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Pentamethylnitrosobenzene as a Spin-trapping Agent

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Pentamethylnitrosobenzene synthesized readily from pentamethylbenzene was studied for utilization in a spin-trapping technique. In a benzene solution it forms a dimer with a dissociation constant of $10^{5.26}\exp(-50/RT)$ in units of kJ/mol. It traps the *t*-butyl radical with the trapping rate constant of 1.4×10^8 $\mathrm{mol^{-1}\,dm^3\,s^{-1}}$ at 299 K. It is thus an efficient spin-trapping agent, even though only a fraction of it is reactive with the short-lived free radicals because the equilibrium lies more on the side of the dimeric form. Electron spin resonance parameters were determined for the spin-adduct radicals derived from alkyl, alkoxyl, and phenyl radicals with this trapping agent. These free radicals were found to attach exclusively to the nitrogen atom of the nitroso compound.

Aliphatic and aromatic nitroso compounds have been widely used as spin-trapping agents for the spin-trapping technique, whereby short-lived free radicals in a reaction system attach to the trapping agents to form stable nitroxide (or anilino-type) radicals and are indirectly identified by means of conventional electron spin resonance (ESR) measurements.[1,2] Although available rate constant is very scanty for reactions between a trapping agent and a short-lived free radical,[3-5] nitrosobenzene appears more reactive compared with its alkyl-substituted derivatives. A drawback of this trapping agent is that its spin-adduct radicals generally show complex hyperfine structures in ESR spectra because of the ring protons, which renders difficult the identification of the trapped radicals.[6] On the other hand, 2,4,6-tri-*t*-butylnitrosobenzene (BNB) yield well-resolved hyperfine structures of its adduct radicals, but is much less reactive with short-lived free radicals.[7] Pentamethylnitrosobenzene (PMNB) is expcted to give a simpler hyperfine structure and to be moderately reactive, as is nitrosodurene,[8] thus being a useful spin-trapping agent. However, PMNB has not been studied as yet. This particular nitroso compound has one advantage as a spin-trapping agent in that it can be synthesized very readily from commercially-available pentamethylbenzene.[9,10] The present report will present several aspects of PMNB as a spin-trapping agent.

Results and Discussion

ESR Spectra of Spin-adduct Radicals. A typical ESR spectrum of spin-adduct radicals is shown in Fig. 1A. When a methyl radical generated in a benzene solution of methyl iodide and tributylstannane is trapped with PMNB, an adduct radical of the nitroxide type is formed and can be identified from the hyperfine splittings due to one nitrogen nucleus and three protons at the β-position with respect to the oxygen atom of the nitroxyl group (see the observed hyperfine splitting constants given in Table 1). Figure 1 also shows methyl-radical adducts from nitrosobenzene and BNB, for comparison. The adduct from PMNB shows broader

Table 1. Hyperfine splitting constants and g-values at 299 K for several nitroxide-type spin adduct radicals formed from pentamethylnitrosobenzene as a spin-trapping agent in benzene solutions. Previous results for tri-*t*-butylnitrosobenzene are also shown for comparison

		PMNB, Present results			BNB, by Terabe *et al.*[a]		
Trapped radical	Radical source	g-Value	Splitting const		g-Value	Splitting const[b]	
			a_N	$a_{\beta\text{-}H}$		a_N	$a_{\beta\text{-}H}$
$\cdot CH_3$	$CH_3I+(n\text{-}C_4H_9)_3SnH$	2.0058	1.38	1.23	2.0060	1.303	1.233
$\cdot CH_2CH_2CH_3$	$n\text{-}C_3H_7Cl+\gamma$	2.0058	1.42	1.12	2.0060	1.339	1.783
$\cdot CH_2CH_2CH_2CH_3$	$(n\text{-}C_4H_9)_3SnH+h\nu$	2.0060	1.37	1.13	2.0061	1.344	1.797
$\cdot CH(CH_3)_2$	$CHCl(CH_3)_2+\gamma$	2.0059	1.39	0.97	2.0060[c]	1.329	2.219
$\cdot CH(CH_3)CH_2CH_3$	$CHCl(CH_3)C_2H_5+\gamma$	2.0058	1.37	0.78	2.0061[c]	1.333	2.225
$\cdot C(CH_3)_3$	$t\text{-}C_4H_9NO+h\nu$	2.0060	1.36	—	Anilino-type		
$c\text{-}\dot{C}_6H_{11}$	$c\text{-}C_6H_{12}+\gamma$	2.0058	1.40	0.76	Anilino-type		
$\cdot CH(CH_3)C_6H_5$	$CH_3CHClC_6H_5+\gamma$	2.0060	1.39	0.85	Anilino-type		
$\cdot C_6H_5$	$[C_6H_5C(O)O:]_2+h\nu$	2.0057	1.00	0.28[d] 0.09[d]	2.0057	0.988	0.286[d] 0.261[d] 0.092[d]
$\cdot CH(CH_3)OC_2H_5$	$(C_2H_5)_2O+\gamma$	2.0058	1.40	0.46	—		
$\cdot C(CH_3)O$	$(CH_3CO)_2+h\nu$	2.0058	1.32	—	—		
$\cdot C(CN)(CH_3)_2$	$[(CH_3)_2C(CN)N:]_2+h\nu$	2.0063	1.30	—	Anilino-type		

a) Ref. 11. b) Other small coupling constants are omitted. c) Anilino-type adduct is also generated. d) Splitting constants due to ring protons.

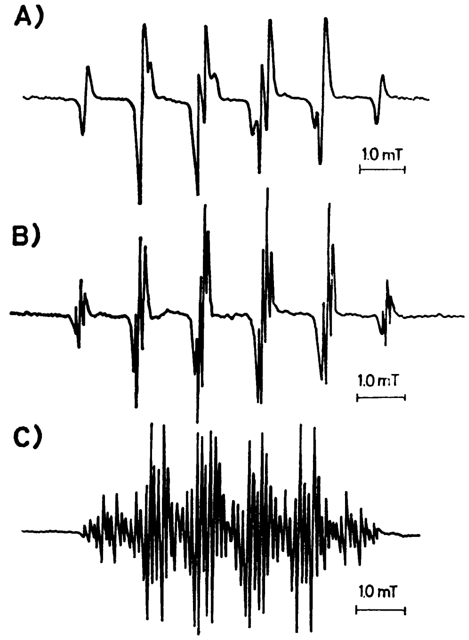

Fig. 1. ESR spectra of the spin adduct radicals generated by trapping methyl radical with (A) PMNB, (B) BNB, or (C) nitrosobenzene in benzene solution. The methyl radical was generated by the photolysis of tributylstannane in the presence of methyliodide.

hyperfine lines than do the adducts from nitrosobenzene and BNB, but it gives a much simpler hyperfine structure facilitating the identification of the trapped radical.

Table 1 summarizes the observed ESR parameters at 299 K for a number of adduct radicals generated from short-lived free radicals with PMNB in benzene. The short-lived free radicals were in turn generated by the photolysis or γ-radiolysis of appropriate radical sources. The observed ESR parameters are similar to those reported for nitrosodurene.[8] The hyperfine splitting due to the nitrogen atom lies in the range 1.42—1.30 mT, except for the phenyl radical adduct. Hyperfine splitting due to the β-proton(s) of the alkyl-radical adducts tends to decrease with the number of hydrogen (or with an increasing number of carbon) atoms attached to the β-carbon atom (the α-carbon in the trapped alkyl radicals). This trend is similar to that for nitrosobenzene and nitrosodurene,[8] being opposite to that for BNB[11] as shown in Table 1.

All the short-lived free radicals examined were found to attach to the nitrogen atom rather than to the oxygen atom of the nitroso compound, thereby giving nitroxide radicals. No formation of anilino-type adduct radicals was observed.

Monomer-Dimer Equilibrium. As in the case of aliphatic nitroso compounds[12] and nitrosodurene,[8] PMNB is present in solution mostly as a dimer, which is inactive in trapping short-lived free radicals. PMNB shows a weak optical absorption band with a maximum at 790 nm and an intense band with a maximum at 324 nm. The former band is due to the $n\pi^*$ transition of the monomeric form, and the latter to the dimeric form. Changing the temperature causes complementary change in the intensity of both the bands, higher temperature favoring the monomeric form. According to the well-known relationship, $c/OD = 1/2\varepsilon + 1/K\varepsilon^2 OD$, where OD represents the optical density at 790 nm and c represents the total concentration of PMNB based on its dimeric form, the dissociation constant K was determined at several temperatures, as shown in Fig. 2. The extinction coefficient ε was also determined to be 83.3 mol^{-1} dm^3 cm^{-1}, almost independent of temperature.

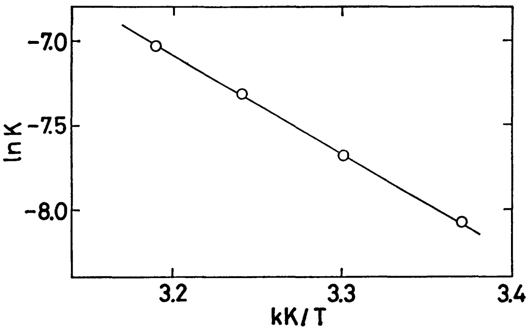

Fig. 2. Dependence of the dimer-monomer equilibrium constant for PMNB in benzene on reciprocal temperature.

The temperature dependence of the equilibrium constant is expressed by the equation, $K = 10^{5.26}\exp(\Delta H/RT)$, where the heat of dissociation is -50 kJ/mol. This means that only 12% of the 10 mmol dm^{-3} PMNB in a benzene solution is in monomeric form and is effective in the trapping reaction at 300 K. This behavior is very similar to that of nitrosodurene.[8]

Rate Constant for the Spin-trapping Reaction. In a separate investigation, the rate constant for the spin-trapping reaction of 2-methyl-2-nitrosopropane with the *t*-butyl radical, being 3.3×10^6 mol^{-1} dm^3 s^{-1} at 299 K in benzene solution, was investigated.[7] Based on this figure, the rate constant for PMNB was determined by studying the competition between PMNB and 2-methyl-2-nitrosopropane in trapping the *t*-butyl radical generated by the photolysis of the latter. Figure 3 shows the linear increase in the concentration of the

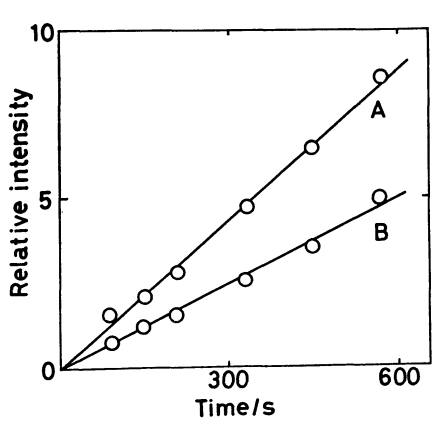

Fig. 3. Yield of the *t*-butyl radical adducts formed from (A) PMNB and (B) 2-methyl-2-nitrosopropane in benzene at 299 K as a function of photolysis time. The *t*-butyl radical was generated by the photolysis of the latter spin trapping agent 0.0276 mol dm^{-3} in benzene solution, where the former trapping agent (0.0012 mol$\cdot$dm^{-3}) was coexisting.

t-butyl adducts with both the trapping agents coexisting in the benzene solution during the early period of photolysis. From the observed slopes and the concentration of the trapping agents present, the rate constant for PMNB was determined to be 1.4×10^8 mol^{-1} dm^3 s^{-1}, based on the concentration of PMNB in monomeric form, in the reaction with the *t*-butyl radical at 299 K.

Although very little has been reported on spin-trapping rate constants, the data so far available indicate that trapping reactions proceed with rate constants of 10^5—10^8 mol^{-1} dm^3 s^{-1}, depending on the spin-trapping agent used and the radical trapped.[3-5] PMNB appears to be a comparatively reactive spin-trapping agent. It was also found to be a more efficient trapping agent than BNB, even when the monomer-dimer equilibrium of PMNB is taken into account.

Experimental

Synthesis. According to McKillop *et al.*,[9] pentamethylbenzene is converted to $C_6(CH_3)_5Tl(OCOCF_3)_2$, with the yield of this organothallium compound being *ca.* 60%. It was then converted into PMNB upon treatment with nitrosyl chloride with a yield of almost 100% by applying the method reported by Taylor and Danforth for the general synthesis of aromatic nitroso compounds.[10] The PMNB thus obtained was purified by recrystallization from an acetone solution three times. Its observed melting point of 427 K was unchanged by further purification. This value is in agreement with the previously-reported melting point of 425—428 K.[13] Elementary analysis gave the following results. Found: C, 74.51; H, 8.56; N, 7.8%. Calcd for $C_{11}H_{15}NO$: C, 74.52; H, 8.54; N, 7.9%.

PMNB was synthesized much more easily than nitrosodurene. This is an advantage of PMNB as a spin-trapping agent over nitrosodurene, although PMNB shows similar behavior in spin-trapping reactions and gives similar features of the hyperfine structures of the adduct radicals as does nitrosodurene.

Photolysis and Radiolysis. The short-lived free radicals trapped were generated by photolysis or radiolysis at room temperature from appropriate radical sources present in a benzene solution of 10 mmol dm^{-3} PMNB sealed in a quartz ESR tube after degassing by the freeze-pump-thaw technique. The solvent and the radical sources were of the highest purity commercially available and were used as received. The photolysis was carried out with light from an ultra-high pressure Hg lamp using a wavelength selected by a set of filters, so that only the radical sources were excited. The radiolysis was carried out with ^{60}Co γ-rays to a dose of approximately 0.1 Mrad.

ESR Measurements. Spin-adduct radicals were observed using a conventional X-band ESR spectrometer (JEOL, Model 2X) at 299 K. Their *g*-value was determined with reference to that of polycrystalline DPPH, 2.0036.[14] The hyperfine splittings were corrected with reference to that of Fremy's salt in aqueous solution, 1.300 mT.[15]

Optical-absorption Measurements. The optical absorption of PMNB in benzene was recorded with a recording spectrophotometer (Hitachi, Model EPS-3T). The sample solutions in a quartz cell having an optical path length of 1.0 cm were examined without degassing. Temperature was controlled in a water bath using a Dewar vessel with quartz windows.

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