ESR DETECTION OF OH AND H RADICALS GENERATED BY CONTACT GLOW DISCHARGE IN AQUEOUS SOLUTIONS

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(Abstract)
Contact glow discharge (CGD) was applied for a few minutes to the surface of an aqueous solution containing DMPO, a spin-trapping compound, and the solution was subjected to ESR measurement at room temperature. The spectra obtained are characteristic of OH – DMPO and H – DMPO adducts in acid and basic conditions, respectively. This is the first, direct evidence for the generation of OH and H radicals under CGD conditions.

(Key words)
OH and H radicals, ESR, Spin trapping, Aqueous solutions

Introduction
It has been known that water molecule is the most abundant molecule in the Universe, and also the most fundamental molecule in evolutionary processes on the primitive Earth. Water is an essential solvent and participates in various chemical reactions. In addition, water molecule dissociates to OH and H radicals under high energy conditions such as electric discharge.

Electric discharge of gaseous mixtures consisting of methane, ammonia and water was shown to result in the formation of various organic compounds [1]. However, the chemical process of this gaseous reaction proceeds in an uncontrolled way. Subsequently, Harada and coworkers reported on aqueous reactions under high energy conditions such as contact glow discharge (CGD) [2]. What they did is a matter of great significance as the simulation of the lightning striking on the surface of the hydrosphere of the primitive Earth. Under the CGD conditions, water molecule presumably dissociates to OH and H radicals, and the radicals immediately react with substrates to form substrate radicals. The reactions proceed stepwise, followed by the formation of various organic compounds in aqueous solutions. Thus the chemical process in each step could be seen in the time course of the products in aqueous reactions under CGD conditions. Although a certain amount of indirect evidence for the formation of OH and H radicals has been accumulated [3], no direct physical evidence is reported yet.

It is the advantage of spin-trapping method that primary short-lived radicals react with such diamagnetic nitroso compounds as 5,5-dimethyl-1-pyrrroline-1-oxide (DMPO) to form long-lived nitrooxide radicals which can be detected and identified by ESR at room temperature. In this study, we have employed the spin-trapping method in order to get direct evidence for the generation of OH and H radicals under CGD conditions.

Experimental
The CGD reaction apparatus consists of dual glass tubes as illustrated in Fig.1. Cold water was led into the outer tube to cool the solution of inside reaction tube so that the reaction temperature was always kept at 20 – 30° C. CGD was applied for a few minutes to the surface of aqueous solution (30 ml) containing 5x10^{-3} M DMPO together with a small amount of sulfuric acid or sodium hydroxide (~0.01 mmol). Argon gas was first bubbled in the solution and then filled the reaction tube during CGD. The applied electric current was 40 – 50 mA at 500 – 700 V.

Fig.1. Reaction apparatus for CGD, a, platinum anode; b, platinum cathode; c, thermometer; d, magnet; e, magnetic stirrer.

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After the reaction was over, the solution of 0.25 ml was transferred into a quartz flat cell for ESR measurement at room temperature. ESR spectra were recorded on a Varian E-9 X-band spectrometer with following settings: modulation frequency, 10 kHz; modulation amplitude, 0.1 mT; microwave output power, 0.2 mW; time constant, 0.3 sec.

**Results and Discussion**

CGD of argon-saturated solutions containing DMPO gave different ESR spectra in acid and basic conditions. This is illustrated in Fig.2 (A) and (B), respectively. As shown by the stick diagrams for (A) and (B), the observed spectra are characteristic of two nitroxides: (A) is due to OH – DMPO adduct and (B) to H – DMPO adduct. It follows that OH and H radicals are produced by CGD of water by the following reactions:

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
N & \quad O \\
H & + \cdot \text{OH} \rightarrow \text{Me} & \quad \text{Me} \\
& \quad \text{O} \\
& \quad H
\end{align*}
\]

\( (1) \)

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
N & \quad O \\
H & + \cdot \text{H} \rightarrow \text{Me} & \quad \text{Me} \\
& \quad \text{O} \\
& \quad H
\end{align*}
\]

\( (2) \)

The absence of H – DMPO adduct in acid condition may be due to a high rate constant of hydrogen recombination reaction to yield molecular hydrogen, i.e. 1.5x10⁷ M⁻¹ sec⁻¹ in 0.2 - 0.8 N H₂SO₄ [4], in comparison with the rate constant of H – DMPO formation. In basic condition, on the other hand, OH radical can be converted to O⁺ by reaction (3)[5]:

\[
\text{OH} + \cdot \text{OH}^- \rightarrow \text{O}^+ + \text{H}_2\text{O} \quad (3)
\]

This may lead to absence of OH – DMPO adduct and appearance of H – DMPO adduct formed by H radical which escapes from recombination with OH radical.

The hyperfine coupling constants are determined as follows: \( a_H = 1.4 \text{ mT} \) and \( a_Q = 1.4 \text{ mT} \) for OH – DMPO adduct and \( a_H = 1.6 \text{ mT} \) and \( a_Q = 2.15 \text{ mT} \) for H – DMPO adduct. These values are in good agreement with those reported for radiolyzed [6] or sonicated [7] aqueous solutions.

**References**