PERKIN 2 COMMUNICATION

Spin adduct formation from the spontaneous reaction between spin traps and weak electron acceptors, as exemplified by trichloroacetonitrile. An acid promoted version of the Forrester–Hepburn addition–oxidation mechanism

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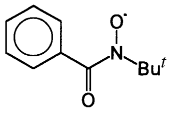
The thermal reaction between *N-tert*-butyl-α-phenylnitrone (PBN) and trichloroacetonitrile is promoted by acids HA, giving spin adducts A–PBN$^\bullet$ and $CCl_2{=}C{=}N$–PBN$^\bullet$, presumably *via* addition of HA to the nitrone with formation of a hydroxylamine and oxidation of the latter by trichloroacetonitrile (the Forrester–Hepburn mechanism).

It was recently reported[1] that the spin trap, *N-tert*-butyl-α-phenylnitrone (PBN)† undergoes spin adduct formation upon thermal reaction with certain cyanohalocarbons, for example, trichloroacetonitrile. This reaction type, spontaneous formation of spin adducts from a spin trap and a compound seemingly devoid of any appropriate reactivity, is common but little understood.[2] In view of our interest in non-conventional spin trapping mechanisms[3,4] and an ongoing study of cyanoalkyl radicals and their spin adducts, we attempted to repeat one of these experiments, namely the thermal reaction between PBN and trichloroacetonitrile in hexane.

However, the basic features described, slow formation (within hours) of substantial concentrations of *N-tert*-butylbenzoylnitrone (**1**, PBNOx), an undefined *O*-centred spin adduct (**2**, $a^N = 1.35$, $a^H = 0.17$ mT) and an *N*-centred spin adduct (**3**, $a^N = 1.45$, $a^H = 0.27$, $a^{N'} = 0.16$ mT) could not be reproduced in spite of much effort, using four commercial trichloroacetonitrile samples of different origin and age. Very long reaction times (4–8 h) sometimes gave extremely low concentrations of **3**, just enough to allow for the determination of approximate coupling constants. This behaviour pointed to some sort of catalytic influence of an impurity. Small amounts of added bases (1,4-diazabicyclo[2.2.2]octane or 2,6-di-*tert*-butylpyridine) had no effect, whereas dibenzoyl peroxide promoted the build-up of low concentrations of **3** (exp. 7 of Table 1), but unconvincingly and far from the reported levels.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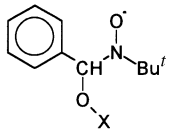
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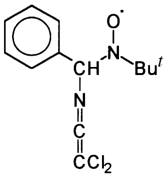
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We then suspected that an acidic species might cause the catalytic effect. Hydrogen chloride is a possible impurity in trichloroacetonitrile, and is known[4] to react with PBN and form the unstable chloro spin adduct in the presence of a weak electron transfer (ET) oxidant, in all probability by addition of HCl to the nitrone and oxidation of the intermediate hydroxylamine.[5] In the case of the trichloroacetonitrile–PBN system, such a reaction would lead to a mechanism of the type shown in eqns. (1)–(3), with A = Cl. Hydroxylamines are easily oxidized, in the range of −(0.2–0.3) V *vs.* SCE,[6] and Cl_3CCN should be a weak electron transfer oxidant with an estimated $E°(Cl_3CCN/Cl^-Cl_2C{-}CN^\bullet)$ around −0.5 V, as judged from a comparison with carbon tetrachloride.[7] The alternative cleavage mode of $Cl_3CCN^{\bullet-}$ to give $Cl^\bullet$ and $^-CCl_2CN$ is ruled out since such a step is *ca.* 2 eV less favourable, as judged by a consideration of the redox potentials of the various couples involved. Thus eqn. (2) is feasible from the viewpoint of ET theory.[8] The attack of $^\bullet CCl_2CN$ *via* the nitrogen [eqn. (3)] has precedents in the formation of ketenimines by self-coupling of other α-cyanoalkyl radicals, generated photochemically or electrochemically.[9] A similar autocatalytic mechanism was demonstrated[4] for the formation of the benzotriazolyl spin adduct from PBN and *N*-chlorobenzotriazole, a good electron acceptor, with benzotriazole as the autocatalytic species.

$$\text{PBN} + \text{HA} \longrightarrow \text{PBN(H)A} \tag{1}$$

$$\text{PBN(H)A} + Cl_3CCN \longrightarrow \text{A–PBN}^\bullet + H^+ + Cl^- + Cl_2C{=}C{=}N^\bullet \tag{2}$$

$$Cl_2C{=}C{=}N^\bullet + \text{PBN} \longrightarrow Cl_2C{=}C{=}N\text{–PBN}^\bullet \tag{3}$$

This assumption was seemingly verified by the addition of a deficit of tetraphenylphosphonium chloride–trifluoroacetic acid (simulating HCl) to [α-^{2}H]PBN (to simplify the EPR spectrum) and trichloroacetonitrile in hexane, leading to relatively fast growth of spin adduct [^{2}H]**3** and a second spin adduct [^{2}H]**4** with $a^N = 1.27$ mT and an unresolved hydrogen coupling (see Table 1, exp. 2). However, the reproducibility of this experiment was not satisfactory, the EPR intensity varying by an order of magnitude between runs. Also, experiments in which solely gaseous HCl had been added to the hexane solvent failed to give any spin adducts.

The next trace impurity suspected was the Fe^{III}/Fe^{II} system. Trichloroacetonitrile is prepared commercially by treatment of acetonitrile with chlorine, conditions which might leave trace impurities of iron chloride in the final product.[10] Addition of a deficit of anhydrous $FeCl_2$ (at 'saturation level' in hexane) and trifluoroacetic acid to the mixture of PBN and CCl_3CCN caused a rapid growth of the EPR spectrum of **3** and **4** (now also showing the hydrogen coupling of 0.14 mT, expt. 3, Table 1). Again, the reproducibility of this experiment was not convincing; spectra appeared in most cases but their intensities varied greatly between runs.

The coupling constants of spin adduct **4**, $a^N = 1.27$ and $a^H = 0.14$ mT, are characteristic of an acyloxyl spin adduct,[11] in all probability CF_3COO–PBN$^\bullet$. Thus, it was possible that trifluoroacetic acid itself could play the role of the HA species in eqns. (1)–(3). This was verified by expts. 1 and 4 of Table 1, in which only trifluoroacetic acid was added as the promoter, leading for the first time to reproducible experiments. Trichloroacetic acid, a possible trace impurity in trichloroacetonitrile, worked equally well as a promoter (expts. 5 and 6, Table 1, and Fig. 1).

In order to increase the nucleophilicity of the A moiety, 3-chloroperoxybenzoic acid was used as a promoter, giving spin adduct **3** and PBNOx **1** (Fig. 2, see also expts. 8 and 9, Table 1) in rapid reactions. The spin adduct initially formed from the

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† IUPAC name: *N*-(Benzylidene)-*tert*-butylamine *N*-oxide.

Table 1 Hyperfine coupling constants of the spin adducts observed from the reaction between PBN or [α-^{2}H]PBN (0.10 mol dm^{-3}) and trichloroacetonitrile (0.3 mol dm^{-3}) in hexane in the presence of acid, HA (0.02–0.04 mol dm^{-3})

		Spin adduct **3**			Second spin adduct		PBNOx **1**
Expt.	HA	a^N/mT	$a^{N'}$/mT	a^H/mT	a^N/mT	a^H/mT	a^N/mT
1	CF_3COOH	1.42	0.15	0.29	1.25	0.14	—
2	CF_3COOH–Ph_4PCl[a]	1.44	0.16	*b*	1.27	*b*	—
3	CF_3COOH–$FeCl_2$	1.43	0.15	0.27	1.26	0.14	0.78
4	CF_3COOH[a]	1.44	0.16	*b*	1.27	*b*	—
5	CCl_3COOH	1.44	0.14	0.26	1.25	0.13	—
6	CCl_3COOH[a]	1.44	0.16	*b*	1.24	*b*	—
7	$(PhCOO)_2$[a]	1.43	0.16	*b*	1.30	*b*	—
8	$3\text{-}ClC_6H_4CO_3H$	1.44	0.14	0.27	—	—	0.79
9	$3\text{-}ClC_6H_4CO_3H$[a]	1.44	0.16	0.040[d]	—	—	0.79
10	HCN	1.45	0.15	0.28	—	—	—
11	'Uncatalysed'[c]	1.45	0.16	0.27	1.35	0.17	0.80

[a] [α-^{2}H]PBN was used. [b] Could not be resolved. [c] Data from Sang *et al.* [d] Coupling to deuterium.

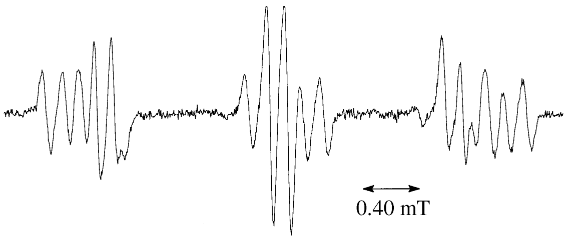

Fig. 1 EPR spectrum of a solution of PBN (0.1 mol dm^{-3}), trichloroacetonitrile (0.3 mol dm^{-3}) and trichloroacetic acid (0.02 mol dm^{-3}) in hexane, recorded 1 h after mixing (Table 1, expt. 5)

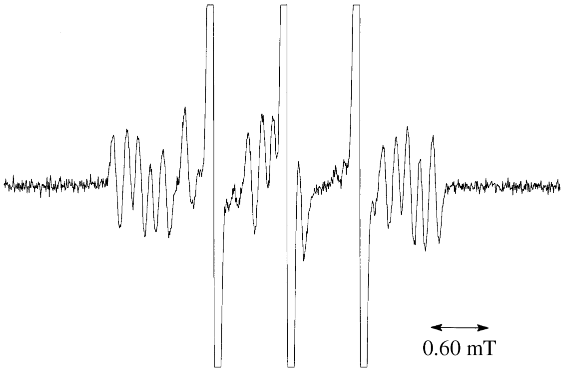

Fig. 2 EPR spectrum of a solution of PBN (0.1 mol dm^{-3}), trichloroacetonitrile (0.3 mol dm^{-3}) and 3-chloroperoxybenzoic acid (*ca.* 0.004 mol dm^{-3}) in hexane, recorded 20 min after mixing (Table 1, expt. 8)

peracid, of type ArCOOO–PBN$^•$, is apparently unstable and rapidly converted to PBNOx. Finally, the promoting ability of HCN was demonstrated in expt. 10, yielding **3**; no other spin adduct could be seen. In hexane, NC–PBN$^•$ gave an EPR spectrum of $a^N = 1.47$ and $a^H = 0.17$ mT when generated by air oxidation of the hydroxylamine NC–PBN(H)‡ but its stability was low, $\tau_{1/2} = 22$ min, explaining why no second spin adduct was seen on the timescale of expt. 10 (several hours).

In the study by Sang *et al.*,[1] the second spin adduct **2** was found to have the coupling constants $a^N = 1.35$ and $a^H = 0.17$ mT. It was assumed to be an *O*-centred spin adduct, and in view of the results described above it seems that an impurity of hydroperoxide type might be the origin of **2**.

Thus we conclude that the reaction between PBN and trichloroacetonitrile is promoted by acids HA, in all likelihood by a version of the Forrester–Hepburn mechanism[5] in which HA is added to PBN, followed by oxidation of the hydroxylamine derivative formed. Trichloroacetonitrile is a weak electron acceptor, capable of slowly oxidizing PBN(H)A to give A–PBN$^•$ and the dichlorocyanomethyl radical which is trapped by PBN to give **3**. This explains the appearance of the two spin adducts in approximately equal concentrations and, in addition, the appearance of PBNOx, the product formed by further reaction of a reactive spin adduct.

This type of mechanism is probably the origin of many spin trappings in which a spin trap and a weak acceptor react 'spontaneously', for example *N*-haloimides,[13] 3-chloroperoxybenzoic acid,[14] *N*-chlorosulfonamides[15] and *N*-fluorodibenzenesulfonimide.[16]

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‡ NC–PBN$^•$ was prepared in an unambiguous way, namely by treatment of PBN by trimethylsilyl cyanide[12] to give NC–PBN($SiMe_3$), followed by hydrolysis of the latter and oxidation of the hydroxylamine NC–PBN(H) by air.