August, 1979] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (8), 2339—2342 (1979) 2339

Relative Spin-trapping Ability of *N*-Benzylidene-*t*-butylamine Oxide, *N*-Benzylideneaniline Oxide, and 2,3,5,6-Tetramethylnitrosobenzene towards Phenyl and Phenylcyclohexadienyl Radicals

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(Received September 27, 1978)

N-Benzylidene-*t*-butylamine oxide (PBN), *N*-benzylideneaniline oxide (DPN), and 2,3,5,6-tetramethylnitrosobenzene (ND) trap phenyl radicals in a relative rate of 1: 0.72: 2.6, whereas they trap phenylcyclohexadienyl radicals in a relative rate of 1: 2.3: 130. The origin of such different spin-trapping abilities of these spin traps towards phenylcyclohexadienyl radicals is discussed.

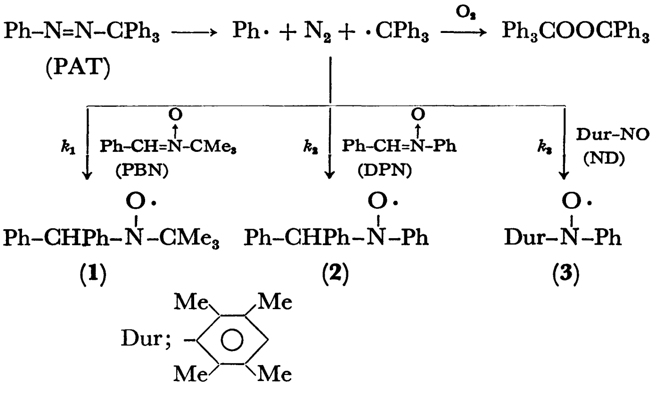
The spin-trapping technique has been widely employed for the characterization of transient reactive free radicals, and various kinds of spin traps have been reported.[1] However, the spin-trapping abilities of various spin traps towards a given free radical have remained obscure.

It is well known that the thermal decomposition of phenylazotriphenylmethane (PAT) in benzene produces triphenylmethyl and phenyl radicals. The latter radicals add to benzene to give phenylcyclohexadienyl radicals, which subsequently either recombine or disproportionate with triphenylmethyl radicals, thus leading to 1,4-dihydro-4-triphenylmethylbiphenyl or triphenylmethane and biphenyl.[2] We have reinvestigated this reaction in the presence of such spin traps as *N*-benzylidene-*t*-butylamine oxide (*N*-*t*-butyl-α-phenylnitrone, PBN), *N*-benzylideneaniline oxide (α,*N*-diphenylnitrone, DPN), and 2,3,5,6-tetramethylnitrosobenzene (nitrosodurene, ND), and have found that while all these spin traps gave their spin adducts with phenyl radicals, only ND afforded the spin adduct with phenylcyclohexadienyl radicals also.[3] Obviously, these facts indicate that spin traps have different reactivities towards phenyl and phenylcyclohexadienyl radicals. In order to confirm this, we have undertaken to determine the relative spin-trapping ability of the spin traps towards phenyl and phenylcyclohexadienyl radicals by competitive methods; our results are described in this paper.

Results

Relative Reactivity of PBN, DPN, and ND towards Phenyl Radicals. PAT was allowed to decompose at a low conversion rate in carbon tetrachloride in the presence of PBN, DPN, and ND under an argon atmosphere at 80 °C. The subsequent examination of the reaction solution by ESR showed signals attributable to phenyl spin adducts of the respective spin traps,[4] along with those attributable to triphenylmethyl radicals. The signals attributable to the triphenylmethyl radicals disappeared on the exposure of the reaction solution to oxygen, but the signals of the nitroxides remained. With authentic specimens of the nitroxides, their stability against oxygen, prolonged heating, and the spin traps was confirmed. Since the nitroxides were produced only in minor amounts (*ca.* 10^{-7} mol l^{-1}), their scavenging by phenyl radicals under the present reaction conditions is very inconsiderable. These results enabled us to determine the relative reactivity of the spin traps towards phenyl radicals by the competitive method.

When PAT was decomposed in the presence of a mixture of PBN (1.5×10^{-2} mol l^{-1}) and DPN (5.0×10^{-3} mol l^{-1}) in carbon tetrachloride at 80 °C, the ESR signals due to the phenyl spin adducts of PBN and DPN (**1** and **2**) were observed (Scheme 1) (Fig. 1). The ratio



Scheme 1.

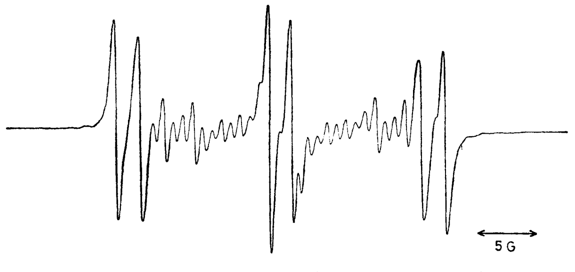


Fig. 1. The ESR spectrum of **1** and **2** obtained from the decomposition of PAT in carbon tetrachloride at 80 °C in the presence of PBN (5.0×10^{-3} M) and DPN (1.5×10^{-2} M). For **1**, $a_N=14.1$, $a_{\beta\text{-H}}=2.1$ G; for **2**, $a_N=10.1$, $a_{\beta\text{-H}}=3.4$, $a_{o,p\text{-H}}=2.5$, $a_{m\text{-H}}=0.9$ G.

of the concentrations of the two spin adducts ([**2**]/[**1**]) was obtained as 0.24 by means of the double integration of the ESR signals. Combining this value with the concentrations of PBN and DPN, the ratio of the rate constants of the addition of phenyl radicals to PBN (k_1) and DPN (k_2) was obtained as $k_2/k_1=0.72$ at 80 °C by the use of this equation: [**2**]/[**1**] $=k_2[\text{DPN}]/k_1[\text{PBN}]$. Triplicated runs afforded the same value within the limits of experimental error. At the concentrations of DPN $=5.0\times10^{-2}$ mol l^{-1} and PBN $=1.5\times10^{-2}$ mol l^{-1}, k_2/k_1 is 0.68 and is almost unchanged as to the relative concentrations of the spin traps.

The decomposition of dibenzoyl peroxide (BPO) in the presence of DPN (5.0×10^{-3} mol l^{-1}) and PBN (1.5×10^{-2} mol l^{-1}) in carbon tetrachloride gave their phenyl spin adducts in a ratio of [**2**]/[**1**] $=0.23$, which led to the value of k_2/k_1 ($=0.69$), similar to that obtained from PAT. Apparently, the relative reactivity towards phenyl radicals (k_2/k_1) is independent of the sources of phenyl radicals. Thus, the possibility that the nitroxides are scavenged by triphenylmethyl radicals concurrently formed in the decomposition of PAT can be disregarded. Accordingly, it is concluded that PBN traps phenyl radicals 1.4 times faster than does DPN.

Likewise, the decomposition of PAT in the presence of ND (4.9×10^{-3} mol l^{-1}) and PBN (5.2×10^{-3} mol l^{-1}) in carbon tetrachloride at 80 °C gave the phenyl spin adducts of ND (**3**) and PBN (**1**) in a ratio of [**3**]/[**1**] $=$ 2.5 (Fig. 2). This value leads to this ratio of the rate constants: $k_3/k_1=2.6$, in which k_3 is the rate constant for the addition of phenyl radicals to ND. The same value was obtained in the decomposition of BPO in the presence of ND (4.5×10^{-3} mol l^{-1}) and PBN (5.5×10^{-3} mol l^{-1}). Therefore, the rate constant for the addition of phenyl radicals to ND (k_3) is approximately 3 times larger than that to PBN (k_1) at 80 °C.

All the above reactions were carried out in carbon tetrachloride, from which phenyl radicals are known to abstract a chlorine atom to yield trichloromethyl radicals. However, none of the spectrum caused by the trichloromethyl spin adduct was hitherto observed. This finding suggests either that phenyl radicals add to the spin traps more rapidly than they abstract a chlorine atom from carbon tetrachloride or that trichloromethyl radicals are not efficiently captured by the spin traps. Therefore, it can safely be said that this side reaction, even if it occurs concurrently, does not affect the rate ratios, k_2/k_1 and k_3/k_1.

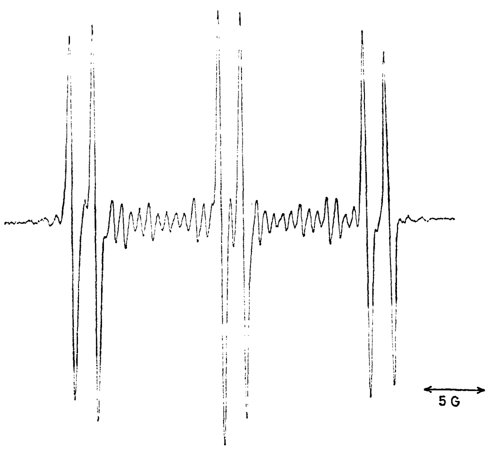


Fig. 2. The ESR spectrum of **1** and **3** obtained from the decomposition of PAT in carbon tetrachloride at 80 °C in the presence of PBN (5.2×10^{-3} M) and ND (4.9×10^{-3} M). For **1**, $a_\text{N}=14.4$, $a_{\beta\text{-H}}=2.1$ G; for **3**, $a_\text{N}=9.5$, $a_{o,p\text{-H}}=2.7$, $a_{m\text{-H}}=0.9$ G.

Relative Reactivity of PBN, DPN, and ND towards Phenylcyclohexadienyl Radicals. In an attempt to determine the relative reactivities of the spin traps towards phenylcyclohexadienyl radicals, 1,4-dihydro-4-triphenylmethylbiphenyl (DTB) was used as the source of this radical. The thermal decomposition of 2-chloro-1,4-dihydro-4-triphenylmethylbiphenyl in benzene was previously shown to generate triphenylmethyl and 1-chloro-6-phenyl-2,4-cyclohexadienyl radicals, which subsequently disproportionate into 2-chlorobiphenyl and triphenylmethane.[5]

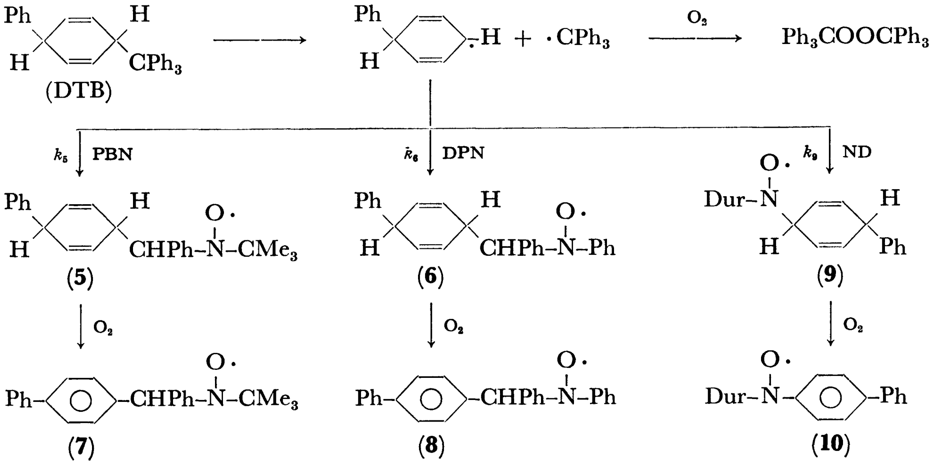
The decomposition of DTB in benzene at 80 °C in the presence of PBN, DPN, and ND under an argon atmosphere produced their phenylcyclohexadienyl spin adducts (**5**, **6**, and **9**) and biphenylyl spin adducts (**7**, **8**, and **10**) along with triphenylmethyl radicals (Scheme 2). On the exposure of the reaction mixture to atmospheric oxygen, the triphenylmethyl radicals were eliminated and the phenylcyclohexadienyl spin adducts were converted to the biphenylyl spin adducts, the concentration of which was subsequently determined quantitatively. The stability of the biphenylyl spin adducts to oxygen, prolonged heating, and spin traps was previously confirmed.[2,6]

The thermal decomposition of DTB in benzene in the presence of a mixture of PBN (3.0×10^{-2} mol l^{-1}) and DPN (3.0×10^{-2} mol l^{-1}) under an argon atmosphere at 80 °C produced triphenylmethyl radicals and nitroxides (**5**, **6**, **7**, and **8**). When oxygen was passed into the reaction mixture, two nitroxides (**5** and **6**) were completely oxidized to **7** and **8** respectively. The ratio of their concentrations ([**8**]/[**7**]) was determined to be 2.3, which gives the realtive reactivity of DPN (k_6) and PBN (k_5) towards phenylcyclohexadienyl radicals as $k_6/k_5=2.3$ in benzene at 80 °C.

Likewise, the decomposition of DTB in benzene in the presence of PBN (9.8×10^{-2} mol l^{-1}) and ND (4.9×10^{-3} mol l^{-1}) at 80 °C, followed by treatment with oxygen, gave their biphenylyl spin adducts (**7** and **10** respectively). The ratio of their concentrations, [**7**]/[**10**], was determined to be 0.15, from which the relative reactivity of PBN (k_5) and ND (k_9) towards phenylcyclohexadienyl radicals was obtained as $k_5/k_9=7.7\times10^{-3}$ at 80 °C. Therefore, ND traps phenylcyclohexadienyl radicals 130 times faster than does PBN.

Discussion

The present results indicate that the nitrones (PBN and DPN) and ND trap phenyl radicals with similar rate constants. Janzen and Evans reported that phenyl radicals add to PBN in methanol at a rate constant of 1.2×10^7 mol l^{-1} at 80 °C.[7] The activation energy for the above reaction probably does not exceed that for the addition of benzoyloxyl radicals to benzene, which



Scheme 2.

has been found to be 6 kcal mol^{-1}.[8] If it is assumed that the rate constant for the spin trapping in carbon tetrachloride is the same as in methanol, and that the activation energy is equal to 6 kcal mol^{-1}, the rate constant for the addition of phenyl radicals to PBN (k_1) in carbon tetrachloride at 80 °C can be estimated as 1.0×10^8 mol l^{-1} s^{-1}. The combination of this value with the observed rate ratios (k_2/k_1 and k_3/k_1) gives k_2 and k_3 as 7.2×10^7 and 2.6×10^8 mol l^{-1} s^{-1} respectively at 80 °C. The above large rate constants for the spin-trapping processes, as much as 10^8 mol l^{-1} s^{-1}, may be responsible for the lower selectivity between the spin traps in these reactions.

On the other hand, ND is now found to trap phenylcyclohexadienyl radicals nearly 130 times faster than the nitrones. A triphenylmethyl radical does not add at all to PBN,[9] DPN,[6] and ND,[10] probably because its addition to the spin traps is highly endothermic. The absolute rate constants for the addition of phenylcyclohexadienyl radicals to the spin traps cannot be estimated. However, as phenylcyclohexadienyl radicals are stabilized, though to a lesser extent, like triphenylmethyl radicals through the delocalization of the unpaired electron, it is suspected that phenylcyclohexadienyl radicals do not react with the spin traps so rapidly as do phenyl radicals.

Recently, Schmid and Ingold reported that 5-hexenyl radicals react with PBN at a rate constant of 1.3×10^5 mol l^{-1} s^{-1} at 40 °C in benzene and more rapidly with ND (3.9×10^7 mol l^{-1} s^{-1} at 40 °C).[11] It is worthwhile noting that ND tends to trap phenylcyclohexadienyl radicals and 5-hexenyl radicals more rapidly than the nitrones, whereas ND and the nitrones capture phenyl radicals with similar rate constants. The above fact may be interpreted in terms of the fact that phenylcyclohexadienyl radicals and 5-hexenyl radicals would suffer more steric hindrance on approaching to the nitrones to give the spin adducts than would phenyl radicals, whereas none of these radicals would suffer any serious steric hindrance in the reaction with ND.

Experimental

Materials. Nitrosodurene (ND),[12] *N-t*-butyl-α-phenylnitrone (PBN),[13] α,*N*-diphenylnitrone (DPN),[14] phenylazotriphenylmethane (PAT),[15] and 1,4-dihydro-4-triphenylmethylbiphenyl (DTB)[2] were prepared according to the methods in the literature.

*Examination of the Stability of the Nitroxides, **1**, **2**, and **3**.* Benzhydrylphenylnitroxide (**2**) was prepared by the oxidation of benzhydrylphenylhydroxylamine[16] with silver oxide in carbon tetrachloride. A mixture of the precipitates was removed by filtration, and the filtrate was used in situ for examining the stability of **2**.

2,3,5,6-Tetramethyldiphenylnitroxide (**3**) was prepared by the complete decomposition of PAT in carbon tetrachloride at 80 °C in the presence of ND; oxygen was passed through the solution to eliminate triphenylmethyl radicals.

Benzhydryl-*t*-butylnitroxide (**1**) was prepared according to the method in the literature.[17]

Each nitroxide solution in carbon tetrachloride was heated for 30 min at 80 °C, was treated with oxygen by passing it in for 3 min, or was mixed with the corresponding spin traps. The intensity of the ESR signals of each nitroxide did not vary under the above conditions.

Decomposition of PAT, DTB, and BPO in the Presence of the Spin Traps. A solution (0.3—0.4 ml) of PAT (2.0×10^{-3} mol l^{-1}) and the spin traps (PBN, 5.0×10^{-3}—5.0×10^{-2} mol l^{-1}; DPN, 1.5×10^{-2} mol l^{-1}; ND, 4.9×10^{-3} mol l^{-1}) in carbon tetrachloride was heated at 80 °C for 3 min under an atmosphere of argon, and then oxygen was passed through the solution in order to remove the triphenylmethyl radicals. The reaction mixture was subsequently purged with argon, and the ESR spectra were recorded.

DTB (8.0×10^{-3} mol l^{-1}) was similarly decomposed in benzene in the presence of the spin traps (PBN, 3.0—9.8×10^{-2} mol l^{-1}; DPN, 3.0×10^{-2} mol l^{-1}; ND, 4.9×10^{-2} mol l^{-1}) at 80 °C for 30 min. The reaction mixture was then treated similarly.

The decomposition of BPO (2.0×10^{-3} mol l^{-1}) was carried out in carbon tetrachloride in the presence of the spin traps (PBN, 5.0×10^{-3} mol l^{-1}; DPN, 1.5×10^{-2} mol l^{-1}; ND, 4.5×10^{-3} mol l^{-1}) at 80 °C for 3 min. Thereafter, the ESR spectra were measured immediately.

The ESR spectra were recorded on a JEOL JES-ME-1X spectrometer. The peak heights were converted to area units by the use of a double integrator. The ratio of the concentrations of the two spin adducts was determined by double integration.[18] The peak-overlap effects of two nitroxides were taken into account by a computer simulation of the summed spectra.

The authors are grateful to Professors Kunio Nakano and Hiroshi Tadano of Rikkyo University for their suggestions regarding the construction of the double integrator.

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