An Electron Spin Resonance Study of the Arylsilyl Adducts of Phenyl *tert*-Butyl Nitrone and Their Decomposition Kinetics

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The formation and the stability of some arylsilyl adducts of phenyl *tert*-butyl nitrone were studied in a photochemical system using di-*tert*-butyl peroxide as solvent. The β-proton splittings of all the arylsilyl adducts, ranging from 5.6 to 8.3 G, are relatively larger than their carbon analogs, which are usually less than 4 G. The arylsilyl adducts are found to decompose in di-*tert*-butyl peroxide solvent by a first-order kinetics. The activation energy involved in the decomposition of a series of arylsilyl adducts varies from about 14 to about 9 kcal/mol, as the size of the silyl group increases. In all cases, very low values of the *A* factors (between 10^6 and 10^{10}) were observed.

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On a étudié la formation et al stabilité de quelques produits d'addition arylsilylés de la phényl *tert*-butyl nitrone dans un système photochimique utilisant le peroxyde de di-*tert*-butyle comme solvant. Les couplages des protons β de tous les produits d'addition arylsilylés qui s'étalent entre 5.6 et 8.3 G sont relativement plus larges que ceux de leurs dérivés carbonés analogues qui sont généralement de l'ordre de 4 G. On a trouvé que les produits addition arylsilylés se décomposent dans un solvant comme le peroxyde de di-*tert*-butyle par une cinétique du premier ordre. L'énergie d'activation impliqué dans la décomposition d'une série de produits d'addition arylsilylés varie de 14 à 9 kcal/mol au fur et à mesure que la grosseur du groupe silylé augmente. Dans tous les cas ou observe des valeurs très basses (entre 10^6 et 10^{10}) pour les facteurs *A*.

[Traduit par le journal]

Introduction

The technique of spin trapping (1) has been increasingly popular in mechanistic studies involving elusive free radical intermediates. The persistent failure of observing the e.s.r. spectrum of the triphenylsilyl radical in liquid solution in our laboratory has led us to consider the application of spin trapping methods. Thus in a related study we have shown that the presence of triphenylsilyl radicals can be detected by using benzophenone as the spin trap at high temperatures (2). Because the phenyl *tert*-butyl nitrone (PBN) has been widely used as a spin trap, we chose PBN in this study as traps to react with various arylsilyl radicals produced in a conventional photochemical system using *tert*-butyl peroxide as the solvent. Quantitative kinetic studies on the subsequent decomposition of these arylsilyl adducts were carried out. The results suggest that under the same experimental conditions, various arylsilyl radicals give spin adducts of different stability, hence different steady-state concentrations of the resulting adducts. The conclusion illustrates the point that for quantitative studies of the relative reactivity of free radicals in solution using the spin trapping techniques, steady-state intensities of the e.s.r. spectra of the various spin adducts are not reliable indications of the relative reactivity.

Experimental

Triphenylsilane (Alfa), diphenylsilane (K & K), phenylsilane (Alfa), phenyl *tert*-butyl nitrone (Eastman), and di-*tert*-butyl peroxide (K & K) were used as received. Use of zone-refined triphenylsilane gave identical results.

About 0.05 *M* solution of each of the nitrone and the silane was prepared in liquid di-*tert*-butyl peroxide (BOOB). Attempts have been made to use BOOB in a variety of common solvents, including benzene, cyclohexane, and carbon tetrachloride. The best results were obtained with BOOB as solvent.

In a typical experiment, the sample solution in a Pyrex tube was degassed thoroughly under 10^{-5} Torr vacuum. The sample tube was sealed and placed in an optical microwave cavity equipped with a variable temperature controller. The sample was irradiated *in situ* using a 200 W high pressure mercury lamp with Pyrex optics. The

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TABLE 1. Experimental e.s.r. parameters of the arylsilyl and B$\dot{O}$ adducts of phenyl *tert*-butyl nitrone in *tert*-butyl peroxide

Radical adduct	a_N (G)	$a_\beta{}^H$ (G)	g value
$Ph_3\dot{S}i$	14.5 ± 0.1	5.6 ± 0.1	2.0056 ± 0.0002
$Ph_2\dot{S}iH$	14.5 ± 0.1	7.5 ± 0.1	2.0057 ± 0.0002
$Ph\dot{S}iH_2$	14.8 ± 0.1	8.3 ± 0.1	2.0056 ± 0.0002
$(CH_3)_3\dot{S}i$	14.5 ± 0.1	6.0 ± 0.1	2.0057 ± 0.0002
$(CH_3)_3C\dot{O}$	14.0 ± 0.1*	1.6 ± 0.1	2.0056 ± 0.0002

*Somewhat larger values of a_N (14.22 G) and $a_\beta{}^H$ (1.95 G) observed in benzene solvent have been given by Janzen and Evans (3).

decay of the e.s.r. spectra between −20 and 30 °C was followed using a Hewlett Packard fast speed recorder with a response time better than 0.5 s. The decay curve of the e.s.r. signal monitored at the maximum of one of the outermost hyperfine lines was obtained after the light beam was cut off.

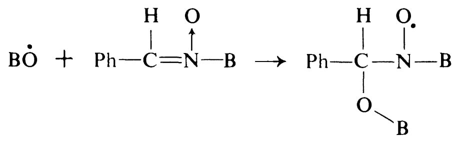
Electron spin resonance spectra were recorded with a Varian X-band spectrometer with 100 kHz modulation. The magnetic field was calibrated with a Varian F-8A fluxmeter and the g-value measurements were made with DPPH as a standard at 2.0036. Calibration of the absolute concentration of the radicals studied was found to be unnecessary, since they decay by first-order kinetics.

Results

Photolysis of BOOB in the Presence of Phenyl tert-Butyl Nitrone

At room temperature and without specific irradiation, the solution of phenyl *tert*-butyl nitrone in BOOB exhibits a weak e.s.r. signal. The intensity and resolution of the signal increased greatly upon irradiation. This spectrum has parameters similar to those of the butoxy radical adduct (3) (**1**) formed in the following reactions

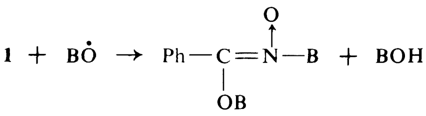
[1] $$BOOB + h\nu \rightarrow 2B\dot{O}$$

[2] 

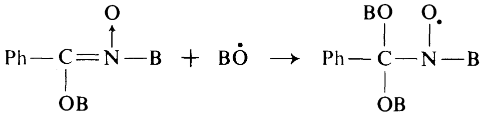
$$B\dot{O} + Ph{-}\overset{H}{C}{=}\overset{\overset{O}{\uparrow}}{N}{-}B \longrightarrow Ph{-}\underset{O-B}{\overset{H}{C}}{-}\overset{\dot{O}}{N}{-}B$$

1

The experimental hyperfine coupling constant for adduct **1** is listed in Table 1. Upon further irradiation, the doublet fine structure of the main triplet spectrum disappeared, leaving only a three-line spectrum with a splitting of 13.6 g. This is consistent with the following reaction scheme:

[3] 

$$\mathbf{1} + B\dot{O} \longrightarrow Ph{-}\underset{OB}{C}{=}\overset{\overset{O}{\uparrow}}{N}{-}B + BOH$$

[4] 

$$Ph{-}\underset{OB}{C}{=}\overset{\overset{O}{\uparrow}}{\dot{N}}{-}B + B\dot{O} \longrightarrow Ph{-}\underset{OB}{\overset{BO}{C}}{-}\overset{\dot{O}}{N}{-}B$$

2

It is reasonable to expect the radical adduct (**2**) to give a simple triplet spectrum with a nitrogen splitting in the order of 13 G. Further experiments show that in the presence of a better hydrogen donor such as silane, the triplet spectrum was not observed.

Photolysis of BOOB in the Presence of Triphenylsilane and Phenyl tert-Butyl Nitrone

Photolysis of this solution led to the observation of an e.s.r. spectrum shown in Fig. 1. This spectrum is analyzed into three component radicals; two of them are readily recognized by their hyperfine splittings as the BN($\dot{O}$)OB radical (4) and the butoxy adduct (**1**). The third radical has a triplet splitting of 14.5 G and a smaller doublet splitting of 5.6 G. Both the BN($\dot{O}$)OB radical and the third radical are found to be unstable in the dark. Considering analogous reactions (5) we *tentatively* assign the third radical to be the triphenylsilyl adduct, $PhCH(SiPh_3)N(\dot{O})B$. To support this assignment, we have made a thorough search for the ^{29}Si splitting. All attempts were unsuccessful and we suspect that the ^{29}Si splitting may be too small to be resolved, since the Si is in the γ-position (6). Nevertheless, in the absence of observable ^{29}Si splitting, the identification of this radical must remain tentative.

It is noted here that all reported spin adducts of the phenyl *tert*-butyl nitrone and either hydrocarbon radicals[2] or oxygen radicals have β-proton splittings less than 4 G and nitrogen splittings between 12 and 16 G (7). Only the

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[2] One of the referees had pointed out to us that the trifluoroacetyl spin adduct of PBN (see E. G. Janzen *et al.* (13)) is reported to have a β-proton splitting of 5.4 G.

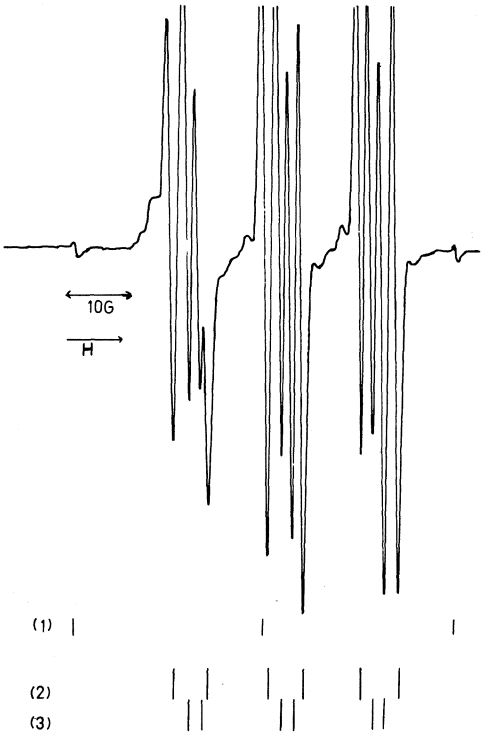


FIG. 1. Electron spin resonance spectrum obtained upon photolysis of BOOB in the presence of phenyl *tert*-butyl nitrone and triphenylsilane: (*1*) BN(Ȯ)OB; (*2*) the triphenylsilyl adduct; and (*3*) the butoxy adduct.

hydrogen adduct, $PhCH_2N(\dot{O})B$, has a larger β-proton splitting of 7.13 G (7). It is thus interesting to observe that the radical adducts in the arylsilane systems all have β-proton splittings substantially greater than 4 G (see Table 1).

Photolysis of BOOB in the Presence of Diphenylsilane and Phenyl tert-Butyl Nitrone

At room temperature and without irradiation, a liquid mixture of phenyl *tert*-butyl nitrone and diphenylsilane undergoes a thermal reaction producing the hydrogen adduct $PhCH_2N(\dot{O})B$. In the presence of BOOB, both the hydrogen adduct and the butoxy adduct (**1**) were observed without irradiation (Fig. 2). Upon photolysis of the solution, the hydrogen adduct disappeared and two other radicals were produced (Fig. 3): one is the BN(Ȯ)NB radical and the other radical has a triplet splitting of 14.5 G and a smaller doublet splitting of 7.5 G. This radical is *tentatively* assigned to the diphenylsilyl adduct $PhCH(SiHPh_2)N(\dot{O})B$.

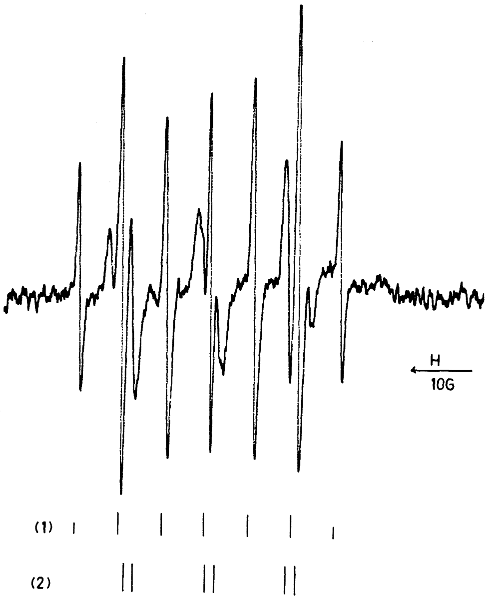


FIG. 2. Electron spin resonance spectrum obtained upon mixing at room temperature BOOB and diphenylsilane in the presence of phenyl *tert*-butyl nitrone: (*1*) $PhCH_2N(\dot{O})B$; (*2*) the butoxy adduct.

The disappearance of the hydrogen adduct upon photolysis is probably due to the reaction with the photo generated BȮ radicals.

Photolysis of BOOB in the Presence of Phenylsilane and Phenyl tert-Butyl Nitrone

Photolysis of this solution led to the observation of an e.s.r. spectrum which can be tentatively assigned to two component radicals: the butoxy adduct (**1**) and the corresponding phenylsilyl adduct $PhCH(SiH_2Ph)N(\dot{O})B$. The parameters of the latter radical having a large doublet splitting of 8.3 G, are given in Table 1.

Photolysis of BOOB in the Presence of Trimethylsilane and Phenyl tert-Butyl Nitrone

Photolysis of this solution gave an e.s.r. spectrum which is tentatively assigned to the trimethylsilyl adduct $PhCH(Si[CH_3]_3)N(\dot{O})B$. The experimental parameters are given in Table 1. Unlike the arylsilyl adducts, the trimethylsilyl adduct was found to be very stable in the dark.

Decay of the Arylsilyl Adducts

The decay of arylsilyl adducts in the dark was found to follow the first-order kinetics. Figure 4 shows a typical first-order plot obtained from the decay curves of the diphenylsilyl adduct. The decay rate constants at various temperatures and the Arrhenius parameters are summarized in Table 2 for the three arylsilyl adducts studied.

TABLE 2. Kinetic parameters for the decay of arylsilyl adducts

Adduct	Temperature (°K)	First-order rate constants k × 10^2 (s^{-1})	Activation energy (kcal/mol)	log *A*
Phenylsilyl	265	13 ± 1	13.7±0.3	10.6±0.2
	273	36 ± 1		
	282	69 ± 2		
	291	139 ±10		
	300	212 ±12		
Diphenylsilyl	247	4.5± 0.3	11.7±0.3	9.0±0.3
	255	8.1± 0.7		
	265	22 ± 1		
	273	47 ± 3		
	282	69 ± 2		
Triphenylsilyl	264	2.4± 0.2	9.3±0.3	6.1±0.3
	273	4.7± 0.5		
	282	7.1± 0.5		
	291	15 ± 4		
	319	50 ± 4		

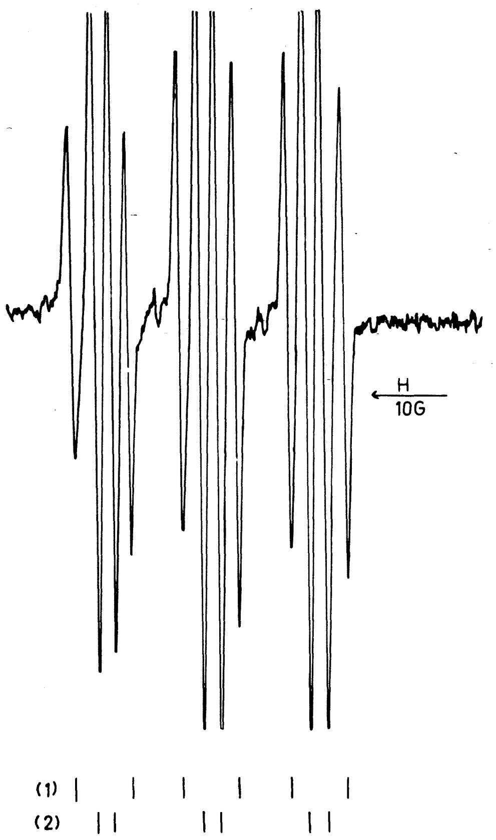


FIG. 3. Electron spin resonance spectrum obtained upon photolysis of BOOB solution of diphenylsilane and phenyl *tert*-butyl nitrone: (*1*) the diphenylsilyl adduct; and (*2*) the butoxy adduct.

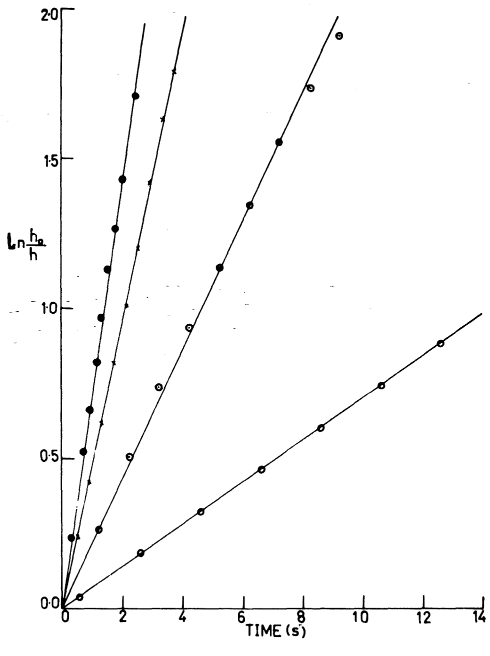
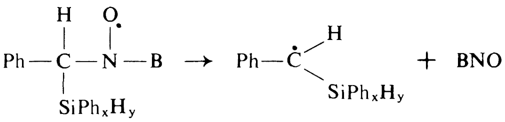


FIG. 4. A first-order plot for the decay of the diphenylsilyl adduct; h_0/h is the relative e.s.r. signal heights at initial time t_0 and time *t*.

Discussion

In all three arylsilanes systems studied, the adduct radical spectra consistently exhibit a relatively large doublet splittings *presumably* due to the β-proton of the adduct radical. This is a rather interesting observation. In the case of spin adducts of hydrocarbon and oxygen radicals, the variation in the β-proton splittings of the nitroxide seems to be related to the size of the carbon or oxygen radical group. For example, the β-proton splitting in $CH_3N(\dot{O})B$ is 12.7 G (8). Upon replacing one of the methyl protons with a phenyl group, the β-proton splitting of the resultant nitroxide drops to 7.13 G (7). In this respect, we observe (Table 1) the similar trend in the arylsilyl adducts; the phenylsilyl adduct has a larger β-proton splitting than that of the diphenyl and triphenyl substituted silyl adducts. However, on the basis of group size alone, it would be expected that the arylsilyl adducts should have smaller β-proton splittings than their carbon analogs. In a solid state pulse n.m r. study, it has been determined (9) that the activation energy for the C_3 rotation in the solid state of the methyl group in $(CH_3)_3SiCl$ and in CH_3SiCl_3 is substantially lower than the values for their carbon analogs $(CH_3)_3CCl$ and CH_3CCl_3. Perhaps despite the larger size of the arylsilyl group there is less steric strain in these arylsilyl adducts as compared to their carbon analogs.

While the triphenylmethyl radicals do not seem to add to the phenyl *tert*-butyl nitrone (7), arylsilyl radicals including the triphenylsilyl radical appear to add readily to the nitrone and their resultant adducts can be observed by e.s.r. during irradiation. These arylsilyl adducts are unstable in the dark and they decompose with various first-order rate constants. In all three systems studied, the $BN(\dot{O})OB$ radicals were also observed. These observations are consistent with the following reaction scheme:

[5]


$$Ph{-}\underset{SiPh_xH_y}{\overset{H}{C}}{-}\overset{\dot{O}}{N}{-}B \rightarrow Ph{-}\dot{C}\begin{smallmatrix}H\\SiPh_xH_y\end{smallmatrix} + BNO$$

[6] $BNO + B\dot{O} \rightarrow BN(\dot{O})OB$

Similar schemes of reactions of carbon analogs have been proposed by Maender and Janzen (10).

The fate of the silyl substituted benzyl radical formed in reaction 5 is not known.

The present experiments show that among the three arysilyl adducts the activation energy of their decomposition decreases with the increasing size of the arylsilyl group. This is also consistent with the observation of Maender and Janzen (10) for carbon adducts. It should be emphasized that the present experiments were carried out in BOOB solvent. However, the use of BOOB as solvent does not seem to interfere with the decomposition of the adducts. For example, we had used liquid diphenylsilane itself as solvent and the decay of the diphenylsilyl adduct was virtually the same as in BOOB. Indeed, the use of BOOB as solvent for radical studies is relatively common in recent years.

Finally the low values of the *A* factor determined and given in Table 2 cannot be satisfactorily explained at the present time. While there have been a few other low values of *A* factors reported for unimolecular reactions (11, 12), further systematic studies of unimolecular decomposition of free radicals are required before this can be explained.

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