Spin Trapping and Identification of the Radicals Formed in the Photolysis of Methane–Ammonia–Water Gaseous Mixtures

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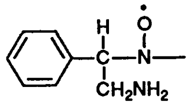
Spin trapping of the gas-phase photoreaction system methane–ammonia–water and the related methylamine–water–oxygen system have been performed using α-phenyl-*N*-t-butylnitrone (PBN). In the former case, methoxyl and aminomethyl radicals were trapped and in the latter, nitromethyl radical was trapped under a higher molar fraction of oxygen and aminomethyl radical was trapped under a lower and zero molar fraction of oxygen. The trapped radicals were identified by comparison of their ESR spectroscopic parameters with those of synthetically-obtained homologues.

Spin trapping is now well-known as a useful method with which to detect the short-lived free radicals formed in a variety of reaction systems. We have recently reported that the radicals in photoreaction gases can be trapped by nitrone spin traps in the liquid-phase by repeated photolysis and trapping of the reactant gas mixtures.[1,2] In this study, the method was applied to the photochemical methane activation system CH_4–NH_3–H_2O and the related CH_3NH_2–H_2O–O_2 system where in the former, methylamine and ethylenediamine were produced very selectively.[3]

Spin trapping of the photoreaction gases of CH_4–NH_3–H_2O yielded a carbon-centred radical adduct of PBN in additon to the methoxyl radical adduct which had been identified in the spin-trapping experiment of the photolysis gases of CH_4–H_2O.[1] The former radical adduct was also obtained from the photolysis gases of CH_3NH_2–H_2O–O_2 under zero or relatively lower molar fraction of oxygen (χ_{O_2}), while another radical adduct was detected under higher χ_{O_2}. The hyperfine coupling constants (hfcc) of these nitroxide radicals, reaction conditions and product analyses of these photoreaction systems suggest that the former radical is $^{\bullet}CH_2NH_2$ and the latter $^{\bullet}CH_2NO_2$. To get a firm basis for this assignment, syntheses of the radicals **1** and **2** were carried out and ESR spectroscopic measurements on these nitroxide radicals were performed.



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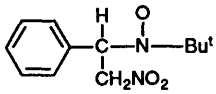

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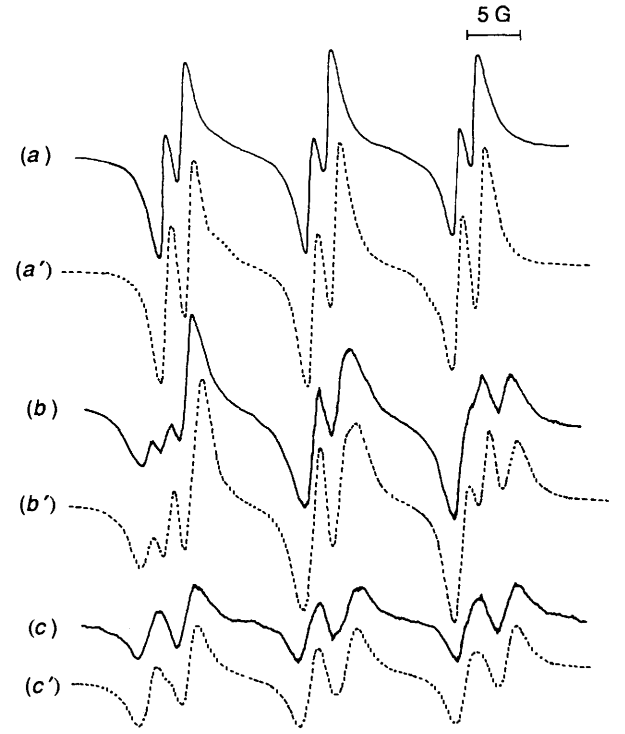


Fig. 1. ESR spectra obtained from the spin trapping of photolysis gas mixture of CH_4–NH_3–H_2O with $\chi_{H_2O} = 0.03$ and (*a*) $\chi_{NH_3} = 0.09$; $\chi_{CH_4} = 0.88$; (*b*) $\chi_{NH_3} = 0.13$; $\chi_{CH_4} = 0.84$; and (*c*) $\chi_{NH_3} = 0.33$; $\chi_{CH_4} = 0.64$. (*a′*), (*b′*) and (*c′*) are the simulated ESR spectra of (*a*), (*b*) and (*c*).

Results and Discussion

The ESR spectra obtained in the spin trapping experiments of the photolysis gas mixture CH_4–NH_3–H_2O by PBN in benzene are shown in Fig. 1. As the molar fraction of ammonia increased from 0.09–0.33 the spectrum obtained changed from Fig. 1(*a*) to 1(*c*). These spectra are clearly not due to a single species but to two species which are seen mainly in Fig. 1(*a*) and (*c*), respectively. Simulation calculations were able to reproduce these spectra using the following variable parameters: the hfccs of nitroxide nitrogen (a^N) and the hydrogen atom at β-C ($a_\beta{}^H$); the peak-to-peak line width (ΔH^{pp}); the *g*-shift (relative position of the centre of the hyperfine splitting, hfs, expressed with respect to the magnetic field); and the spectral weight (relative concentration of the free radical which causes the hfs, $\leqslant 1$). In fact, Fig. 1(*a*) was reproduced by $a^N = 13.97$, $a_\beta{}^H = 2.04$, $\Delta H^{pp} = 0.5$, *g*-shift = 0 G, weight = 0.95 (species 1) and $a^N = 14.97$, $a_\beta{}^H = 3.54$, $\Delta H^{pp} = 1.5$, *g*-shift = +2 G, weight = 0.05 (species 2); Fig. 1(*b*) by weight = 0.6 (species 1) and 0.4 (species 2); and Fig. 1(*c*) by weight = 0.2 (species 1) and 0.8 (species 2); the others were the same as those for Fig. 1(*a*). In the same way, computer simulation enabled us to estimate the relative weight of these two species detected under a series of molar fractions of ammonia (χ_{NH_3}) (Fig. 2). It is evident that the superiority of the weight of species 1 and 2 alternated depending on χ_{NH_3}, *i.e.* production of the radicals in the photolysis of the CH_4–NH_3–H_2O mixture responsible for species 1 and 2 depended inversely on χ_{NH_3} for species 1 and directly for species 2.

Lack of ammonia in the reaction-gas mixture resulted in the spectrum shown in Fig. 1(*a*). Product analysis after 1 h photolysis of the gas mixture CH_4–NH_3–H_2O showed that the main

Table 1. Hfccs/G of PhCHR–N(O$^{\bullet}$)–Bu^{t} (in benzene) obtained through the spin trapping of photolysis gases.

System	R	a^N	a_β^H	
CH_4–NH_3–H_2O	OCH_3	13.79	2.04	Fig. 1(*a*) (species 1)
	CH_2NH_2	14.97	3.54	Fig. 1(*c*) (species 2)
CH_3NH_2–H_2O	CH_2NH_2	14.87	3.62	Fig. 4(*a*) (species 2)
CH_3NH_2–H_2O–O_2	CH_2NH_2	14.87	3.62	Fig. 4(*b*), (*c*) (species 2)
	CH_2NO_2	14.94	5.20	Fig. 4(*d*), (*e*) (species 3)
PBN/CH_3NO_2/Et_2NH[a]	CH_2NO_2	15.32	5.15	Fig. 5(*a*) (species 3)
PBN–CH_2NO_2/Fe/AcOH[b]	CH_2NH_2	15.2	3.8	Fig. 5(*b*), R_1 (species 2)
	OAc	14.7	2.5	Fig. 5(*b*), R_2

[a] Produced by the addition of $CH_2NO_2^-$ to PBN in solution. [b] Produced by the reduction of PBN–CH_2NO_2 in solution.

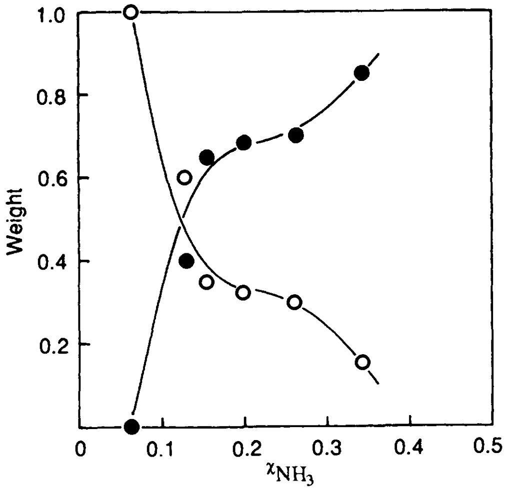


Fig. 2. Changes in spectral weight of species 1 (○) and species 2 (●) *versus* the molar fraction of ammonia obtained from the CH_4–NH_3–H_2O system. $\chi_{H_2O} = 0.03$ and $\chi_{CH_4} = 0.97 - \chi_{NH_3}$.

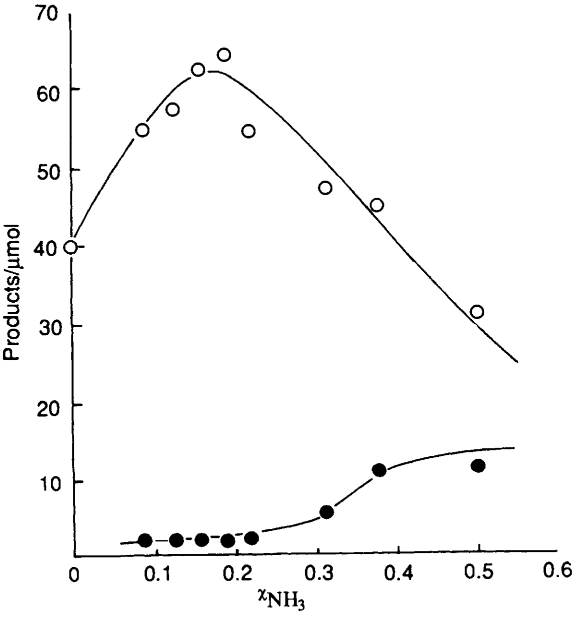


Fig. 3. Changes of production of methanol (○) and methylamine plus ethylenediamine (●) *versus* the molar fraction of ammonia in the photolysis of CH_4–NH_3–H_2O. $\chi_{H_2O} = 0.01$ and $\chi_{CH_4} = 0.99 - \chi_{NH_3}$. Error limits are 8% at $\chi_{NH_3} > 0.2$ and 3% at $\chi_{NH_3} \leqslant 0.2$.

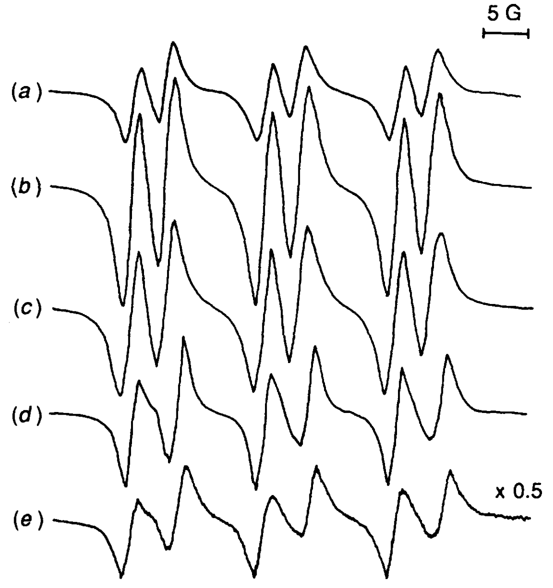


Fig. 4. Spectral changes in the spin trapping of photolysis gas mixture of CH_3NH_2–H_2O–O_2 *versus* χ_{O_2}: (*a*) 0, (*b*) 0.20, (*c*) 0.27, (*d*) 0.33 and (*e*) 0.49. $\chi_{H_2O} = 0.02$ and $\chi_{CH_3NH_2} = 0.98 - \chi_{O_2}$.

products were methanol, methylamine and ethylenediamine. The amount of these products also changed depending on χ_{NH_3} (Fig. 3). Comparing Fig. 3 with Fig. 2, it is evident that the dependence of methanol production on χ_{NH_3} is similar to that of the weight of species 1 and that the dependence for production of methylamine and ethylenediamine is similar to that of species 2. Hfccs of the spin adducts, species 1 and 2, are listed in Table 1.

In our previous report,[1] it was confirmed that methoxyl radical was produced and trapped in the photolysis of CH_4–H_2O and CH_3OH. That the hfccs of species 1 are very close to those reported for PBN–OCH_3[1,4] and that methanol production is relatively high under the same conditions which yield species 1 leads us to the conclusion that species 1 is the methoxyl radical adduct of PBN.

As for the radical responsible for species 2, the hfccs shown in Table 1 suggest a carbon-centred radical adduct yet the radical added has a structure and electronic character which resembles that of the ethyl radicals. No hfs due to the β-nitrogen atom was observed, which rules out a nitrogen-centred radical, and the hfccs are similar to those of PBN–C_2H_5 ($a^N = 13.93$; $a_\beta^H = 3.21$ G)[5] although the values in this study are somewhat large due to the polar-solvent effect caused by the contaminated polar products.[6] Moreover, the similarity of the above-mentioned χ_{NH_3} dependence of methylamine and ethylenediamine production and of the weight of species 1 strongly suggests the aminoalkyl radical. Therefore, as control experiments, spin trapping experiments on the photolysis gas mixture of CH_3NH_2 and H_2O were performed. The resulting spectrum is shown in

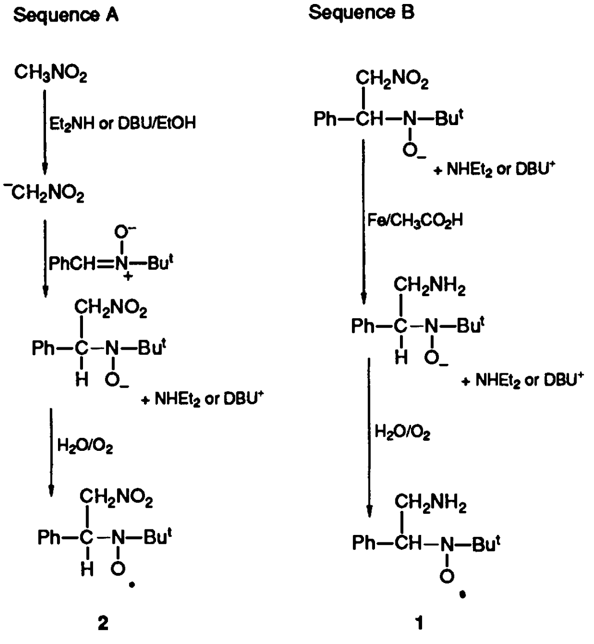
Fig. 4(*a*) and the hfccs are displayed in Table 1. It is evident that the nitroxide radicals of species 2 and Fig. 4(*a*) are the same.

Product analysis of the photolysis of CH_3NH_2–H_2O under the same experimental conditions as those for Fig. 4(*a*) showed that H_2 production is extremely high (217 μmol for $[CH_3NH_2]_{\text{initial}}$ = 2.8 mmol). Production of CH_3OH, HCHO and CH_4 was 41.6, 48.7 and 12.7 μmol, respectively. Very little ethylenediamine and ammonia were produced. Previous reports for the photolysis of methylamine[7] showed that the main primary products were $CH_3NH^{\bullet}$ and $^{\bullet}CH_2NH_2$ and that directly-dissociated products such as $CH_3NH_2 \longrightarrow {}^{\bullet}CH_3 + {}^{\bullet}NH_2$, $CHN + 2H_2$ were minor, even following photolysis at 147 nm. Therefore, it is reasonable to assume that the primary products of this study were either $CH_3NH^{\bullet}$ or $^{\bullet}CH_2NH_2$. Concomitantly produced H atoms could abstract H from CH_3NH_2, which is abundant in the system, to produce H_2 and $^{\bullet}CH_2NH_2$ (preferentially to $CH_3NH^{\bullet}$).[7] Hydroxyl radicals derived from the photolysis of water also join this H-abstraction. Since $^{\bullet}CH_2NH_2$ is more stable than $CH_3NH^{\bullet}$ due to the conjugative delocalization of an unpaired electron onto the adjacent electron lone-pair,[8] the radical trapped in the experiment shown in Fig. 4(*a*) is clearly $^{\bullet}CH_2NH_2$. The lack of hfs by the β-N atom also supports this assignment. Methane and its derivatives might arise from the decomposition of $CH_3NH^{\bullet}$ by, *e.g.*, $2CH_3NH^{\bullet} \longrightarrow 2^{\bullet}CH_3 + N_2 + H_2$. Details of this process will be described elsewhere.[9]

In the photolysis of CH_4–NH_3–H_2O, as already reported,[3,9] the primary products are $^{\bullet}NH_2$, $^{\bullet}OH$ and H ($NH_3 \longrightarrow {}^{\bullet}NH_2 + H$, ν 185 nm; $H_2O \longrightarrow {}^{\bullet}OH + H$, ν 185 nm) and the hydroxyl radical, which possesses a high H-abstracting ability, produces $^{\bullet}CH_3$ ($CH_4 + {}^{\bullet}OH \longrightarrow {}^{\bullet}CH_3 + H_2O$), The main products shown in Fig. 3 are considered to form through a recombination of the corresponding radicals. Therefore, $^{\bullet}CH_2NH_2$ detected in this system seems to be produced from CH_3NH_2 in the same manner as mentioned above. In contrast to the CH_3NH_2–H_2O system, however, $^{\bullet}CH_2NH_2$ might be protected from the secondary photolysis due to the existence of photoactive ammonia and as a result, a detectable amount of ethylenediamine could be produced under higher χ_{NH_3} (see Fig. 3), while only a trace of ethylenediamine was detected in the photolysis of CH_3NH_2–H_2O.

Addition of oxygen to the photolysis system CH_3NH_2–H_2O changed the radical trapped [Fig. 4(*b*) (*c*) to 4(*d*) (*e*)]. Product analysis of the system ($\chi_{CH_3NH_2} = 0.66$; $\chi_{O_2} = 0.33$; $\chi_{H_2O} = 0.01$) revealed an increase in oxidized species, *i.e.*, CO_2, NO_2 and CH_3NO_2 and a drastic decrease in H_2, CH_4 and C_2H_6. The hfccs shown in Table 1 indicate that the radicals responsible for the spectra 4(*b*) and (*c*) are the same as that of species 2, *i.e.* $^{\bullet}CH_2NH_2$. The radical which caused spectra 4(*d*) and (*e*) (species 3) introduced distinctive large hfs of β-H. This suggests that a radical consisting of an electron-withdrawing group such as $^{\bullet}NC{=}O$ has been trapped by PBN.[10] Taking account of the fact that the trapped radical in question seems to come from an oxidized species of CH_3NH_2 and that CH_3NO_2 was detected under large χ_{O_2}, the $^{\bullet}CH_2NO_2$ adduct is the most probable candidate for species 3.

To obtain proof of the identity of $^{\bullet}CH_2NH_2$ and $^{\bullet}CH_2NO_2$ as species 2 and 3, syntheses of PBN–CH_2NO_2 **2** and PBN–CH_2NH_2 **1** were planned, as outlined in Scheme 1. A solution of PBN–CH_3NO_2–Et_2NH in ethanol was refluxed for 3 h to ensure hydrolysis (sequence A). The hydrolysed product was oxidized (O_2 bubbling) and extracted into benzene then its ESR spectrum was recorded. The spectrum shown in Fig. 5(*a*) was obtained and estimated hfccs are given in Table 1. Use of DBU * instead of Et_2NH increased the intensity of the ESR signal (× 4), which suggests the effective production of nitromethanide in this case. The fact that similar values of the hfccs were obtained from Fig. 5(*a*) to those of species 3 thus confirms that the radical trapped in the photolysis gas of CH_3NH_2–H_2O–O_2 is $^{\bullet}CH_2NO_2$.



Scheme 1.

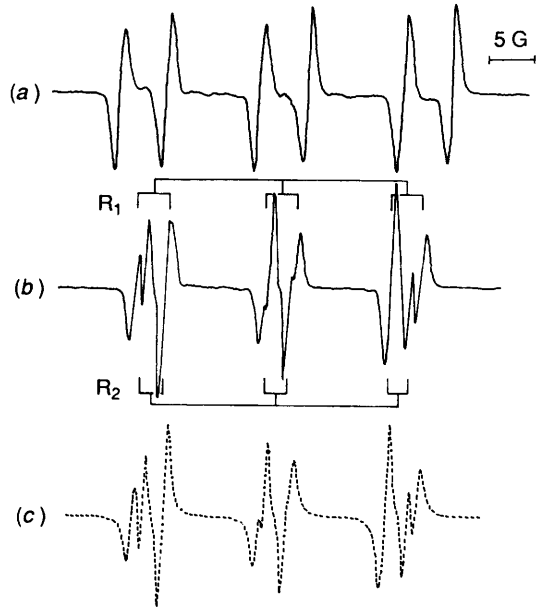


Fig. 5. ESR spectra of the synthesized nitromethyl adduct (*a*) and aminomethyl adduct [R_1 in (*b*)] of PBN. Spectrum (*b*) is derived from the superposition of two spectra (R_1 and R_2) and these are analysed respectively by the simulation (*c*).

Next (sequence B) a solution of the nitromethanide adduct of PBN in ethanol was evaporated to dryness and the resulting solid was dropped into an acetic acid solution containing electrolytic iron powder. Reduction was continued for 2 h under reflux with stirring and the reduction product was hydrolysed, oxidized and extracted with benzene. The ESR spectrum of this benzene solution yielded the spectrum shown in Fig. 5(*b*), in which two species of nitroxide radical (R_1 and R_2) can be

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* DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

recognized. This superimposed spectrum was simulated with the following parameters: (R_1) $a^N = 15.2$, $a_\beta{}^H = 3.8$, $\Delta H^{pp} = 0.8$, g-shift = 0 G, weight = 0.6; (R_2) $a^N = 14.7$, $a_\beta{}^H = 2.5$, $\Delta H^{pp} = 0.6$, g-shift = 0 G, weight = 1.0 [Fig. 5(*c*)]. The hfccs obtained are also listed in Table 1. It is evident that the hfccs of R_1 are almost the same as those of species 2, *i.e.* the $^{\bullet}CH_2NH_2$ adduct of PBN **1**. R_2 in Fig. 5(*b*) is probably the acetoxyl radical adduct since this is likely to produce acetate anion during the reduction of the nitro group in compound **2**. The hfccs obtained (Table 1, R_2) are reasonable as those of the PBN acetoxyl adduct although they are somewhat large compared with the reported values ($a^N = 14.0$, $a_\beta{}^H = 2.0$ G).[11]

Conclusions

A carbon-centred radical trapped by PBN from the photolysis gas mixture CH_4–NH_3–H_2O (in addition to methoxyl radical) was strongly suggested to be $^{\bullet}CH_2NH_2$ by the hfccs of its PBN adduct and the χ_{NH_3} dependence of its production, which also showed good correlation with production of methylamine and ethylenediamine. This supposition was confirmed through the synthesis of PBN–CH_2NH_2 **1** from PBN and CH_3NO_2 *via* PBN–CH_2NO_2 **2** and ESR spectroscopic measurements of **1** and **2**. In addition, a radical detected along with $^{\bullet}CH_2NH_2$ from the photolysis gas mixture CH_3NH_2–H_2O–O_2, which was tested as a control experiment, was eventually shown to be $^{\bullet}CH_2NO_2$.

Experimental

Materials.—α-Phenyl-*N*-t-butylnitrone (PBN) was obtained from the Aldrich Chemical Co. and used without further purification. Methane, ammonia and oxygen (Seitetsukagaku Co.) had purities 99% (main impurities: CO_2, 0.5%; N_2, 0.2%; O_2, 500 ppm), 99.9% and 99.5%, respectively, and were used without purification. Methylamine was obtained by vacuum evaporation from a 40% water solution (Katayama Chemical Co.). Water was treated with an ion-exchanging column. Benzene used as a solvent for PBN was Dotite spectrosole reagent. Chemicals used for the synthesis of **1** and **2** were all reagent grade.

Photolysis and Spin-trapping Experiments.—The whole reaction system was built up in a vacuum line made of Pyrex glass and consisted of a photocell (262 cm^3), a spin trapping cell (5 cm^3), two manometers and three gas inlets. The photocell, spin trapping cell, and gas circulator with a flow meter were connected in series. An illustration of this apparatus can be seen in ref. 1. The detailed method of photolysis and spin trapping experiments are also described in ref. 1.

Preparation of Nitromethylbenzyl-t-butyl Nitroxide **2** *and Aminomethylbenzyl-t-butyl Nitroxide* **1**.—CH_3NO_2 (44.1 mg), PBN (88.6 mg) and Et_2NH (23.3 mg) or DBU (76.1 mg) were dissolved in ethanol (1 cm^3) and the solution was refluxed at 80 °C for 3 h. The product **2** was extracted with benzene using a small amount of water for separation. Oxygen and nitrogen were bubbled through the benzene solution and this was used for ESR spectroscopic measurements.

In contrast, the ethanol solution containing the product (the nitromethanide adduct of PBN) was dried and the resulting solid was gradually added to a mixture of CH_3CO_2H (1.5 cm^3) and iron (1.0 g). The solution was kept for 2 h while being stirred at 0 °C. The product **1** was extracted with benzene and subjected to similar treatment as above.

Product Analysis.—In the product analysis experiments a product trap containing water was set in place of the spin trapping cell. All other conditions were same as those in the spin trapping experiments. Products in the gas phase were taken from a gas sampler on the photocell and analysed by FID-GC (Shimadzu, GC-8A) with a Porapak Q column at 100 °C. Among the water-soluble products, alcohols and aldehydes were analysed by a steam chromatograph (Ohkura, SSC-1) with a Porapak R-O column at 130 °C and FID, and amines were prelabelled by FDNB (1-fluoro-2,4-dinitrobenzene) and analysed by HPLC (Hitachi, 655A).

ESR Measurements and Spectral Simulation.—ESR spectra were recorded on a JES-ME-1X spectrometer at ambient temperature. Microwave frequencies, microwave power and 100 kHz field modulation amplitude were 9.45 GHz, 2 mW and 1 G, respectively. Field calibrations were performed based on the signals from Mn^{2+} in MgO and DPPH.

ESR spectral simulations were carried out on an NEC 9801vm personal computer based on the program given in ref. 12. The total components were set at 625 points and the highest resolution is 0.08 G to the calculation region of 50 G. Input parameters are given in the text.

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