Photoactivated formation of hydrogen spin adduct from phenylsilane. A new example of inverted spin trapping?

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Photodissociation of phenylsilane was studied by EPR spectroscopy using *N*-benzylidene-*tert*-butylamine *N*-oxide (PBN) and bis(benzene)chromium (BBC) as spin trapping systems. Under controlled UV irradiation and in the presence of dioxygen, hydrogen spin adducts were detected. Conditions for the formation and stability of the adducts have been studied. A mechanism involving "inverted spin trapping" was propounded that implies photoactivation of the spin traps followed by the formation of the superoxide radical ion $O_2^{\bullet-}$ and the abstraction of H^- from phenylsilane.

Introduction

It is well known[1] that arylsilanes have a tendency to decompose in the presence of light but the corresponding pathway for this reaction is still not clear. Attention was focused on the possible formation of arylsilyl radicals[2,3] and the use of spin traps to detect spin adducts by EPR, but some of these results did not seem to be conclusive.

In the course of our investigations on bis(benzene)chromium [$(\eta^6\text{-}C_6H_6)_2Cr$] (BBC) (**I**), we have recently shown that this sandwich compound under certain circumstances acts as a spin trap,[4] for instance towards hydrogen radicals generated by photodissociation of phenylsilane, $PhSiH_3$. Subsequent studies revealed that **I** is also an active catalyst for hydrosilylation and dehydrocoupling reactions.[5]

This prompted us to investigate more thoroughly the mechanism of interaction between **I** and arylsilanes. However, as we showed in our previous work,[4] identification of spin adducts with **I** is not straightforward by EPR and requires tedious ENDOR measurements. As a model spin trap system, we were therefore led to use *N*-benzylidene-*tert*-butylamine *N*-oxide, $PhCH{=}N(O)C(CH_3)_3$ (PBN)[6,7] (**II**). In this work we propose a possible pathway for the formation of the hydrogen adduct of **I** that involves the "inverted spin trapping" mechanism previously reported for **II**, throwing new light on the unusual reactivity of **I**.

Experimental

EPR spectra were recorded with a Bruker 220 D X-band spectrometer equipped with a standard TE102 cavity and a variable temperature accessory for temperatures in the range 100 K < T < 300 K. Photolysis was performed with a 250 W Xe lamp or in daylight either inside the cavity for **I** or outside the cavity for **II**. **I** was obtained following a literature procedure[8] or purchased from STREM. **II** and phenylsilane were used as received and kept under argon. Toluene and hexane were dried and distilled before use. In a typical experiment, degassed solvent was introduced under argon into a quartz tube containing **I** or **II**. After vigorous shaking to ensure complete dissolution of the solid, phenylsilane was then added to obtain **I**–silane or **II**–silane in molar ratios of *ca.* 1 : 50. In this case, traces of air are considered to be unavoidably present in the reaction media.

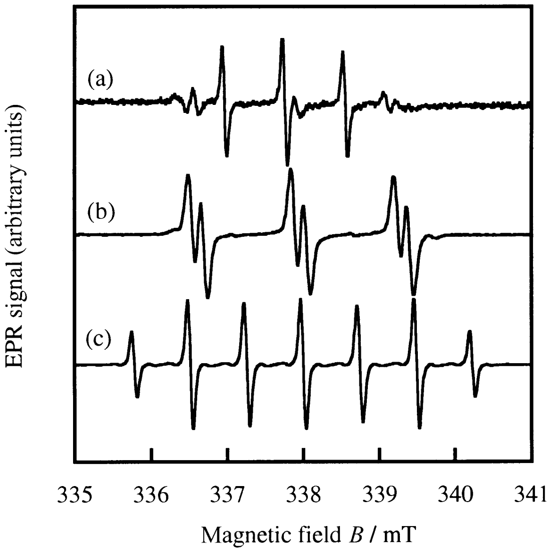

Fig. 1 EPR spectra recorded at room temperature of irradiated PBN solution (a) and (b) without phenylsilane, (c) in the presence of phenylsilane.

Results

Spin adduct formation

As a first step, and in the absence of silane, the effect of irradiation of solutions of **I** in toluene and of **II** in toluene and hexane was monitored by EPR. When exposed to daylight at room temperature, **II** gave rise to two superimposed weak signals: a 1 : 1 : 1 triplet ($a(^{14}N) = 0.79$ mT) due to the carbonylaminoxyl radical [$PhCON(O^{\bullet})t$Bu][9] (Fig. 1(a)) and a doublet of triplets ($a(^{14}N) = 1.35$ mT, $a(^{1}H) = 0.17$ mT) that could be tentatively attributed to peroxy adducts[10] (Fig. 1(b)). The relative intensities of these two signals depend on the solvent and irradiation time, the peroxy contribution being enhanced

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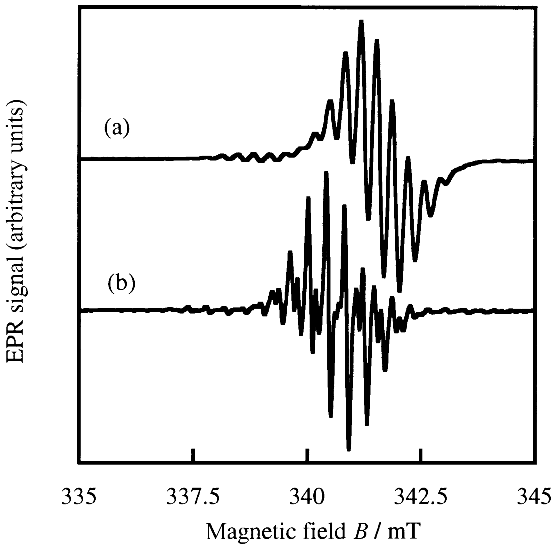

Fig. 2 EPR spectra recorded at 240 K of (a) BBC$^{\bullet +}$ and (b) BBC–H$^{\bullet}$.

when the Xe lamp was used as a focalized source of light. In the case of **I** at 240 K, irradiation leads to a multiplet centered at $g = 1.987$ ($a(^{1}H) = 0.35$ mT, $a(^{53}Cr) = 1.81$ mT) characteristic of the BBC$^{\bullet +}$ radical cation[11] (Fig. 2(a)). It is therefore clear that irradiation of these two systems mainly leads to their oxidation. In the presence of $PhSiH_3$, irradiation of solutions of **I** and **II** in toluene results in the formation of their previously described[4] hydrogen spin adducts (BBC–H$^{\bullet}$ and PBN–H$^{\bullet}$). The EPR spectrum of PBN–H$^{\bullet}$ at 300 K is a triplet (N) of triplets (2H) ($a(^{14}N) = 1.53$ mT, $a(^{1}H) = 0.73$ mT) (Fig. 1(c)) while BBC–H$^{\bullet}$ exhibits at 240 K an octet ($a = 0.39$ mT) of triplets ($a = 0.635$ mT) centered at $g = 1.991$ (Fig. 2(b)). However, it is worth noting that no $PhSiH_2^{\bullet}$ radical adduct could be detected with certainty, in agreement with previous observations.[2,3] Moreover, the same H-adducts were detected with diphenylsilane but not with triphenylsilane.

Influence of light

These studies also revealed that daylight was sufficient for the rapid formation of spin adducts of **I** and **II** in the presence of $PhSiH_3$. This contrasts with conditions required for the generation of silyl radicals from silanes (photosensitisation of *tert*-butyl peroxide,[2] long irradiation time using a Hg lamp or ^{60}Co γ-rays[3])[12] and led us to compare the conditions for the formation of **II** adducts using two different sources of light, daylight and a Xe lamp. As shown in Fig. 3, daylight irradiation leads to the slow formation of the PBN–H$^{\bullet}$ adduct while with a Xe lamp the EPR signal increases rapidly but then falls dramatically after 10 minutes.

Further information was obtained when samples of **II** in quartz tubes (transparent to UV) and glass tubes (filtering most of the UV component of the spectrum) were irradiated at 300 K in daylight. As is clearly seen in Fig. 4, cutting off UV light suppresses the EPR signal, thus indicating that UV light is necessary for the formation of the PBN–H$^{\bullet}$ adduct signal. Finally, when samples were kept in the dark, no signal appeared.

Influence of temperature

Another question we addressed was the possible thermal activation of the reaction. We first noted that a sample of **II** kept in the dark and heated from 300 to 350 K did not show any significant EPR signal. However, a clear difference in behaviour was observed when comparing irradiation at 300 and 340 K in daylight. As shown in Fig. 5, after 20 minutes, the higher temperature gives a more intense signal. If the light is then turned off,

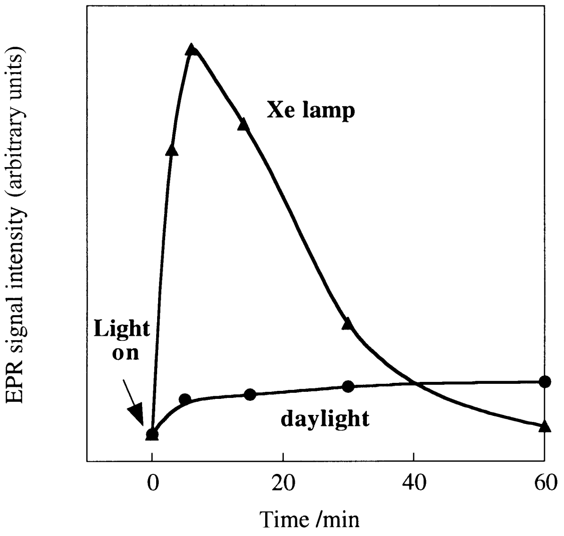

Fig. 3 Variation of the intensity of the EPR signal of a $PhSiH_3$–PBN solution in toluene at 300 K under: ▲, Xe lamp irradiation; ●, daylight irradiation.

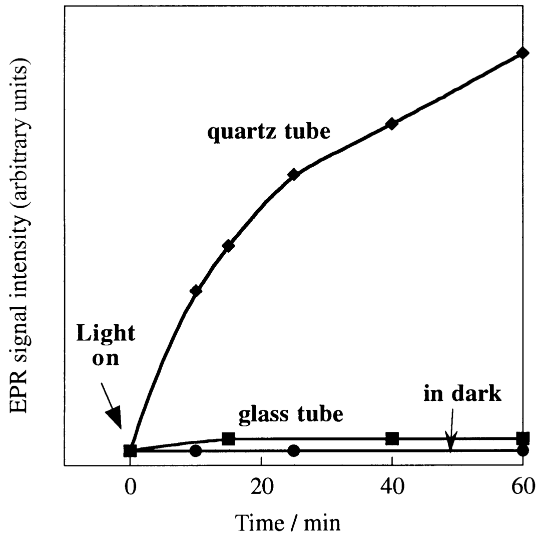

Fig. 4 Variation of the intensity of the EPR signal of a $PhSiH_3$–PBN solution in toluene at 300 K: ◆, in a quartz tube under daylight irradiation; ■, in a glass tube under daylight irradiation; ●, kept in the dark.

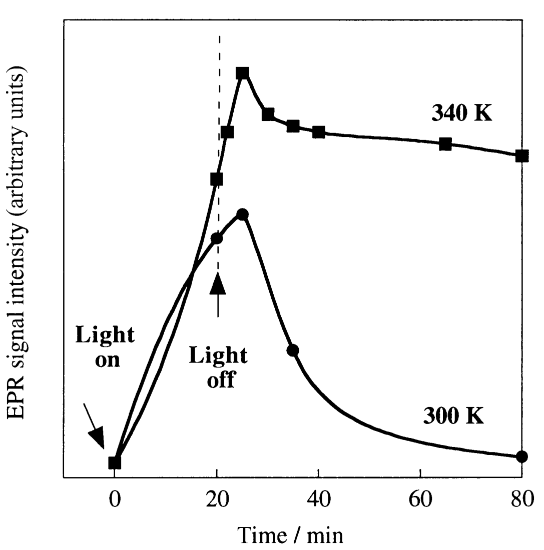

Fig. 5 Variation of the intensity of the EPR signal of a $PhSiH_3$–PBN solution in toluene: ■, at 340 K; ●, at 300 K. The solution was irradiated for 20 min under daylight and then kept in the dark.

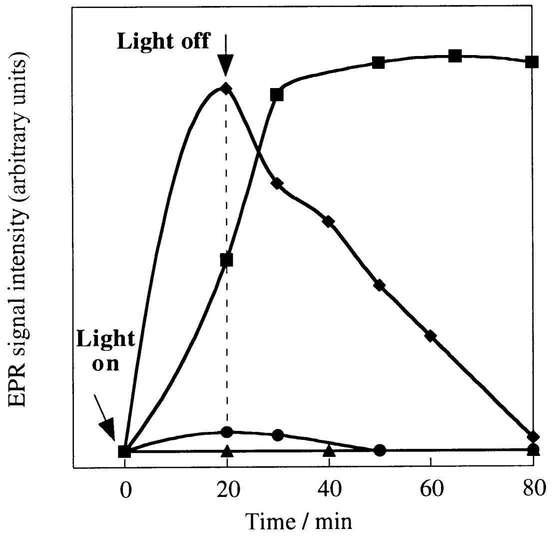

Fig. 6 Variation of the intensity of the EPR signal of a $PhSiH_3$–BBC solution in toluene at 240 K under daylight irradiation: ●, kept under argon; ■, with traces of air; ◆, air-prepared sample; ▲, after O_2 bubbling. The solution was irradiated for 20 min under daylight and then kept in the dark.

the signals continue to increase for about 5 minutes. Subsequently, the 300 K sample signal undergoes a rapid decay while a slower decrease is observed at 340 K. Similar experiments with **I** were not conclusive because spectra had to be recorded at 240 K so that the effect of temperature was difficult to monitor.

Influence of dioxygen

In the course of this study, the poorly reproducible EPR signal intensities of some of our experimental data led us to investigate the effect of sample preparation conditions. Of particular interest was the role of the dioxygen content that is frequently involved in metal-centered reactions. Solutions of **I** in toluene were therefore prepared in the presence of variable amounts of dioxygen. For this purpose, samples prepared in the manner described in the Experimental section, thus containing traces of air, were compared with samples carefully kept under argon, with samples left *ca.* one minute in the presence of air and with solutions submitted to O_2 bubbling for *ca.* one minute. Fig. 6 shows that the presence of oxygen is necessary for the formation of the BBC–H$^\bullet$ signal but that an excess of oxygen is detrimental to the stability of this adduct, an EPR signal corresponding to BBC$^{\bullet+}$ being observed in the case of the O_2-bubbled sample. The same trends were observed for **II** (not shown here).

Discussion

It has been previously demonstrated[4] that **I** is able to trap radicals with well-known radical sources and forms H-adducts in the presence of phenylsilane under photolysis. However, $PhSiH_3$ for instance has not been reported to release easily radical species so that the role of **I** in this system was to be investigated. Moreover, hydrogen spin adducts were also obtained with the widely studied PBN spin trap offering a basis for comparison.

In this context, it has been reported[9,13] that, parallel to the traditional trapping route involving the addition of a radical R$^\bullet$ to PBN [eqn. (1)], two other pathways could lead to the formation of the PBN–R$^\bullet$ adduct. The first one is related to the possibility of nucleophiles/bases (R$^-$) adding to PBN [eqn. (2)],

$$\mathrm{R^\bullet + ST \longrightarrow R{-}ST^\bullet} \qquad (1)$$

$$\mathrm{R^- + ST \leftrightarrow R{-}ST^- \xrightarrow{Ox} R{-}ST^\bullet} \qquad (2)$$

the addition product being then easily oxidized to PBN–R$^\bullet$. The other mechanism, denoted "inverted spin trapping", implies oxidation of PBN to its radical cation PBN$^{\bullet+}$ which then reacts with R$^-$ to give the same spin adduct [eqn. (3)].

$$\mathrm{ST \xrightarrow{-e^-} ST^{\bullet+} \xrightarrow{R^-} ST{-}R^\bullet} \qquad (3)$$

Moreover, it was shown[9] that photoactivation of PBN using UV irradiation could either favour nucleophilic attack [eqn. (2)] or, in the presence of a weak electron acceptor, lead to PBN$^{\bullet+}$ formation [eqn. (3)]. This is all the more important in that the EPR spectrum of BBC–H$^\bullet$ was initially reported as the result of the reaction between the cation BBC$^{\bullet+}$ and H$^-$ sources.[14] Moreover, we have shown in this study that irradiation of **I** under trace amounts of oxygen tends to favour its oxidation to BBC$^{\bullet+}$. However, such an "inverted spin trapping" pathway implies that bond breaking of phenylsilane is of a heterolytic (and not homolytic) nature. Note that such an ionic mechanism is in agreement with the fact that silane decomposition occurs here under far milder conditions than those usually reported for silyl radical formation. Moreover, it provides an explanation as to why we could not detect silyl spin adducts during our EPR investigations. The question then arises: by what mechanism does H$^-$ abstraction from $PhSiH_3$ occur?

The determining role of dioxygen in the adduct formation suggests that activated forms of O_2 could be involved in the reaction. In the course of our studies on the catalytic properties of BBC, we have recently demonstrated that the KO_2–crown ether system was also an efficient catalyst for hydrosilylation reactions.[15] Such a system leads to stable superoxide $O_2^{\bullet-}$ anion solutions in aprotic media.[16] $O_2^{\bullet-}$ was reported to make a nucleophilic attack on various substrates.[17] On the other hand the electronegativity (Pauling scale) of silicon is lower than that of hydrogen so that the Si atom in phenylsilane can undergo nucleophilic attack. Therefore, it seems plausible that interaction between superoxide[18] and $PhSiH_3$ could weaken the Si–H bond and lead to the release of H$^-$, this process being thermally enhanced. In this context, the absence of spin adduct formation with $(Ph)_3SiH$ would be attributed to steric hindrance.

Therefore, a mechanism for the spin trapping reaction can be proposed [eqn. (4)]. Steps (*i*) and (*iii*) have been discussed

$$\mathrm{ST \xrightarrow{(\mathit{i})\ \mathit{h\nu}} ST^* \xrightarrow{(\mathit{ii})\ O_S} ST^{\bullet+} + O_2^{\bullet-}}$$

$$\mathrm{ST^{\bullet+} + O_2^{\bullet-} \xrightarrow{(\mathit{iii})\ PhSiH_3} ST{-}H^\bullet + PhSiH_2^{+}{-}O_2^{\bullet-}} \qquad (4)$$

above. The fate of the reaction products is, at this time, difficult to determine.

The last point remaining to be addressed concerns $O_2^{\bullet-}$ formation (step (*ii*)). The redox potential for $O_2/O_2^{\bullet-}$ is reported to lie between −0.2 and −0.5 V *vs.* NHE depending on the reaction solvent.[16] As far as spin trap systems are concerned, PBN has an oxidation potential $E^{ox}_{1/2}$ (PBN/PBN$^{\bullet+}$) of 1.7 V *vs.* NHE in acetonitrile[9] whereas the half-wave reduction potential of BBC$^{\bullet+}$/BBC was found to be −0.50 V *vs.* NHE in DMF.[19] In both cases, we have shown that irradiation favours oxidation of photoactivated species so that step (*ii*) appears plausible. Finally, it is clear that direct interactions between **I** and phenylsilane could play a role in this process as reported for other organometallic catalytic systems[18] so that steps (*ii*) and (*iii*) proposed in eqn. (4) could in fact involve a single three-component (BBC, O_2, $PhSiH_3$) reaction. In such a system, we can postulate a cluster-like structure where dioxygen would act as a bridge for H$^-$ transfer between phenylsilane and BBC *via* electron transfer from BBC* to O_2. In this case, the formation of BBC–H$^\bullet$ would depend on the O_2 : BBC ratio. For

O_2 : BBC ≤ 1, all the dioxygen molecules are in the cluster so that only hydrogen adduct formation is possible. When O_2 is in excess, the possibility of direct interaction between BBC–H$^•$ and O_2 will arise so that BBC–H$^•$ adducts would be reoxidized. Larger O_2 contents would only give the BBC$^{•+}$ compound. Such a mechanism would be in good agreement with the observed effect of dioxygen content shown in Fig. 6.

Conclusion

This study is aimed at the understanding of the formation of hydrogen spin adducts from irradiated phenylsilane solutions and provides a new example of the "inverted spin trapping" phenomenon. Under the working conditions described, it appears that the photoactivated species formed are not the silane derivatives but the spin trap systems themselves due to the presence of dioxygen. However, it is clear that the rather unusual behaviour of bis(benzene)chromium as a rare example of a metal-centered spin trap is far from being fully understood.

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