PERKIN 2

Authentic *versus* alternative mechanisms in spin trapping. Formation of azide spin-adducts in biphasic and non-aqueous systems by the oxidation of azide anion with a variety of hydrazyl radicals

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The formation of azide spin-adducts of a number of spin-traps, including PBN, DMPO, DEPMPO and TBNB, in biphasic and organic media has been studied by EPR spectroscopy. A series of hydrazyl radicals has been employed to oxidise the azide anion to the corresponding short-lived azido radical, which is subsequently trapped. The approach has typically involved the presence of the ether 18-crown-6 in order to facilitate the transport of the azide anion from water into the organic media, with further experiments in non-aqueous systems. The results can largely be rationalised in terms of a "conventional" spin-trapping mechanism, with an efficiency that depends on the relevant redox potentials, which are themselves solvent dependent; however, conditions that favour direct oxidation of the trap have also been identified. It is also established that the azide spin-adducts of some nitrones can be transformed, under certain conditions, into secondary spin-adducts by nucleophilic substitution reaction of the first-formed nitroxides.

Introduction

It is well established that the so-called "stable" free radical 2,2-diphenyl-1-picrylhydrazyl [DPPH (**1**, $R^1 = R^2 = H$)] can act as an effective one-electron oxidant.[1–4] The related radicals 2-*p*-nitrophenyl-2-phenyl-1-picrylhydrazyl [NO_2DPPH (**1**, $R^1 = H$, $R^2 = NO_2$)] and 2,2-bis(*p*-nitrophenyl)-1-picrylhydrazyl [$(NO_2)_2$DPPH (**1**, $R^1 = R^2 = NO_2$)] have also been prepared and some of their reactions reviewed;[1–4] although the oxidation potential of only DPPH itself has been reported ($E_{\frac{1}{2}} = 0.03$ V *vs.* SCE in acetonitrile,[5] $E_{\frac{1}{2}}$ from 0.18 V *vs.* SCE in acetonitrile up to 0.35 V *vs.* SCE in DMSO[6]) it is expected that NO_2DPPH, and $(NO_2)_2$DPPH would be more powerful oxidants.

The reactivity of these organo-soluble oxidants has also been extended by the use of crown ethers to bring about phase transfer, and hence to encourage oxidation, of water-soluble reagents (see *e.g.* ref. 4). Investigation of this type of novel chemistry has led to the use of EPR spectroscopy, with spin trapping, to study the reaction of DPPH and its derivatives with a number of anions (including HO^-, NO_2^-, CN^- and BPh_4^-) in a two-phase system (liquid–liquid or liquid–solid), in the presence of a crown ether and a nitrone spin-trap.[1–4] Detection of the appropriate nitroxides by EPR spectroscopy suggests the occurrence of reactions (1) and (2), whereby one-

$$\text{DPPH}^{\bullet} + \text{Nu}^{-} \longrightarrow \text{DPPH}^{-} + \text{Nu}^{\bullet} \qquad (1)$$

$$\text{Nu}^{\bullet} + \text{ST} \longrightarrow \text{ST–Nu}^{\bullet} \qquad (2)$$

electron oxidation of the anion (transported into the organic phase) is evidently brought about by the hydrazyl radical: signals of "$HO^{\bullet}$ adducts" and species derived from $^{\bullet}NO_2$ were obtained from DPPH itself with the spin-trap PBN, and adducts of $^{\bullet}CN$ and $Ph^{\bullet}$ were detected with the better oxidant $(NO_2)_2$DPPH.[4] However, at this stage two further possible mechanisms of reaction of the oxidant should be considered—namely, nucleophilic addition followed by oxidation [the so-called Forrester–Hepburn mechanism, reactions (3) and (4)],[5,7]

$$\text{ST} + \text{Nu}^{-} \longrightarrow \text{ST–Nu}^{-} \qquad (3)$$

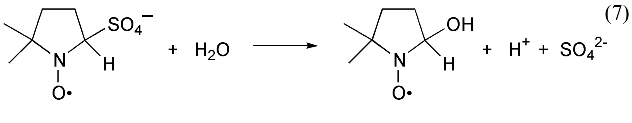
$$\text{ST–Nu}^{-} + \text{DPPH}^{\bullet} \longrightarrow \text{ST–Nu}^{\bullet} \qquad (4)$$

and oxidation of the trap to a radical-cation followed by nucleophilic attack [a process which Eberson named "inverse spin-trapping", as shown in reactions (5) and (6)].[5,7] A further

$$\text{DPPH}^{\bullet} + \text{ST} \longrightarrow \text{DPPH}^{-} + \text{ST}^{+\bullet} \qquad (5)$$

$$\text{ST}^{+\bullet} + \text{Nu}^{-} \longrightarrow \text{ST–Nu}^{\bullet} \qquad (6)$$

mechanistic possibility for formation of adducts of this type involves the nucleophilic substitution reaction of a first-formed adduct, as described for the conversion of the sulfate radical-anion adduct of DMPO into the "hydroxyl" radical-adduct, in aqueous solution [reaction (7)].[8–10]



(7)

In a programme designed to explore the possible occurrence of alternative mechanisms under specific circumstances, we have utilised the azide anion as the nucleophile (Nu^-), with several spin-traps including, *N-tert*-butyl-α-phenylnitrone (PBN, **2**), 5,5-dimethyl-4,5-dihydro-3*H*-pyrrole *N*-oxide (DMPO, **3**), 5-diethoxyphosphoryl-5-methyl-4,5-dihydro-3*H*-pyrrole *N*-oxide (DEPMPO, **4**) and 2,4,6-tribromonitrosobenzene (TBNB, **5**); most of our experiments have involved the use of the oxidants DPPH, NO_2DPPH and $(NO_2)_2$DPPH in dichloromethane together with aqueous solutions of sodium

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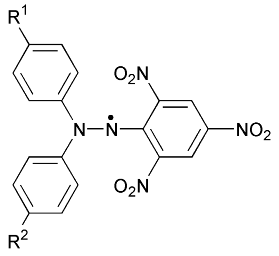

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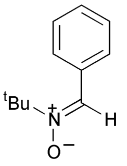
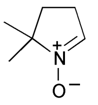


PBN

2



DMPO

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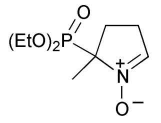
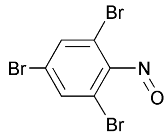


DEPMPO

4



TBNB

5

azide, and in the presence or absence of the ether 18-crown-6 as potential interphase carrier. We have examined the EPR spectra of any aminoxyls formed and also followed the disappearance of the DPPH radicals by EPR and UV–vis spectroscopy.[3] Water-soluble reagents (hydrazyl and spin-traps) have also been employed, and similar experiments conducted in organic and mixed organic solvents. Cyclic voltammetry has been employed to determine the oxidation potentials of the hydrazyl radicals in organic media.

Results and discussion

(a) Background EPR experiments with hydrazyl radicals (1), spin-trap and crown ether: experiments in dichloromethane and in biphasic media

The hydrazyl radicals were prepared as described previously[2] and used as (stable) solutions in dichloromethane. We first performed experiments to establish whether there is any reaction between the hydrazyl radicals and some individual reaction components (spin-traps or crown ether).

(i) Experiments with DPPH (1, $R^1 = R^2 = H$). EPR and UV–vis measurements established that DPPH itself (at concentrations of 10^{-3} mol dm^{-3}) did not react with any of the spin-traps (STs) **2**–**5** employed (at concentrations of typically 10^{-3}–10^{-2} mol dm^{-3}) in CH_2Cl_2 (experiment 1, see Table 1). DPPH was also found to be long-lived in the presence of 18-crown-6 (10^{-3}–10^{-2} mol dm^{-3}, experiment 2), and with a mixture of 18-crown-6 and the spin-traps (experiment 3). Experiment 4 involved a liquid–liquid biphasic system (DPPH in dichloromethane, sodium azide in water); again no reaction was observed as indicated by experiments involving EPR and UV–vis studies of both phases. Further, no reaction was found to occur when experiments 1–3 were repeated in biphasic systems (dichloromethane–water, 1 : 1 v/v) or when experiment 4 was carried out in a solid–liquid biphasic system (DPPH in dichloromethane, solid sodium azide). Addition of N_3^- (10^{-1} mol dm^{-3}) to experiments with spin-traps and/or 18-crown-6 (experiments 5–7) had no observable effect. At this stage, we can rule out the occurrence of reactions (1) and (2) and also (5) and (6); if any nucleophilic adduct is formed then it is presumably not oxidised under these conditions. We note, however, that it has been shown that DPPH can oxidise the nucleophilic adducts formed from reaction of N-heteroaromatic bases with spin-traps.[5]

Table 1 Results for the reactions of hydrazyl radicals (**1**) in biphasic (dichloromethane–water) systems monitored by EPR and UV–vis spectra

Experiment	Hydrazyl	ST	18-Crown-6	NaN_3	Reaction
1	+	+	−	−	No
2	+	−	+	−	No
3	+	+	+	−	No
4	+	−	−	+	No
5	+	+	−	+	No
6	+	−	+	+	No[a]/Yes[b]
7	+	+	+	+	No[a]/Yes[b]

[a] Only in the case of DPPH. [b] For $NO_2DPPH^•$ or $(NO_2)_2DPPH^•$ radicals.

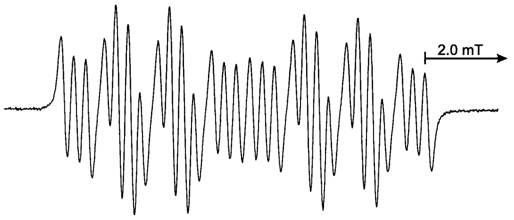
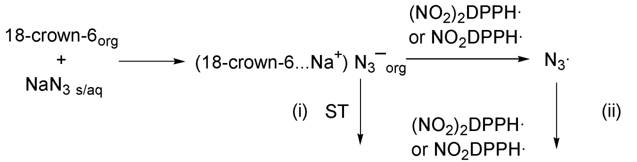


Fig. 1 EPR spectrum of **8**, the azide radical adduct of DEPMPO in dichloromethane, formed in the reaction of $(NO_2)_2DPPH$ with azide anion in the presence of DEPMPO and using the ether 18-crown-6 as a phase-transfer catalyst.

(ii) Experiments with NO_2DPPH and $(NO_2)_2DPPH$. As with DPPH, there was found to be no reaction with the spin-traps (with or without 18-crown-6). However, in the presence of N_3^-, spin-trap (**2**, **3** or **4**) and phase-transfer agent the EPR spectra showed the rapid disappearance of the hydrazyl radical (confirmed by UV–vis spectroscopy) and the appearance of the characteristic signals of the azide spin-adducts **6**–**8**[11,12] (for EPR parameters, see Table 2: see also Fig. 1). Similar experiments with the inclusion of the nitroso spin-trap **5** also led to the disappearance of the hydrazyl and the appearance of a new EPR signal, attributed to the azido-derived species **9**. (Reactions of this type and the appropriate assignments have been discussed previously.[13,14])

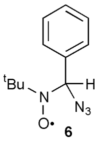
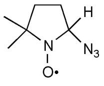
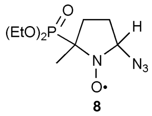
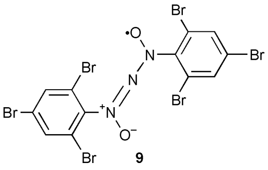
We conclude that the hydrazyls NO_2DPPH and $(NO_2)_2$-DPPH are considerably more effective oxidants than DPPH itself, that the crown ether is essential (presumably to carry N_3^- into the organic layer) and that two mechanistic possibilities remain: firstly, nucleophilic addition of azide to the spin-trap, followed by oxidation of the nucleophile-adduct $ST–N_3^-$ to a spin-adduct $ST–N_3^•$, and secondly generation of the $N_3^•$ radical (by one-electron oxidation by hydrazyl) followed by the conventional spin-trapping mechanism (see Scheme 1). Since the nitrated hydrazyls were found to react extremely rapidly with N_3^- itself [as indicated by an immediate disappearance of the typical hydrazyl colour on addition of the anion (in experiment 6) *i.e.* without the spin trap], we believe that the initial electron-transfer, pathway (ii) occurs, and that our results point to the occurrence of a *bona fide* spin-trapping process. We note that oxidation of N_3^- occurs readily in dichloromethane and expect that nitrated hydrazyls are much more effective when there is no (stabilising) hydration of the anion (see later for investigations in different solvents and for discussion of $E^\ominus$ values).



Scheme 1

Reaction of $(NO_2)_2DPPH$ with azide in the presence of 18-crown-6 and *N-tert*-butyl-α-(2-sulfophenyl)nitrone (2-SPBN used as the sodium salt, which is soluble only in the aqueous

Table 2 EPR hyperfine splittings (in mT ± 0.005) for the spin-adducts of the azide radical (in dichloromethane)

Spin adduct		a_N	a_H	a_N(Azide)	a_P
 6	PBN–$N_3^{\bullet}$	1.405	0.195	0.195	—
 7	DMPO–$N_3^{\bullet}$	1.335	1.22	0.335	—
 8	DEPMPO–$N_3^{\bullet}$	1.295	1.05	0.300	4.595
 9	“TBNB–$N_3^{\bullet}$”[a]	0.700	—	0.700(1) 0.305(1)	—

[a] See references 13 and 14.

phase) gave no EPR signals in the aqueous phase and, perhaps surprisingly, weak EPR signals from the azide adduct in the organic phase. We believe this observation reflects the presence of a small amount of the spin-trap carried into the organic phase by the crown ether, with other reactions as noted above.

(iii) Reaction of a water-soluble hydrazyl ^-O_3S–DPPH (1, $R^1 = SO_3^-$, $R^2 = H$) with azide. Addition of sodium azide to an aqueous solution of the sodium salt of the water-soluble hydrazyl ^-O_3S–DPPH (**1**, $R^1 = SO_3^-$, $R^2 = H$) and spin-trap (**2**–**5** or 2-SPBN) showed no apparent reaction detectable by either UV–vis or EPR spectroscopy. Negative results were also obtained using biphasic systems (water–dichloromethane) which contained ^-O_3S–DPPH, sodium azide and any of the spin-traps.

(iv) Attempted formation of spin-adducts using other oxidants. We also employed another organo-soluble oxidant, galvinoxyl (itself a “stable” free radical) as potential oxidant in the biphasic system, but no reaction occurred, as with DPPH; this is perhaps not surprising since the redox potential of galvinoxyl is less than that of DPPH ($E_{\frac{1}{2}}$ −0.32 V *vs.* SCE in acetonitrile).[5]

However, by stirring solid sodium azide with the spin-trap (PBN) and 18-crown-6 in dichloromethane, followed by addition of the stronger oxidant lead dioxide, we detected the corresponding azide adduct by EPR [for spin-trap **2**], but only after a few minutes and at low intensity. These findings are in marked contrast with the results for NO_2DPPH and $(NO_2)_2$DPPH, which react to give very strong EPR signals. The lack of a strong signal (as described above) suggests there is little effective electron-transfer in this case and that a nucleophilic adduct (which we would expect to be oxidisable by PbO_2) has not been formed.

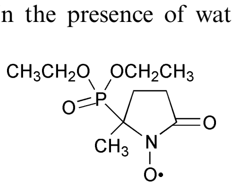
(b) Reactions in other solvent systems (monophasic)

We extended our study to the investigation of the reactions of the hydrazyl radicals [DPPH, NO_2DPPH and $(NO_2)_2$DPPH] in the presence of sodium azide, with spin-traps PBN and DEPMPO, but without the phase-transfer agent, in methanol as well as the dipolar aprotic solvents acetonitrile and DMF.

In methanol, a very weak EPR signal of the azide–PBN adduct was detected for reaction with NO_2DPPH and $(NO_2)_2$DPPH; there was no change on addition of *ca.* 20% water. Reaction of the azide anion with NO_2DPPH and $(NO_2)_2$DPPH in methanol with DEPMPO as the spin trap gave an EPR spectrum from the methoxide adducts. Under these conditions, nucleophilic substitution of the initially formed DEPMPO–azide adduct occurs to give the methoxide adducts (see below) by reaction with the methanol. In the absence of azide, no adducts were observed.

In acetonitrile, we were unable to detect spin-adducts in the presence of PBN using any of the hydrazyl oxidants, possibly on account of the relative insolubility of the sodium azide in the organic solvent. However, on addition of water (*ca.* 20%), to bring about dissolution, we recorded relatively strong signals from the azide–PBN adduct in the reactions of NO_2DPPH and $(NO_2)_2$DPPH. Experiments with DEPMPO and NO_2DPPH or $(NO_2)_2$DPPH in acetonitrile, in the presence or absence of azide anion, led to the detection of an EPR signal of the radical **10** (with a_P 37.26, a_N 6.85 and a_H 3.29 mT)[14] evidently formed by direct oxidation of the trap; addition of water (*ca.* 20% v/v) led to an increase in signal intensity. This process may involve reactions (5) and (6), followed by further oxidation.

In DMF (in which all reagents are soluble), signals from the azide–PBN adduct were obtained from all three hydrazyl oxidants, these being relatively strong for NO_2DPPH and $(NO_2)_2$DPPH. With DEPMPO, reaction of NO_2DPPH and $(NO_2)_2$DPPH, in the absence of azide, led to the observation of the radical **10**. In the presence of water, signals from the appropriate hydroxyl adduct (see Table 3) were observed. We believe that this is formed *via* reactions (5) and (6), but under these conditions the adducts are less prone to further oxidation.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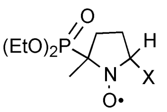
The positive results for azide ion oxidation in acetonitrile and DMF can be rationalised in terms of the increased solubility and lower $E^{\ominus}$ values for oxidation of N_3^- in dipolar aprotic solvents (a value of 0.8 V *vs.* SCE has been reported for dichloromethane and acetonitrile, compared with the value of 1.1 V *vs.* SCE in water[15]). This decrease is believed to reflect the decreased solvating ability for the anion (N_3^-) in the aprotic

Table 3 EPR hyperfine splittings (in mT ± 0.005) for DEPMPO spin-adducts (in dichloromethane)

	X	a_N	a_H	a_P
	H$^•$	1.40	1.85 (2H)	5.10
	HO$^{•a}$	1.34	1.29	4.685
	MeO$^•$ *cis*^{b}	1.30	0.758	3.955
	MeO$^•$ *trans*^{b}	1.265	0.62	4.67

^{a} In DMF. ^{b} *cis* and *trans* isomers, relative concentrations *ca.* 1 : 3.

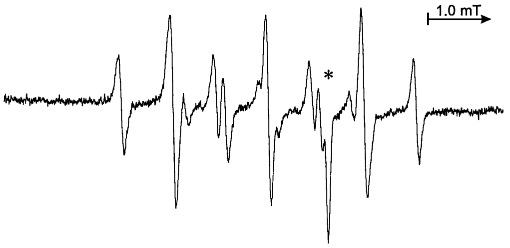


Fig. 2 EPR spectrum of the hydrogen-atom adduct of PBN in dichloromethane formed by reaction of the PBN–azide adduct, **6**, with sodium borohydride using the ether 18-crown-6 as a phase-transfer catalyst. The peak marked * is due to the quartz cell.

solvents, as noted above. The oxidation by NO_2DPPH and $(NO_2)_2DPPH$ of the trap DEPMPO (as shown by the detection of radical **10** and the hydroxyl adduct) presumably reflects more effective electron-transfer [reaction (5)] brought about by an increase in $E^{\ominus}$ for the nitrosubstituted hydrazyls and an apparent decrease in the oxidation potential of this trap in polar solvents (see next section).

(c) Electrochemical measurements and mechanistic conclusions

In order to allow a more quantitative assessment of the likelihood of direct electron-transfer reactivity (rather than addition–oxidation) of the series of hydrazyl radicals, we recorded cyclic voltammograms of each hydrazyl in acetonitrile (for details, see Experimental section). The values (*vs.* SCE) for the redox potentials were found to be 0.30 (DPPH), 0.49 (NO_2DPPH) and 0.60 V [$(NO_2)_2DPPH$]. For the sulfonated derivative (**1**, $R^1 = SO_3^-$, $R^2 = H$) $E^{\ominus}$ is 0.34 V. These results confirm that, as expected, the introduction of the nitro groups increases the oxidation potential, encouraging one-electron oxidation of azide anion in acetonitrile and DMF and, we presume, DEPMPO.

(d) Experiments involving nucleophilic substitution on spin-adducts

We finally explored the possibility that the spin-adducts react with other nucleophiles, thus converting an azide spin-adduct into a new spin-adduct. This type of reaction has previously been observed for the sulfate radical-anion adduct of DMPO,[8–10] which is converted into the DMPO–OH spin adduct in the presence of water [reaction (7)].

When a solution containing the azide spin-adduct of PBN in dichloromethane was allowed to react with added sodium borohydride, sodium tetraphenylborate, sodium hydroxide or sodium methoxide (at concentrations typically 10^{-2} mol dm^{-3}) the characteristic EPR spectrum of the azide adduct was rapidly replaced by that of a different adduct over a period of *ca.* 1–10 minutes (typically with a_N 1.35–1.45 and a_H 0.28 mT). For the borohydride reaction, the adduct is recognisable as that of the hydrogen atom by two large proton splittings (a_N 1.507, a_{2H} 0.795 mT, see Fig. 2). The identity of the other adducts is more difficult to determine since resolution is limited, hence experiments were carried out using DEPMPO.

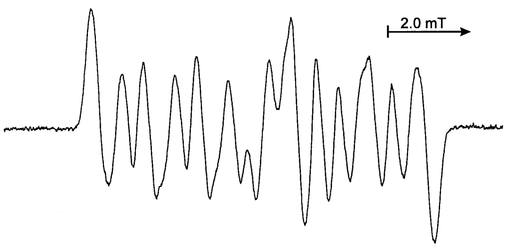


Fig. 3 EPR spectrum of the *cis* and *trans* methoxide adducts of DEPMPO (~1 : 3) in dichloromethane formed by reaction of the DEPMPO–azide adduct, **8**, with sodium methoxide using the ether 18-crown-6 as a phase-transfer catalyst.

Analogous experiments with the azide spin-adduct of DEPMPO showed some interesting features. In the case of sodium borohydride, the initial azide spin-adduct is converted into the hydride adduct of DEPMPO (for coupling constants see Table 3). For sodium methoxide (added as a supramolecular complex with 18-crown-6) the initial spectrum of azide adduct was quickly replaced by that of the methoxide adducts (see Table 3 and Fig. 3), but after a few minutes, a new spectrum appeared, with hyperfine coupling constants a_N 1.37, a_H 2.00, and a_P 4.71 mT. The latter spectrum is similar to that formed during the substitution of the sulfate-radical anion adduct of DEPMPO (where it is accompanied by the HO$^•$ adduct) and is characteristic of the formation and subsequent reaction (inter or intra) of the radical-cation of DEPMPO.[16] The intermediate methoxide adducts formed are a 1 : 3 mixture of the *cis* and *trans* isomers, from which it is inferred that the substitution occurs *via* an S_N1 type process.

Conclusion

It has been shown that azide spin-adducts of the spin-traps PBN, DMPO, DEPMPO and TBNB are readily obtained in the organic phase starting from sodium azide (transferred into the organic phase by 18-crown-6) and a stable nitro-substituted hydrazyl free radical, which acts as a one-electron oxidant; $E^{\ominus}$ values for the latter are considerably higher than DPPH. The pathway leading to spin-adduct formation is a genuine spin-trapping reaction [reaction (1)], but some artefactual reactions may also be invoked to explain other observations (for example, DEPMPO oxidation). Azide spin-adducts can themselves be transformed *via* S_N1 chemistry into other secondary species.

Experimental

All substances were purchased from Aldrich or Lancaster in highest purity and used as received. EPR spectra were recorded at room temperature using a JEOL JES-RE1X spectrometer. NO_2DPPH and $(NO_2)_2DPPH$ free radicals were prepared as described previously.[2]

Generation of the ST–N$_3^•$ spin-adduct

A solution in dichloromethane of 18-crown-6 (10^{-3}–10^{-2} mol dm^{-3}), the spin-trap (10^{-4}–10^{-3} mol dm^{-3}) and the hydrazyl radical (10^{-4}–10^{-3} mol dm^{-3}) was prepared to which solid sodium azide (10–50 mg) was added. The solution was stirred for a few seconds by bubbling oxygen-free nitrogen (OFN) and then the organic layer was studied by EPR or UV–vis. For reactions with NO_2DPPH and $(NO_2)_2DPPH$, on addition of the azide, a rapid colour change of the organic layer was observed (from violet to red) as the hydrazyl radical was reduced to the anion.

Nucleophilic substitution of the ST–N$_3^•$ spin-adduct

To a solution of ST–N$_3^•$, obtained as above, was added supramolecular complexes of sodium borohydride, hydroxide, tetraphenylborate or methoxide (obtained by stirring a solution of 18-crown-6 with the solid sodium salts). The EPR of the organic layer was then recorded.

Electrochemistry

Cyclic voltammetry was performed under nitrogen using a Princeton Applied Research Potentiostat 273A. Pt wire was used for the working and auxiliary electrodes, with Ag/Ag^+ as the reference electrode; the scan rate was typically 0.05–0.75 V s^{-1}. The concentration of hydrazyl was 10^{-2} M in dry acetonitrile containing the supporting electrolyte $(C_4H_9)_4N^+BF_4^-$ (0.1 M).

Acknowledgements

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