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# Relative yields of radicals produced in deuterated methanol by irradiation

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## HIGHLIGHTS

- The deuteration of the methyl in methanol lead to a higher yield of the methoxy radical.
- The deuteration of the hydroxyl in methanol lead to a lower yield of the methoxy radical.
- The rates of proton transfer and hydrogen abstraction influence the relative radical yield.

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## ABSTRACT

The relative yields of radicals produced in four kinds of methanols; i.e., CH<sub>3</sub>OH, CH<sub>3</sub>OD, CD<sub>3</sub>OH and CD<sub>3</sub>OD, by  $\gamma$ -irradiation have been studied using ESR spin trapping with PBN. Both PBN-H and PBN-D were produced from CH<sub>3</sub>OD and CD<sub>3</sub>OH. This means that the proton transfer to the neutral methanol from the cationic one is one of the processes to produce both the methoxy and hydroxy-methyl radicals. The yield of the methoxy radical adduct relative to the hydroxy-methyl radical adduct decreased in the order CD<sub>3</sub>OH > CD<sub>3</sub>OD > CH<sub>3</sub>OH > CH<sub>3</sub>OD. The difference in the rates of the proton transfer and hydrogen abstraction reactions by substitution with deuterium is the reason for the variation in the relative radical yield.

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## 1. Introduction

It is known that three kinds of radicals; i.e., hydrogen, the alkoxy radical and hydroxy-alkyl radical, will be produced by the irradiation of an alcohol (Spinks and Woods, 1990). The spin trapping method was applied to study radicals produced during the radiolysis of an alcohol, and the reaction mechanism to form the radicals was discussed (Mao and Kevan, 1974; Schlick and Kevan, 1976; Sargent and Gardy, 1974; 1976; Shiotani et al., 1976). Recently, the relative yield of radicals produced in methanol by heavy ion irradiation has been studied using the spin trapping method to estimate the effect of localization for the initial distribution of radicals (Nakagawa and Murakami, 2015). Based on these studies, not only the stability of the radical adducts and the reactivity between the spin trapping reagent and the radical, but also the reaction and diffusion rates of the radicals will influence the relative yield of the spin trapped radicals. The substitution of hydrogen in methanol by deuterium is an effective way to vary the reaction and diffusion rates of the radicals, while the stability of the adducts and the reactivity for the production of adducts will be

almost unaffected. Based on this concept, the relative yield of radicals produced in four kinds of methanols; i.e., CH<sub>3</sub>OH, CH<sub>3</sub>OD, CD<sub>3</sub>OH and CD<sub>3</sub>OD, by  $\gamma$ -irradiation have been studied using the ESR spin trapping method.

Previously, 2-methyl-2-nitrosopropane (MNP), tri-*t*-butyl-nitrosobenzene (BNB), and phenyl-*t*-butylnitron (PBN) were used for the spin trapping reagents to study the radicals produced in methanol by irradiation. In this study, PBN was selected as the spin trapper, because both the reagent and the radical adduct are relatively stable to heat and light. The reaction mechanism of radicals depending on the deuteration can be estimated for the first time.

## 2. Experimental

Methanol (Wako-Junyaku), deuterated methanols (Cambridge Isotope Lab.) and PBN (Dojin Chemical) were used as received. Methanol solutions with PBN of 0.1 mol/L were prepared, and 50  $\mu$ L aliquots of them were placed in 2-mm diameter quartz ESR tubes. The samples were sealed after being degassed by a pump and thaw method.

The samples were  $\gamma$ -irradiated by a <sup>137</sup>Cs source. The absorbed

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doses were 30–120 Gy. The irradiation time was set to less than 20 min to minimize the effects of the difference in the lifetimes among the radical adducts. The samples were kept at 77 K immediately after the irradiation.

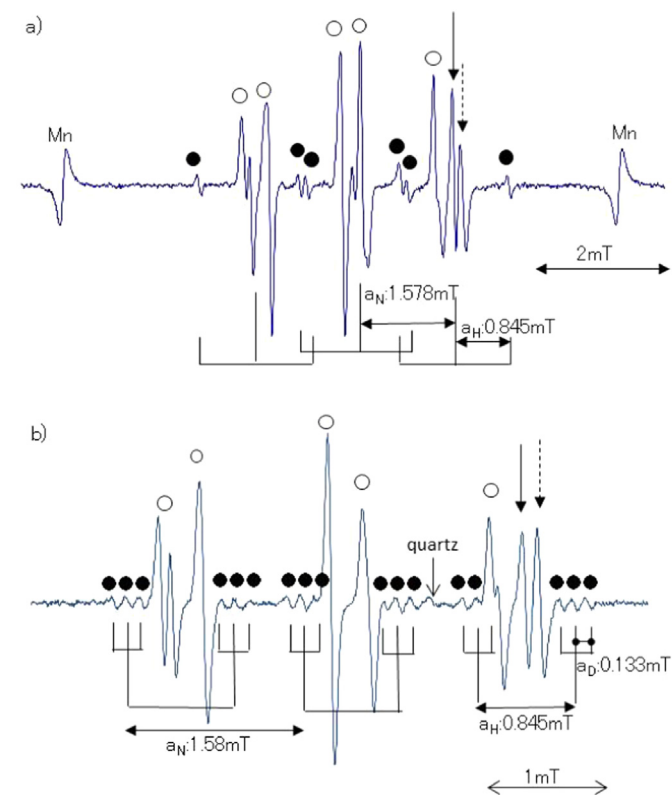
The ESR spectra were measured using a JES-FA-200 (JEOL) spectrometer with a 100-kHz field modulation. The temperature was controlled by an NTV-4 control unit, and ESR measurements were carried out at 263 K. The ESR signals were processed by an ES-PRITS data system. The ESR spectral simulation was performed and the component line shape was taken to be Lorentzian.

### 3. Results and discussion

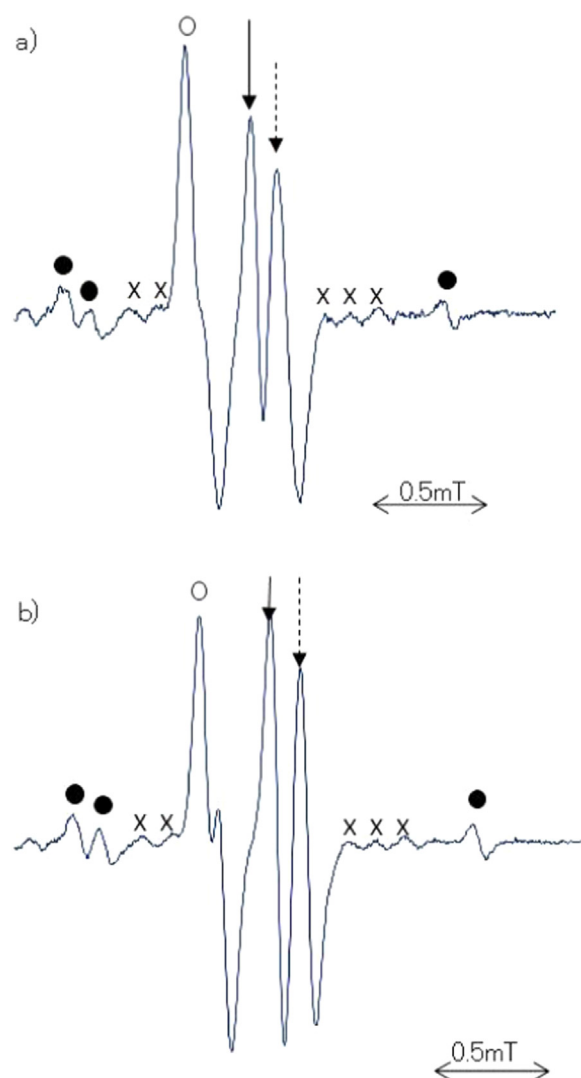
#### 3.1. Determination of the relative yield of the radical adducts

Fig. 1 shows ESR spectra obtained by  $\gamma$ -irradiation of a)  $\text{CH}_3\text{OH}$  and b)  $\text{CD}_3\text{OD}$ . The open circles denote the methoxy radical ( $\text{CH}_3\text{O}$  or  $\text{CD}_3\text{O}$ ) adduct and the hydroxy-methyl radical ( $\text{CH}_2\text{OH}$  or  $\text{CD}_2\text{OD}$ ) adduct overlapping with each other. The black circles and the longitudinal lines show the signals of PBN-H or PBN-D with their hyperfine constants. The hyperfine constants of nitrogen ( $a_N$ ) and hydrogen ( $a_H$ ) for PBN-D were almost consistent with those for PBN-H. The relative value of the hyperfine constant  $a_H/a_D$  was 6.35, which agreed with that of the nuclear magnetic rotation  $\gamma_H/\gamma_D$  (=6.514).

Though the feature of the methoxy radical adduct and that of the hydroxy-methyl radical adduct overlapped in the lower magnetic field region, we can distinguish them in the highest magnetic field as shown by the arrows. Because the feature of PBN- $\text{CH}_3\text{O}$  in the highest magnetic field overlapped with that of PBN-H as shown in



**Fig. 1.** ESR spectra obtained by irradiation of (a)  $\text{CH}_3\text{OH}$  and (b)  $\text{CD}_3\text{OD}$ . The open circles denote the methoxy radical ( $\text{CH}_3\text{O}$  or  $\text{CD}_3\text{O}$ ) adduct and the hydroxy-methyl radical ( $\text{CH}_2\text{OH}$  or  $\text{CD}_2\text{OD}$ ) adduct overlapping with each other. The black circles and the longitudinal lines show the signals of PBN-H or PBN-D with their hyperfine constants. The signals shown by arrows were used to calculate the relative radical yields.



**Fig. 2.** ESR spectra obtained by irradiation of (a)  $\text{CH}_3\text{OD}$  and (b)  $\text{CD}_3\text{OH}$  in the highest magnetic region. The black circles and the crosses denote PBN-H and PBN-D, respectively. The open circles denote the methoxy radical ( $\text{CH}_3\text{O}$  or  $\text{CD}_3\text{O}$ ) adduct and the hydroxy-methyl radical ( $\text{CH}_2\text{OH}$  or  $\text{CD}_2\text{OH}$ ) adduct overlapping with each other. The signals shown by arrows were used to calculate the relative radical yields.

Fig. 1a, the relative yield of the radicals, PBN- $\text{CH}_3\text{O}$ /PBN- $\text{CH}_2\text{OH}$ , was calculated from the differential spectrum between the observed and the simulated one of PBN-H. The relative yield of the radicals, (PBN- $\text{CH}_3\text{O}$ +PBN- $\text{CH}_2\text{OH}$ )/PBN-H, was obtained from the differential spectrum and the simulated one of PBN-H. Fortunately, the feature of PBN- $\text{CD}_3\text{O}$  in the highest magnetic field did not overlap at all with other radicals as shown in Fig. 1b. Both of the relative radical yields, PBN- $\text{CD}_3\text{O}$ /PBN- $\text{CD}_2\text{OD}$  and (PBN- $\text{CD}_3\text{O}$ +PBN- $\text{CD}_2\text{OD}$ )/PBN-D, could be obtained from the observed spectra. Because the lifetime of the methoxy radical adduct is shorter than that of the hydroxy-methyl radical adduct, the relative radical yield decreased with the increasing dose. Therefore, the relative radical yield was plotted versus the dose and the extracted value of the dose at zero was obtained.

Fig. 2 shows ESR spectra obtained by irradiation of a)  $\text{CH}_3\text{OD}$  and b)  $\text{CD}_3\text{OH}$  in the highest magnetic region. The black circles and the crosses denote PBN-H and PBN-D, respectively. Both PBN-H and PBN-D were observed in  $\text{CH}_3\text{OD}$  and  $\text{CD}_3\text{OH}$ . The relative radical yield, PBN-H/PBN-D, could be obtained from these spectra. The open circles denote the overlapping feature of the methoxy radical ( $\text{CH}_3\text{O}$  or  $\text{CD}_3\text{O}$ ) adduct and that of the hydroxy-methyl

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