37,38] Previous recordings include generation by anodic oxidation at −80 °C in dichloromethane–trifluoroacetic acid (5%)–trifluoroacetic anhydride (5%) or SbCl$_5$ oxidation in dichloromethane–sulfur dioxide at −(60–80) °C.

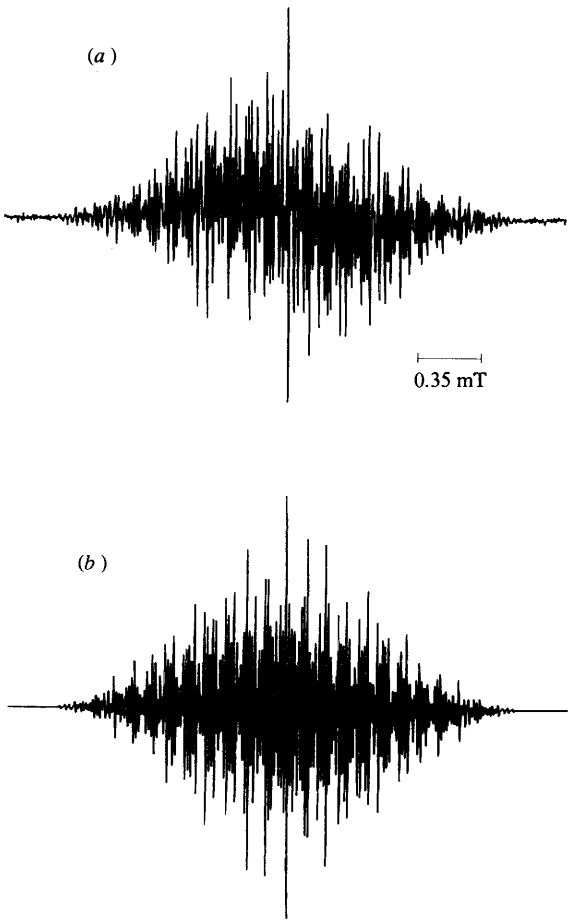
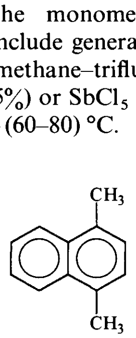


Fig. 5 (*a*) EPR spectrum of a solution of 1,1′-binaphthalene (5 mmol dm^{-3}) and Tl$^{\mathrm{III}}$ (15 mmol dm^{-3}) in HFP at 22 °C. (*b*) Simulated Lorentzian spectrum, using hfs coupling constants given in the text and a linewidth of 0.025 mT.



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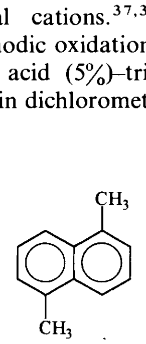

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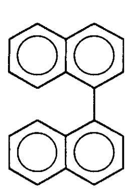

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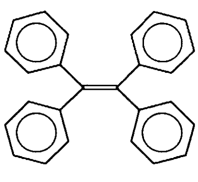
The radical cation of 1,1′-binaphthalene (**19**) was easily generated in HFP–Tl$^{\mathrm{III}}$ at 22 °C and gave a strong and well resolved EPR spectrum (Fig. 5), simulated by the following hfs constants: a^{H} (2 H) 4.58, 2.26 (2 H), 1.87 (2 H), 1.19 (2 H), 1.06 (2 H), 0.54 (2 H) and 0.31 (2 H) mT.

Tetraphenylethylene (**20**) upon oxidation with tolyl-Tl$^{\mathrm{III}}$ in



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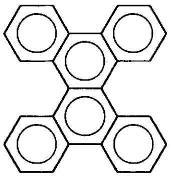

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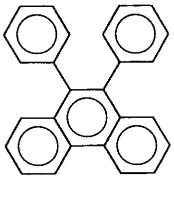

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HFP gave a well resolved spectrum of its radical cation [a (4 H) = 0.201, a (8 H) = 0.150, a (4 H) = 0.090 (4 H), a^{H} (4 H) = 0.0083 mT; lit.,[22] a^{H2} (8 H) = 0.206, a^{H3} (8 H) = 0.052, a^{H4} (4 H) = 0.293 mT]. Clearly these parameters define distinctly different spectra, since the width difference alone is about 0.5 mT; however, the published spectrum (obtained by $SbCl_5$ oxidation at −70 °C) appears to be very similar to ours. We therefore assume that the tetraphenylethylene radical cation was observed in both cases and that this species exists as a less symmetrical conformer than that corresponding to an 8:8:4 hydrogen pattern. When instead the stronger oxidant, Tl^{III}, was employed for oxidation of tetraphenylethylene, further oxidation and double cyclization gave the radical cation of dibenzo[*a*,*c*]triphenylene **21** [a^{H4} (4 H) = 0.230, a^{H3} (4 H) = 0.0, a^{H2} (4 H) = 0.200, a^{H1} (4 H) = 0.059 mT; lit.,[39] a^{H4} (4 H) = 0.228, a^{H3} (4 H) < 0.003, a^{H2} (4 H) = 0.199, a^{H1} (4 H) = 0.060 mT], presumably *via* the monocyclized product, 9,10-diphenylphenanthrene (**22**). The latter in itself was not oxidized by tolyl-Tl^{III}, but gave the radical cation of dibenzo[*a*,*c*]triphenylene when treated by Tl^{III}.

Use of HFP as solvent for anodic electrochemistry

As expected, the radical cation stabilizing properties of HFP also manifested themselves in studies of the anodic oxidation of ArH. With tetrabutylammonium hexafluorophosphate (0.15 mol dm^{-3}) as the supporting electrolyte, cyclic voltammetry demonstrated reversible electrochemical behaviour for the following substrates (sweep rate/V s^{-1}): anthracene (≥0.2), 1,3-benzodioxole (≥0.05), durene (> 1) and phenanthrene (> 5).

Use of 2,2,2-trifluoroethanol as solvent for radical cation generation

With 3,3′,4,4′-tetramethyl-1,1′-binaphthalene as the substrate and Tl^{III} as the oxidant, it was established that this solvent was approximately equivalent with trifluoroacetic acid in its radical cation stabilizing properties ($\tau_{\frac{1}{2}}$ about 0.1 h in both solvents). The radical cation of biphenylene, as generated by Tl^{III}, had $\tau_{\frac{1}{2}}$ = 0.5 h in trifluoroethanol, compared with > 100 h in HFP and 3.5 h in trifluoroacetic acid.

Discussion

Solvent properties of HFP

The persistence of radical cations in HFP is high, as seen from the data described above, and allows for the recording of well resolved EPR spectra of many radical cations which previously had to be generated by flow methods or at low temperatures. Also for normally persistent radical cations, the quality of the EPR spectra is improved significantly. In most cases, HFP is better in this respect than the previously most employed solvent, trifluoroacetic acid. As discussed below, this finding is not expected from a consideration of the measured solvent parameters of HFP which, although favourable for stabilization of electrophilic species, are not nominally as good as those of trifluoroacetic acid.

HFP is a liquid boiling at 59 °C and with a melting point of −4 °C. Its relative permittivity is 22.3, less than that of trifluoroacetic acid (39) but higher than that of dichloromethane (8.9). As shown above, the persistence of radical cations in HFP increases by a factor of about 100 compared with the previously most favourable solvent in this respect, trifluoroacetic acid. Nucleophilicities (*N*, measured by the methyl tosylate method) and p*K*s of a number of solvents of interest[40] are summarized below.

Solvent	p*K*	*N*
HFP	9.3	−4.9
Trifluoroacetic acid	0.3	−5.6
2,2,2-Trifluoroethanol	12.8	−3.0, −2.7
Acetic acid	4.8	−2.4
Ethanol–water (80:20)	≈15	0.0

In spite of the fact the trifluoroacetic acid on this scale is a less nucleophilic solvent than HFP, the ability of the latter to stabilize radical cations is much more pronounced. There is no ready explanation for this effect, unless one is prepared to discuss a differential 'special stabilizing effect' of the CF_3 group of the molecule toward electrophilic centres, as proposed by Dannenberg.[41] This idea has been experimentally tested for stabilization of radical cations by trifluoroacetic acid in a different context,[42] but no special effect was noted for trifluoroacetic in comparison with other strong acids. Only the p*K* appeared to determine the stability of radical cations, indicating that the predominant effect of trifluoroacetic acid would be to protonate nucleophilic impurities and thus suppress their reactivity. However, this property can hardly be of importance of HFP, with a much higher p*K* than trifluoroacetic acid.

We are thus left with somewhat of a paradox: HFP is a much weaker acid and has significantly higher nucleophilicity, as measured by the *N* scale, than trifluoroacetic acid, yet is a far better solvent for sustaining the stability of radical cations. If there is a special stabilizing effect by CF_3, both solvents should possess this property, as also should 2,2,2-trifluoroethanol. Most probably, the *N* scale, defined by the kinetics of methyl tosylate solvolysis, is not an adequate measure of the ability of a solvent to stabilize radical cations.

Properties of oxidants

The data in Table 3 show the very high persistence of radical cations in HFP compared with trifluoroacetic acid when tolyl-Tl^{III} is used as the oxidant. As seen from Tables 1 and 2, this is a relatively mild reagent which does not oxidize aromatic compounds with $E°(ArH^{•+}/ArH)$ ≥ *ca.* 1.6 V. The small effect seen upon addition of 5% trifluoroacetic acid is most likely due to an increase in the oxidizing power of tolyl-Tl^{III} (Table 2). On the other hand, Tl^{III} is far more reactive, with a borderline to unreactive substrates around 2.1 V, and a corresponding capacity to promote further reactions of the primary radical cations formed or, possibly, of dications formed from reactive substrates. Tetraphenylethylene (**20**) exemplifies this behaviour, in that it has been shown by cyclic voltammetry that it can be transformed into the radical cation (at 1.32 V) and that cyclization to 9,10-diphenylphenanthrene (**22**) takes place *via* disproportionation of the radical cation to the dication.[17] This means that oxidation of **20** by tolyl-Tl^{III} will give a solution of the radical cation which will slowly decay *via* disproportionation–cyclization to **22**, the latter not being oxidized by tolyl-Tl^{III}. If Tl^{III} is used instead, direct oxidation to $\mathbf{20}^{2+}$ can take place, cyclization to **22** becomes very fast, and the only EPR spectrum seen will be that of $\mathbf{21}^{\bullet +}$.

We have shown recently[6] that the $1e^-$ oxidation of hexamethylbenzene by Tl^{III} in trifluoroacetic acid proceeds *via* a complex mechanism, in that the 'decay' of the radical cation is actually controlled by its *slow formation* from Tl^{III} and hexamethylbenzene. In itself, the hexamethylbenzene radical cation is a very reactive species, as was indicated from the very early studies of its reactivity.[7] Similar behaviour has been found for 4,4′-bitoluene oxidation by Tl^{III}. Since the same type of behaviour applies to Tl^{III} oxidation of hexamethylbenzene or 4,4′-bitoluene in HFP, it appears possible that the favourable properties of Tl^{III} as a radical cation generating agent are at least partially dependent upon this kinetic feature. Whether tolyl-Tl^{III} displays the same behaviour is not yet established.

It should be emphasized that the low acidity of HFP should be an advantage for generating radical cations from acid-sensitive systems.

Experimental

Materials

1,1,1,3,3,3-Hexafluoropropan-2-ol was of highest commercial quality available (Aldrich, Sigma). 4-Tolylthallium(III) bis(trifluoroacetate) was synthesized according to a literature procedure.[9] Most compounds used were either commercially available or available from earlier work.[5,6,43] The following compounds were prepared according to published procedures: 9,10-diphenylphenanthrene,[44] pentamethylanisole,[45] 4-methoxy-1,3-benzodioxole,[45] 3,3′,4,4′,5,5′-hexamethylbiphenyl,[46] ($^2H_{14}$)-4,4′-bitoluene,[47] 4,4′-($^2H_6$)bitoluene,[47] 4,4′-di-*tert*-butylbiphenyl[48] and dibenzo[*a*,*c*]-triphenylene.[49] 2,2′-Bithiophene, 2,5-dimethylthiophene and 2,5-diphenylselenophene were kindly supplied by Dr A.-B. Hörnfeldt, University of Lund. The diacetonide of 1,2,4,5-tetrahydroxybenzene, as well as 1,2,4,5-tetrahydroxybenzene itself, was a gift from Dr L.-G. Wistrand, Nycomed Innovation AB, Malmö. Phenanthrene, in its commercial quality containing 1–2% of anthracene, was purified by treatment with chromium trioxide in acetic acid.[36]

Methods

EPR spectra were recorded by the Upgrade Version ESP 3220-200SH of a Bruker ER-200D spectrometer. Photolyses were performed in the photolysis cavity (ER 4104 OR), using unfiltered light from a 50 W high-pressure Hg lamp from Bruker (ER 202). The substrate (0.1–0.5 mg) was dissolved (complete dissolution was not always feasible) in 0.70 cm^3 of HFP and the solution bubbled with argon on the EPR sample tube. The oxidant (2–4 mg) was added in solid form and bubbling continued (total period 2 min). The tube was then sealed and the EPR spectrum recorded at room temperature (100 kHz modulation frequency, microwave effect 0.4–1.6 mW, modulation amplitude 0.001–0.02 mT).

Cyclic voltammetry was performed in dichloromethane–Bu_4NPF_6 (0.15 mol dm^{-3}), using a BAS-100 instrument.

Other compounds studied

Except for compounds listed in the tables, the EPR spectra of a number of other compounds were recorded in HFP, using either tolyl-Tl^{III} or Tl^{III} as the oxidant, and generally were found to be of excellent quality. These compounds included (the references given are to earlier reports of EPR spectra; unless otherwise noted, hfs constants of spectra in HFP differed only marginally from those obtained in other systems): 1,4-dimethoxybenzene,[25] 4,4′-dimethoxybiphenyl,[50] octamethyl-4,4′-dimethoxybiphenyl-1,4-benzodioxane,[25] 1,3,5,7-,[51] 1,4,5,7-, 1,4,5,8-[52] and 1,4,6,7-tetramethylnaphthalene,[38] pyrene,[39] 4,4′-dimethoxy-1,1′-binaphthalene,[43b] 4,4′-($^2H_6$)-4,4′-dimethoxy-1,1′-binaphthalene,[43b] 9,10-dimethylanthracene,[39] 9,10-diphenyl-2,3,6,7-tetramethoxyanthracene,[12a] perylene,[39] 1,2,3,4,5,6,7,8-octamethylanthracene,[12a] pentacene,[39] 1,2,3,4,5-pentamethylcyclopentadiene,[53] 1,2-benzanthracene,[39] 9,9′-bianthracene, 9,9′-bifluorenylidene,[39] benzo[*a*]pyrene,[54] *N*-methylphenothiazine,[55] *N*-methyl-2-phenylindole,[56] 2,4,6-tri(*tert*-butyl)nitrosobenzene,[57] 2,5-di-(*tert*-butyl)-1,4-dimethoxybenzene,[43a] tetra(4-methoxyphenyl)ethylene,[58] 4-methyl-1-methoxynaphthalene, the diacetonide and bis(perdeuterioacetonide) of 1,2,4,5-tetrahydroxybenzene, dodecahydrotriphenylene,[59] 2,5-dimethylthiophene[60] and 2,5-diphenylselenophene.[61]

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