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ESR Spectroscopic Detection of Methoxyl Radicals Formed in the Photochemical Gas-Phase Reaction of Methane and Water

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During the photolysis of methane–water gas mixtures, a radical has been trapped by both α-phenyl-*N*-*tert*-butylnitrone and 5,5-dimethyl-1-pyrroline 1-oxide. The analysis of the ESR parameters along with the control experiments and the determination of reaction products strongly suggests the detection of methoxyl radical. It is revealed that the yield of methanol and methoxyl radical depends on the initial concentration of methane and the reaction temperature, and the observed difference between their yields is mainly ascribed to the reaction $CH_3O^{\bullet} + CH_4 \rightarrow CH_3OH + {}^{\bullet}CH_3$, which is favorable at higher concentration of initial methane and at higher reaction temperature. Furthermore, the preferential trapping of the methoxyl radical by the spin traps is discussed.

Introduction

Recent investigations have reported that methane is converted to methanol and other oxygen-containing compounds through the photochemical reaction with water vapor under the conditions of low temperature (<100 °C) and atmospheric pressure.[1,2] On the basis of the precise analysis of reaction products, a formation mechanism of each product has been proposed.[2] Nevertheless, the direct detection of reaction intermediates is of particular interest and is important to understand the complicated gas-phase reaction mechanisms. Here, we report the spin trapping of reaction intermediates in the photolysis of methane and water with α-phenyl-*N*-*tert*-butylnitrone (PBN) and 5,5-dimethyl-1-pyrroline 1-oxide (DMPO).

Spin-trapping techniques have been applied in many fields of reaction systems to detect a short-lived radical intermediate. Most of the applications, however, are restricted to the liquid-phase reactions. First trials of spin-trapping gas-phase radicals were performed by Janzen et al.[3-7] and more recent applications by Pryor et al.[8,9] to detect the free radicals in cigarette smoke. We took a similar method to Pryor et al.'s, but in our system the reaction gases were circulated by passing through the spin-trap solution and returned to the photolytic cell. Moreover, to overcome the disadvantage of PBN that the spin adduct generally shows only hyperfine couplings from α-nitrogen (a(N)) and β-hydrogen ($a(\beta$-H)) of PBN itself and, consequently, ambiguity remains in the identification of the trapped radical, another spin trap, DMPO, was used for comparison. Although DMPO spin adducts also show only a(N) and $a(\beta$-H) in many cases, their $a(\beta$-H) values are more sensitive to the trapped radicals than PBN adducts's.

Experimental Section

Ion-exchanged water was supplied after distillation. Methane gas used (Seitetsu Kagaku Co.) was 99% pure and treated with the molecular sieve 3A. PBN and DMPO (Aldrich Chem. Co.) were used without further purification. Reagent grade benzene was dried with molecular sieve 3A and distilled before use. All other chemicals were reagent grade and used without further purification.

As shown in Figure 1, a photolytic cell (0.26 dm^3) was constructed in a vacuum line, and a 15-W low-pressure mercury lamp (main wavelengths 184.9 and 253.7 nm) made of synthetic quartz was set in the cell. Reaction gases of CH_4 and H_2O were led into the photocell through the vacuum line and quantitated by means of manometers, respectively. Mixed reaction gases were led to the degassed benzene solution of a spin trap (1 mmol dm^{-3} PBN or 50 mmol dm^{-3} DMPO) and returned to the photocell by use of a circulating pump at the rate of 0.1 dm^3 min^{-1}. The trapping reaction was usually begun as soon as the mercury lamp was turned on. A path length from the exit of the photocell to the spin trap solution was ca. 250 nm. The spin-trap solution was kept at 10–15 °C and shielded against light. Reaction temperature was varied by using a ribbon heater around the photocell at higher temperatures and running cold nitrogen gas between the photocell and a jacket made of styroform at lower temperatures.

Product analysis was performed by a gas chromatograph equipped with a Porapak Q column at 100 °C with a flame ionization detector.

ESR spectra were measured at ambient temperature with a JES-ME-1X spectrometer. The ESR signals from Mn^{2+} in MgO and DPPH were used for the field calibrations.

Results and Discussion

The gas mixture of methane and water was photolyzed, and the spin trapping of the reaction gases yielded the ESR spectra shown in Figure 2a with PBN and in Figure 2d with DMPO. Results of the control experiments were as follows: photolysis of N_2–H_2O and N_2–H_2O_2 did not give any ESR signals; that of CH_4 yielded the same spectrum as Figure 2a but in very small intensity and the signal almost disappeared after careful dehydration of methane gas supplied; that of CH_4–D_2O gave the spectrum in Figure 2b; that of CH_3OH gave the spectrum in Figure 2c. The hyperfine coupling constants obtained from Figure 2a–c were all the same, and $a(\mathrm{N}) = 1.36$ mT and $a(\beta\text{-H}) = 0.21$ mT. To examine the possibility of the production of spin adducts originated from the solvent, the spin trapping was conducted in several kinds of solvent. However, benzene, dioxane, toluene, and tetrahydrofran gave the same pattern of ESR spectra and the hyperfine coupling constants obtained showed no significant solvent dependence: $a(\mathrm{N}) = 1.357$–1.371 mT and $a(\beta\text{-H}) = 0.193$–$0.211$ mT. The spectrum of Figure 2d apparently consists of two components but mainly of the triplet of doublets ($a(\mathrm{N}) = 1.30$ mT; $a(\beta\text{-H}) = 0.72$ mT). The minor component of a triplet ($a(\mathrm{N}) = 1.397$ mT) is probably caused by the impurity from DMPO.

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TABLE I: Hyperfine Coupling Constants[a] of PBN-R and DMPO-R

	PBN-R				DMPO-R			
R	a(N)	$a(\beta$-H)	solv	ref	a(N)	$a(\beta$-H)	solv	ref
CH_3O	1.377	0.205	benzene	11	1.36	0.76	benzene	13
	1.36	0.21	benzene	this work	1.30	0.72	benzene	this work
CH_2OH	1.519	0.376	methanol	12	1.47	2.07	benzene	13
OH	1.493	0.288	benzyl alcohol	11	1.49	1.48	water	14
	1.38	0.22	benzene	11				
CH_3	1.469	0.357	benzene	4	1.43	2.05	benzene	13
H	1.484	0.742	benzene	5	1.66	2.25	water	14

[a] Values in mT.

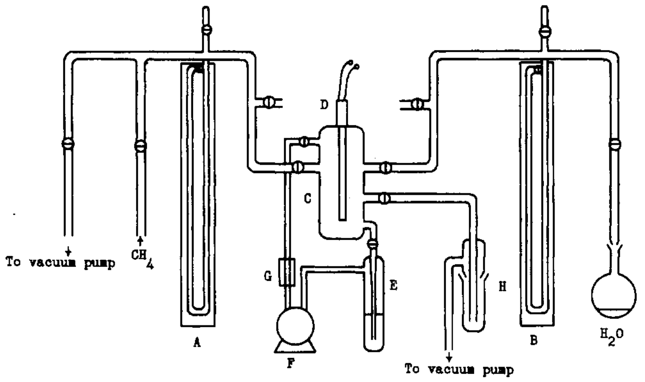

Figure 1. Flow system used for the photolysis of methane-water mixtures: A, B, mercury manometers; C, photocell; D, ultraviolet lamp; E, spin-trapping cell; F, circulating pump; G, flowmeter; H, liquid nitrogen trap.

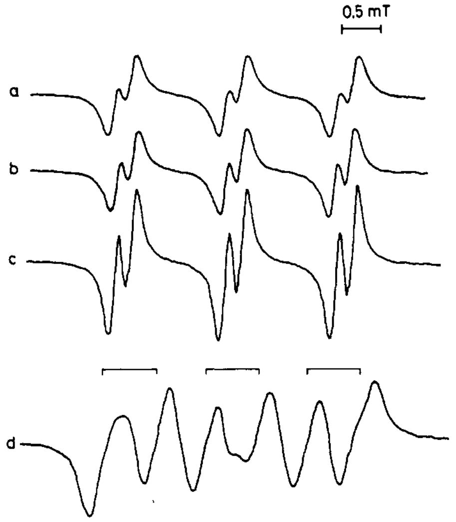

Figure 2. ESR spectra of PBN (a-c) and DMPO (d) spin adducts obtained from the photochemical reaction gases (a) CH_4-H_2O, (b) CH_4-D_2O, (c) CH_3OH, and (d) CH_4-H_2O. Reaction time (=trapping time), 1 h; reaction temperature, 40 °C.

On the other hand, the product analysis for the photolysis of the gaseous CH_4-H_2O system was performed independent of the spin-trapping experiments. The product distribution was basically the same as that in our previous reports[1,2] and the main product was methanol followed by ethanol.

As previous investigations stated,[9] the photochemical reaction of the gaseous CH_4-H_2O system proceeds as follows:

$$H_2O \xrightarrow{h\nu} {}^{\bullet}OH + H \quad (1)$$

$$CH_4 + {}^{\bullet}OH \rightarrow {}^{\bullet}CH_3 + H_2O \quad (2)$$

$${}^{\bullet}CH_3 + H_2O \rightarrow CH_3OH + H \quad (3)$$

$${}^{\bullet}CH_3 + {}^{\bullet}OH \rightarrow CH_3OH \quad (4)$$

Methanol produced should suffer photolytic decomposition and/or an attack of H-atom abstraction by the radicals such as $^{\bullet}OH$ and $^{\bullet}CH_3$ ($^{\bullet}R$).

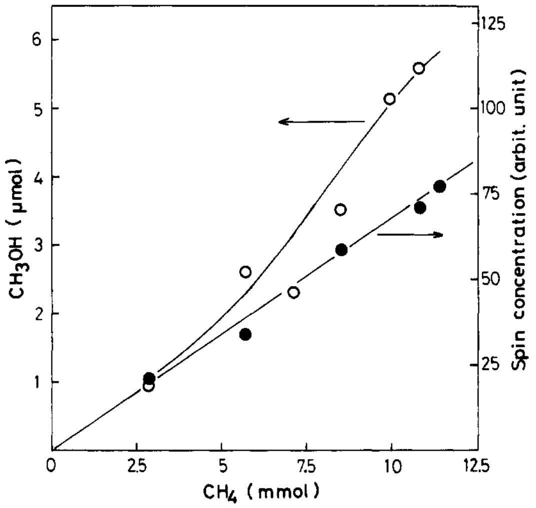

Figure 3. CH_3OH (○) and $CH_3O^{\bullet}$ (●) yields depending on initial concentration of methane. $[H_2O]$ = 0.25 mmol; reaction time (=trapping time), 1 h.

$$CH_3OH \xrightarrow{h\nu} CH_3O^{\bullet} + H \quad (5)$$

$$CH_3OH \xrightarrow{h\nu} {}^{\bullet}CH_2OH + H \quad (6)$$

$$CH_3OH + {}^{\bullet}R \rightarrow {}^{\bullet}CH_2OH + RH \quad (7)$$

$$CH_3OH + {}^{\bullet}R \rightarrow CH_3O^{\bullet} + RH \quad (8)$$

These mechanistic proposals suggest the possibility of the spin trapping of H, $^{\bullet}CH_3$, $^{\bullet}OH$, $CH_3O^{\bullet}$, and $^{\bullet}CH_2OH$. In Table I, data of the hyperfine coupling constants of these radicals trapped by PBN and DMPO are shown together with those obtained in this study. As seen from this table, the hyperfine coupling constants obtained here are in good agreement with the reported values for $CH_3O^{\bullet}$. Therefore, we conclude that the methoxyl radical formed in the photolysis of the CH_4-H_2O mixture was trapped.

It is not very clear why only methoxyl radical was detected in this photochemical reaction. However, the following explanations may be possible: The radical intermediates $^{\bullet}CH_3$, H, $^{\bullet}OH$, $^{\bullet}OCH_3$, and $^{\bullet}CH_2OH$ should vanish through H-atom abstraction, radical-radical recombination, or addition reaction. A general reactivity of these radicals for H-atom abstraction is in the order $HO^{\bullet} > CH_3^{\bullet} > H \simeq CH_3O^{\bullet} > HOCH_2^{\bullet}$.[15] The probability of recombination depends on the radical concentration, and that of

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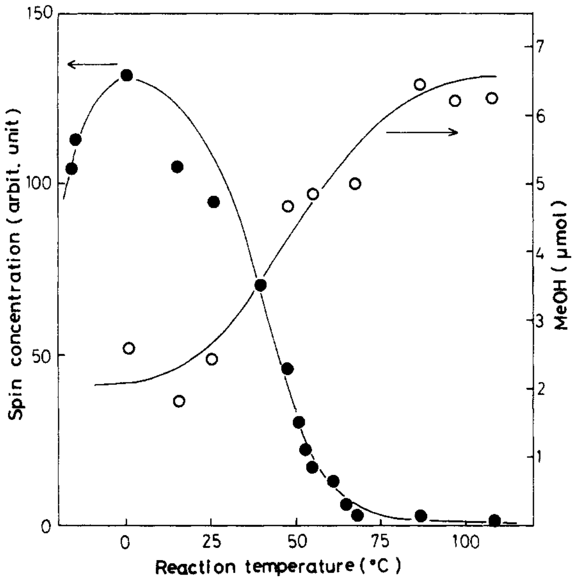

Figure 4. Temperature dependence of CH_3OH (○) and $CH_3O^•$ (●) yield. $[CH_4]$ = 10 mmol; $[H_2O]$ = 0.25 mmol; reaction time (=trapping time), 1 h.

methyl radical and hydrogen atom must be much higher than that of the radicals originated from methanol. Actually, considerable amounts of ethane and hydrogen were obtained. Consequently, the lifetime of the radicals $HO^•$, $CH_3^•$, and H might be shorter than that of $^•CH_2OH$ and $CH_3O^•$ and the probability of the spin-trapping of the former radicals might be low. Compared with $^•OCH_3$, $^•CH_2OH$ should be produced in higher probability.[16] Taking into account this point and the low reactivity for H abstraction, the concentration of $^•CH_2OH$ is expected to be higher than that of $^•OCH_3$. This speculation, however, is inconsistent with the experimental result. Therefore, the preferential trapping of $CH_3O^•$ may be related with the difference in the affinity of $^•CH_2OH$ and $^•OCH_3$ to the $-CH{=}N^+{-}O^-$ fragment of PBN and DMPO. As Paul and Roberts reported,[17] alkoxyl radical is highly electrophilic and the addition reaction of $^•OCH_3$ to PBN or DMPO is considered to be much faster than that of $^•CH_2OH$.

Ledwith et al.[18] also detected $CH_3O^•$ preferentially by 80 mmol dm^{-3} PBN in the liquid-phase photolysis of methanol and water containing an oxidant.

As shown in Figure 3, the production of both methanol and methoxyl radical increases as the initial concentration of methane increases, but the increment of CH_3OH exceeds that of $CH_3O^•$ at higher concentrations of CH_4. The good correspondence between the yields of CH_3OH and $CH_3O^•$ at lower concentrations of CH_4 suggests that methanol produced by (3) and/or (4) decomposes to $CH_3O^•$ via (5). At higher concentrations of CH_4, however, the following reaction is presumably involved in the formation of methanol since added methane shows a catalytic effect on the formation of methanol as seen from Figure 3.

$$CH_3O^• + CH_4 \rightarrow CH_3OH + {}^•CH_3 \qquad (9)$$

This reaction is also probable both energetically and in view of the probability of molecular collision.

In Figure 4, the concentration of spin adduct and methanol are plotted versus reaction temperature. The concentration of the spin adduct decreases with increasing temperature through a maximum at about 0 °C and becomes negligibly small at temperatures over 70 °C. On the other hand, the formation of methanol increases with reaction temperature. These results can be explained by the temperature dependence of a series of reactions involving (9). At low temperatures, the reaction rate of (9) is relatively low, while the photolysis is principally independent of temperature. Therefore, methoxyl radical is produced by (5) whenever methanol exists in the system. At higher temperature, however, the rates of reactions (2)–(4) and (9) are high, which results in the increase of methanol production but in the decrease of methoxyl adduct.

Consequently, it is concluded that (i) methoxyl radical is trapped in the photochemical reaction of gas-phase methane and water by PBN or DMPO, (ii) the photolysis of methanol is the main source of the methoxyl radical, and (iii) the observed change in the yields of methanol and methoxyl radical depending on the initial concentration of methane and the reaction temperature is mostly attributed to the reaction $CH_3O^• + CH_4 \rightarrow CH_3OH + {}^•CH_3$.

Registry No. PBN, 3376-24-7; DMPO, 3317-61-1; CH_4, 74-82-8; H_2O, 7732-18-5; CH_3OH, 67-56-1; $CH_3O^•$, 2143-68-2.

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