5.3 Radiolytic Reduction Reaction of Colloidal Silver Bromide Solution

Yasuhisa Oya, Takehiro Zushi*, Kunihiko Hasegawa* and Tatsuo Matsuura**

Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, Tokyo 152, Japan

* Radiochemistry Research Laboratory, Shizuoka University, Shizuoka 422, Japan

** Institute for Atomic Energy, Rikkyo University, Yokosuka 240-01, Japan

Abstract The reduction reaction of colloidal silver bromide $(AgBr_3)^{2-}$ in nitrous oxide gas saturated solution of some alcohols: methanol, ethanol, 2-propanol and 2-methyl-2-propanol by γ-irradiation was studied spectrophotometically in order to elucidate the mechanism of the formation of colloidal silver bromide $(AgBr_3)^{3-}$ at ambient temperature . The amount of colloidal silver bromide formed increases in the order: i-PrOH, EtOH, MeOH. In t-BuOH, colloidal silver bromide did not form. The relative reactivities of alcohols for colloidal silver bromide was also studied kinetically.

INTRODUCTION

The reduction reaction of colloidal silver bromide $(AgBr_3)^{2-}$ in aqueous solution by γ-ray irradiation has been known to form colloidal silver. However, the mechanism of the formation of colloidal silver bromide $(AgBr_3)^{3-}$ adding alcohols in N_2O saturated solution has not been revealed.

In present paper, the reduction of colloidal silver bromide by γ-irradiation saturated solution in the presence of alcohols, viz., methanol, ethanol, 2-propanol, 2-methyl-2-propanol was studied. The mechanism of reduction of colloidal silver bromide was also studied.

EXPERIMENTAL

All reagents were obtained from Wako Pure Chemical Industries Ltd. methanol, ethanol, 2-propanol, 2-methyl-2-propanol were purified by distillation. Other reagents were used without further purification. Water from a Milli RO60 Millipore filtering system was used throughtout the study. Colloidal silver bromide suspensions were prepared by adding 2×10^{-2}M $AgNO_3$ and adding very slight excess of 2×10^{-2}M ion concentration of KBr solution in 0.05% gelatine solution and then stirring the solution to prepare a homogeneous collidal solution. The colloidal silver bromide solution was produced to a negative charge colloid in the solution. N_2O gas passed through the solution for 10 min to study the reaction between OH radical and colloidal silver bromide. Hydroxy radical, OH, and hydrated electrons, e_{aq}^- are formed by the radiolysis of water. In N_2O saturated solution hydrated electrons are converted to OH radical:

$$e_{aq}^- + H_2O + N_2O \rightarrow N_2 + OH^- + OH. \quad (1)$$

To prevent the effect of UV radiations the solution was quickly wrapped in black paper and then irradiated at the room temperature. The amount of colloidal silver obtained by the irradiation was determined spectrophotometically at the maximum wave length of 405~410 nm, ε = 11500 mol $dm^{-3}cm^{-1}$ and that of 410~420 nm, ε = 13500 $mol^{-3}cm^{-1}$(Johnson, *et al.*,1970). ^{60}Co γ-ray source, 1.35kCi, was used for the irradiation. Dose rate measured with Fricke dosimeter (G=15.5) was $1.3\times10^{17}\sim3.0\times10^{17} eV\cdot g^{-1} h^{-1}$.

RESULTS AND DISCUSSION

The wave lengths of maximal absorption of colloidal silver bromide $(AgBr_3)^{3-}$ in 0.1M MeOH was 409 nm at the absorbed dose $1.8\times10^{18} eV\cdot s^{-1}$. The absorption maximum is shifted to long wave lengths upon increasing the dose. The range of maximum absorption was 409~420 nm. The dose rate for colloidal bromide solution was studied. The amounts of $G(Ag^{\circ}\cdot)$ was found to increase with the dose rate and colloidal silver bromide formed at a given dose in the order: i-PrOH, EtOH and MeOH (Johnson, 1978). The stability of colloidal silver bromide produced by γ-ray irradiation was studied for about 200 hrs. It was found that colloidal silver bromide reduced by irradiation diminished with pseudo first order reaction. After finishing for irradiation, the colloid is stable within about 1 h. For one example, in case of silver bromide solution to add $1.0\times10^{-3}\sim1.0\times10^{-1}$M MeOH, the relation between Ag^{0} (=$(AgBr_3)^{3-}$) produced and the absorbed dose is shown in Fig.1. As can be seen from figure, for MeOH, the amount of Ag^{0} produced is increase with the concentration of alcohol. The initial G(Ag^{0}) was obtained from the slope of curve in the figure.

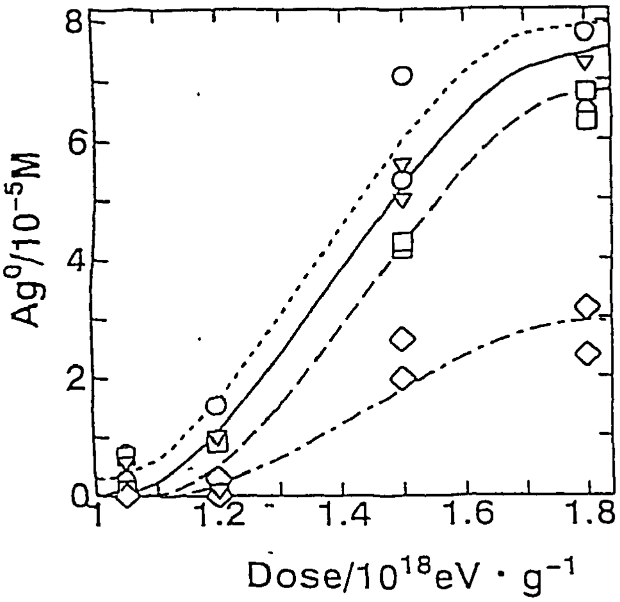

Fig.1 Radiolytic reduction reaction of colloidal silver bromide with methanol; Concentration of MeOH, ○:1.0×10^{-1}M, □:1.0×10^{-2}M, ▽:5.0×10^{-2}M, ◇:1.0×10^{-3}M

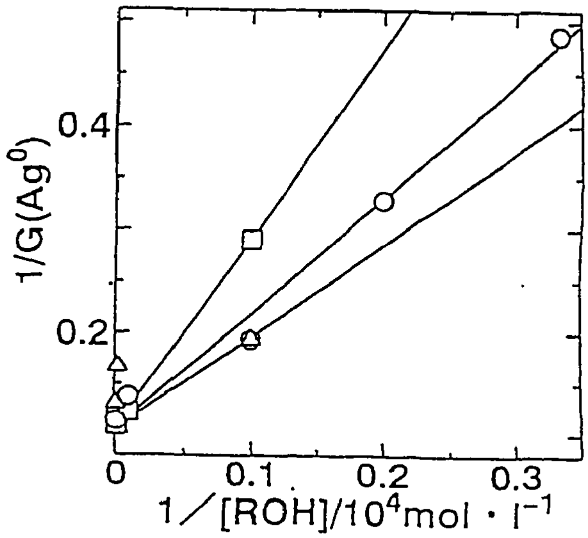

Fig.2 1/G(Ag^{0}) vs. 1/ [ROH] ; □: MeOH, ○: EtOH, △: i-PrOH.

As described above, when excess Br^- ion was added to the solution, the colloidal silver bromide forms $(AgBr_3)^{2-}$ as a chemical form. First of all, this colloid solution was irradiated by γ-ray irradiation:

$$(AgBr_3)^{2-} \rightarrow [(AgBr_3)^{2-}]^{\bullet}. \qquad (2)$$

OH radical(1) produced reacts alcohol to form radical:

$$RCH_2OH + OH \rightarrow RCHOH + H_2O. \qquad (3)$$

The produced radical(3) reacts with $[AgBr_3)^{2-}]^{\bullet}$ to form $(AgBr_3)^{3-}$, rate constant k_1 is reaction (4):

$$[(AgBr_3)^{2-}]^{\bullet} + RCHOH \xrightarrow{k_1} (AgBr_3)^{2-}\cdots RCHO + H^+. \quad (4)$$

On the other hand, the excited colloidal silver bromide make up to the stable colloid, rate constant k_2 is reaction (5):

$$[(AgBr_3)^{2-}]^{\bullet} \xrightarrow{k_2} (AgBr_3)^{2-}, \quad (5)$$

where the radiation yield(G) of colloidal silver denotes $G(AgBr_3)^{2-} = G(Ag^{\circ})$, the intensity of γ-ray is I and the reaction efficiency a , $G(Ag^{\circ})$ can be discribed as follows:

$$G(Ag^{\circ})\,I = k_1' \,[(AgBr_3)^{2-}]^{\bullet}\,[RCHOH]\,. \quad (6)$$

When the rates of production equals to the rate of disapperence in excited colloidal silver bromide, the following equation (7) can be written by the use of stationary state method:

$$G(Ag^{\circ}) = \frac{ak_1\,[RCHOH]}{k_1\,[RCHOH] + k_2}. \quad (7)$$

In order to find a relation $G(Ag^{\circ})$ and the rate constants, k_1 and k_2, eq.(7) is rearranged as:

$$\frac{1}{G(Ag^{\circ})} = \frac{1}{a} + \frac{k_2}{ak_1\,[RCHOH]}. \quad (8)$$

Therefore, if a plot of $1/G(Ag^{\circ})$ against the concentration of alcohol gives a straight line, a and relative rate constant of k_1 and k_2 can be determined from the intercept and slope respectively. This relations is shown in Fig.2.

$$CH_3OH + OH \xrightarrow{k_m} CH_2OH + H_2O, \quad (9)$$

$$CH_3CH_2OH + OH \xrightarrow{k_e} CH_3CHOH + H_2O, \quad (10)$$

$$(CH_3)_2CHOH + OH \xrightarrow{k_p} (CH_3)_2COH + H_2O. \qquad (11)$$

The rate constants of the reaction between OH radical and MeOH, EtOH and i–PrOH, respectively, are the following 0.5, 1.0 and 1.5 × 10^9 M^{-1} s^{-1} (Anbar *et al.*, 1967). Thus, the following relation roughly can be expressed:

$$\frac{1}{3}k_p = \frac{1}{2}k_e = k_m = k_R' \qquad (12)$$

Considering OH radical reacts with radical produced from alcohol, we can derive from (7) equation:

$$\frac{1}{G(Ag^{\cdot})} = \frac{1}{a} + \frac{k_2}{ak_1k_R\,[RCH_2OH]\,[OH]} \qquad (13)$$

For one example of EtOH and MeOH, we can obtain the following relation:

$$\frac{ak_1(EtOH)k_e\,[OH]}{ak_1(MeOH)k_m\,[OH]} = \frac{1.84\times10^{-4}}{1.12\times10^{-4}} \qquad (14)$$

The relative rate constant of MeOH, EtOH and i–PrOH are found to be 1 : 2 : 3 for OH radical and 1 : 3.3 : 6.2 for the reduction by the radicals produced from alcohols by γ–ray irradiation. It became evident that colloidal silver bromide solution can be reduced to faciliate by EtOH and i–PrOH radicals more than MeOH radical. This result show that the relation of the reduction ability is established in the both aqueous solution and colloidal solution.

REFERENCES

Anbar M. and Neta P. (1967) *Intl. J. Appl. Radiation & Isotope* 18, 493. .

Johnson F.J.,Mehrotra K.N. and Huh.Y.(1970) *Radiation Res.* 44, 323.

Johnson F.J. (1978) *Radiation Res.* 75, 286.