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Effect of Hole Scavengers on the Radiolysis of Water

Takeshi SAWAI
Tokyo Metropolitan Isotope Research Center, Fukazawa, Setagaya-ku, Tokyo

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Recently, a model for the radiolysis of water at low LET was proposed by Hamill.[1] According to the model, some charge recombination of the dry electron and the hole, which are produced early in the radiolysis of water, occurs before hydration and is responsible for the formation of molecular hydrogen and hydrogen peroxide, and these ion pairs can be scavenged by suitable solutes prior to hydration. This hypothesis has been supported by the quantitative correlation shown in recent studies[2,3] of aqueous solutions. The reaction of an electron with some solutes prior to hydration has been reported by the recent striking experiments of Hunt *et al.*[4] with pico second-pulsed radiolysis.

If the dry hole in water is trapped by a suitable solute (X^-), one can expect an increase in $G(e^-_{aq})$ by preventing the fast neutralization of the dry-charge pairs in water. The increase in $G(e^-_{aq})$ with an increase in the Cl^- concentration was shown in an earlier paper.[5] Moreover, the increase of $G(e^-_{solv})$ by Cl^- in the radiolysis of ethanol was recently reported by Khorana and Hamill.[6] The change in $G(e^-_{solv})$ is considered to be due to hole trapping by Cl^-.

The negative ions, SO_4^{2-}, ClO_4^-, or F^-, will also trap the hole[7]:

$$H_2O^+(H_3O^+) + X^- \longrightarrow X(HX) + H_2O \qquad (1)$$

The purpose of this work is to provide evidence for the hole trapping by halogen ions and SO_4^{2-}, and to examine the effect of the solutes on the yield of molecular products.

Experimental

Samples (10 m*l*) of aqueous neutral solutions containing 10^{-2}M KNO_3 and 5×10^{-2}M isopropanol (*i*-PrOH) for the testing of $G(e^-_{aq})$, $G(H_2)$, $G(H_2O_2)$, and 2×10^{-2}M KNO_3 aqueous solutions for G_{H_2} were used. These samples in the irradiation vessel with a break seal were purged with nitrogen gas, degassed by repeated freeze-pump-thaw cycles, and then irradiated with ^{60}Co γ-rays. Oxygenated 5 m*l* samples of

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[1] W. H. Hamill, *J. Phys. Chem.*, **73**, 1341 (1969).

[2] P. L. T. Bevan and W. H. Hamill, *Trans. Faraday Soc.*, **66**, 2533 (1970).

[3] T. Sawai and W. H. Hamill, *J. Phys. Chem.*, **74**, 3915 (1970).

[4] R. K. Wolff, M. J. Bronskill, and J. W. Hunt, *J. Chem. Phys.*, **53**, 4211 (1970).

[5] T. Sawai and W. H. Hamill, *ibid.*, **52**, 3843 (1970).

[6] S. Khorana and W.H. Hamill, *J. Phys. Chem.*, **74**, 2885 (1970).

[7] P. N. Moorthy and J. J. Weiss, "Solvated Electrons," Advances Chemistry Series **50**, ed. by R.F. Gould, American Chemical Society Publications, Washington, D.C. (1960), p. 180.

10^{-2}M KNO_3-i-PrOH solutions were used for the G(OH) measurements. The dose rate, determined by means of a ferrous sulfate dosimeter, was 9.31×10^{18} eV/g hr. The methods of the measurement of H_2, acetone, H_2O_2, and NO_2^- are described elsewhere.[8] These yields were calculated from the slope of the linear portions of the product-dose curves. The energy absorbed in the samples was corrected by the use of the electron fraction of each sample.

Results and Discussion

In the deaerated i-PrOH-KNO_3 solutions, NO_3^- reacts with e^-_{aq} to form NO_2^-:

$$NO_3^- + e^-_{aq} \longrightarrow NO_2^- \qquad (2)$$

H and OH radicals react with i-PrOH to form isopropanol radicals:

$$(CH_3)_2CHOH + H \longrightarrow (CH_3)_2COH + H_2 \qquad (3)$$

$$(CH_3)_2CHOH + OH \longrightarrow (CH_3)_2COH + H_2O \qquad (4)$$

In oxygenated solutions, $(CH_3)_2COH$ will react with O_2 to produce acetone and HO_2[9]:

$$(CH_3)_2COH + O_2 \longrightarrow (CH_3)_2CO + HO_2 \qquad (5)$$

Almost all the H reacts with O_2 to form H_2O_2, because $k(H+O_2)[O_2]/k_3[i\text{-PrOH}]$ is about 50. The effect of hole scavengers on the yields of NO_2^-, H_2O_2, H_2, and acetone was measured under each set of conditions. These results are shown in Figs. 1 and 2. $G(NO_2^-)$ increases with an increase in the concentration of F^- and SO_4^{2-}. G(acetone) decreases with an increase in the Cl^- concentration, while in F^- or SO_4^{2-} solutions the yield is independent of the concentration of F^- and SO_4^{2-}. There is no dependence of G_{H_2}, G_H, and $G_{H_2O_2}$ on the solute concentration except for the cases of Br^- and I^-.

In a F^- solution, the reaction of H with F^- is very slow[10] ($k\approx10^4 M^{-1} sec^{-1}$) and the reaction of OH with F^- should not occur. In Fig. 1, $G(e^-_{aq})$ increases and G(acetone) dose not depend on the F^- concentration. The hole trapping by F^- will be:

$$H_2O^+ + F^- + H_2O \longrightarrow HF + OH + H_2O$$

$$\text{or } H_3O^+ + F^- \longrightarrow HF + H_2O,$$

since F_2^- has not been found even in aqueous F^- solutions at 77°K.[11] The increase in $G(e^-_{aq})$ seems to be due to the prevention of the geminate recombination of dry-charge pairs by the hole trapping. By the same expression used previously for the hole trapping,[5] $1/G_2^0$ can be obtained from the intercept of the plot of $\Delta 1/G(NO_2^-)$ vs. $1/[F^-]$. G_2^0 is 0.9 from Fig. 3, and $G(e^-_{aq})$ is 2.7 at $[F^-]=0$ in Fig. 1; therefore, $\sum G(\text{electrons})=3.6$ is obtained.

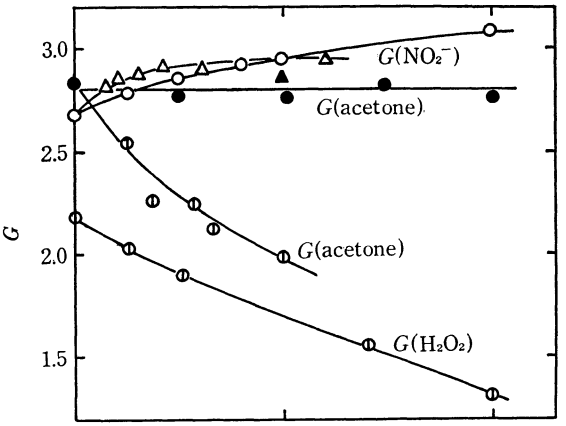

Fig. 1. Effects of solute concentration on $G(NO_2^-)$, $G(H_2O_2)$, and G(acetone) in 10^{-2}M KNO_3-isopropanol solutions.
●, ▲, ⦶: Yields in oxygenated solutions
○, △: Yields in deaerated solutions
○, ●: KF
△, ▲: Na_2SO_4
⦶: NaCl

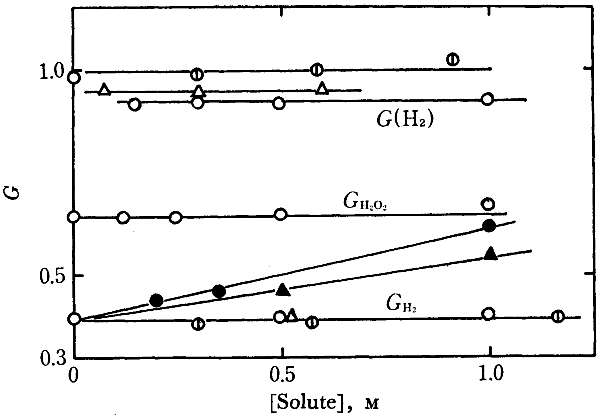

Fig. 2. Effects of solute concentration on G_{H_2}, $G(H_2)$, and $G_{H_2O_2}$ in deaerated solutions.
$G(H_2)$, $G_{H_2O_2}$: H_2 and H_2O_2 yields in 10^{-2}M KNO_3-isopropanol solutions
G_{H_2}: H_2 yield in 2×10^{-2}M KNO_2 solutions
○: KF, ⦶: $NaClO_4$, △: Na_2SO_4, ●: KI, ▲: KBr

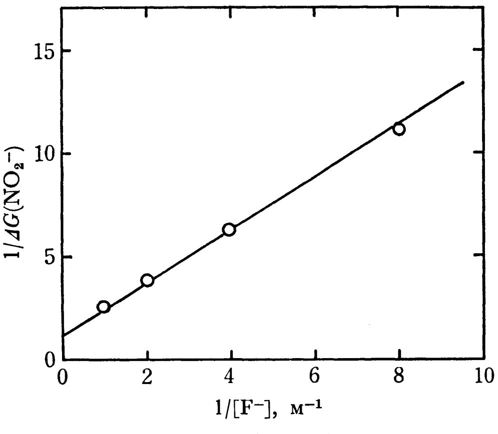

Fig. 3. $G(NO_2^-)$ as a function of the concentration of KF.

In SO_4^{2-} solutions, $G(e^-_{aq})$ increases with an increase in the concentration, and 0.5M SO_4^{2-} has no effect on G(acetone). The reaction of SO_4^{2-} with hole will be:

$$H_2O^+(H_3O^+) + SO_4^{2-} \longrightarrow SO_4^-(HSO_4^-) + H_2O.$$

The reaction of SO_4^- with NO_3^- can be ignored, since $k(SO_4^- + i\text{-PrOH})/k(SO_4^- + NO_3^-)$ is about 100,[12] and SO_4^-, a stronger oxidizing species than

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[8] T. Sawai, This Bulletin, **39**, 955 (1966).

[9] E. Hayon, "Radiation Chemistry of Aqueous Systems," ed by G. Stein, John Wiley & Sons, Inc., N. Y. (1968), p. 157.

[10] M. Anber and P. Neta, *Int. J. App. Radiation and Isotopes*, **18**, 439 (1967).

[11] B. L. Bales and L. Kevan, *J. Phys. Chem.*, **74**, 1098 (1970).

[12] I. Kraljic, *Int. J. Rad. Phys. Chem.*, **2**, 59 (1970).

Cl_2^-,[13] reacts with *i*-PrOH probably to form an isopropanol radical, as in the case of OH. Therefore, $G(e^-_{aq})$ increases upon the hole trapping, while, G(acetone) is constant.

$G(e^-_{aq})$ increased and $G_{H_2O_2}$ decreased with an increase in the Cl^- concentration. We have reported before that these changes might be due to the hole trapping by Cl^-.[5] The Cl radical formed by the hole trapping reacts with Cl^- to produce Cl_2^-. It has been shown that Cl_2^- reacts with NO_3^- and *i*-PrOH:[13]

$$Cl_2^- + NO_3^- \longrightarrow 2Cl^- + NO_3 \qquad (6)$$

$$Cl_2^- + (CH_3)_2CHOH \longrightarrow \text{Products} \qquad (7)$$

Reaction (6) can be ignored because k_7 is much larger than k_6 ($k_6=1.4\times10^6$ and $k_7=6.1\times10^7$ M^{-1} sec^{-1})). Therefore, the increase of $G(e^-_{aq})$ is probably due to the hole trapping. G(acetone) goes down with the Cl^- concentration, as is shown in Fig. 1. If the change in G(acetone) is due to the hole trapping by Cl^-, ΔG(acetone) should be $\leqq \Delta G(e^-_{aq})$. However, at 1 M NaCl, for example, $\Delta G(e^-_{aq})$ is only ~0.3 and ΔG(acetone) is ~1.0. Some other reaction which reduces G(acetone) seems to occur. The reaction of Cl^- with OH is very slow in a neutral solution ($k=10^4\text{M}^{-1}\text{sec}^{-1}$), but the reaction is relatively fast in an acid solution.

$$OH + Cl^- + H_3O^+_{aq} \longrightarrow Cl + 2H_2O \qquad (8)$$

The acetone yield may be decreased by the reaction (8) in the spur, and the decrease in $G_{H_2O_2}$ with the Cl^- concentration[5] may not be due to hole trapping, but to the reaction (8).

According to the model of the radiolysis of water proposed by Hamill,[1] molecular hydrogen and hydrogen peroxide yields should decrease in the presence of hole scavengers, which prevent the reaction of the hole with dry electrons. As is shown in Fig. 2, however, F^- has no effect on $G_{H_2O_2}$, and G_{H_2} is almost independent of the solute concentrations except in the cases of Br^- and I^-. It has also been found that NO_3^-, which is a good scavenger for dry and solvated electrons, diminished G_{H_2} most effectively, while $G_{H_2O_2}$ was not affected at all.[14] These facts suggest that the molecular products in the radiolysis of water are not formed by the reaction of the hole with dry electrons.

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[13] M. E. Langmuir and E. Hayon, *J. Phys. Chem.*, **71**, 3808 (1967).

[14] M. Anbar, "Fundamental Processes in Radiation Chemisty," ed. by P. Ausloos, John Wiley & Sons, Inc., N. Y. (1968), p. 651.