BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (5), 1631—1632 (1975)

The Radiation-induced Dehalogenation of Dichloromethane and Dibromomethane in Methanol Solutions

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(Received October 26, 1974)

Synopsis. The scheme of the radiation-induced dehalogenation of dichloromethane and dibromomethane was investigated in deaerated methanol. The relative rate constants of those solutes toward e_{sol}^- were determined by competition kinetics, using a N_2O scavenger.

Organic halides are generally radiosensitive, and the main reaction in the radiolysis is usually dehalogenation, producing readily determinable halide ions. Therefore, a number of studies concerning the radiation chemistry of organohalogen compounds and their aqueous or alcohol solutions have appeared in the literature.[1-9]

In previous work,[10-12] we ourselves have determined the reactivities of monochlorobenzene and its derivatives toward the solvated electron in alcohols. We now wish to extend those studies to simple aliphatic halogen compounds, such as dichloromethane and dibromomethane, in methanol systems and to elucidate the scheme of the radiation-induced dehalogenation of these methylene halides in methanol solutions.

Experimental

The methanol was purified according to the procedure proposed by Imamura *et al.*[13] The dichloromethane and dibromomethane were treated successively with dilute sulfric acid and a 0.1 M K_2CO_3 solution and washed repeatedly with distilled water. They were subjected to fractional distillation after being dried over $CaCl_2$. A deaerated solution (5 ml) prepared by the conventional vacuum technique with freeze and thaw cycles was sealed in a glass cell. ^{60}Co γ-irradiation was carried out at a dose rate of 1.34×10^{18} eV ml^{-1} h^{-1}. The halide ions were determined by potentiometric titration. The formaldehyde was determined spectrophotometrically by the use of chromotropic acid. The amounts of hydrogen and nitrogen were determined by gas chromatography, using a Molecular Sieve 5A column and argon as the carrier gas.

Results and Discussion

Figure 1 shows the yields of halides ions as a function of the methylene dihalide concentration in deaerated methanol solutions. $G(Cl^-)$ reaches a plateau value of 3.6 at concentrations above 0.07 M CH_2Cl_2. The significantly high yield of $G(Br^-)$, which is, for example, 54 at 0.07 M CH_2Br_2, indicates the occurrence of a chain reaction.

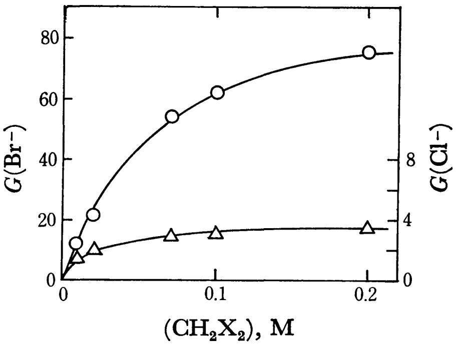

Fig. 1. Dependence of halide ion yields on the initial concentrations of methylene dihalides in methanol.
△: CH_2Cl_2 solution, ○: CH_2Br_2 solution

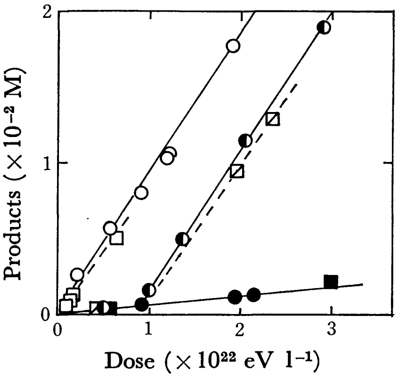

Fig. 2. Yields of bromide ion and formaldehyde as a function of absorbed dose in methanol solution of 7×10^{-2} M CH_2Br_2.
Bromide ion; ●: aerated, ○: deaerated, ◐: sealed
Formaldehyde; ■: aerated, □: deaerated, ⧄: sealed

Figure 2 shows the yields of bromide ions and formaldehyde as a function of the absorbed dose in a 0.07 M CH_2Br_2 solution under the three following experimental conditions; (1) deaerated, (2) aerated, and (3) sealed. The experimental condition is designated as "sealed" when the irradiation ampoule is filled with an aerated solution up to a ground-glass joint stopper. Under this condition, only the oxygen initially dissolved in a solution can participate in the reaction. The condition is designated as "aerated" when the solution is equilibrated with the oxygen present in the air above a solution in a stoppered vial during irradiation. As is illustrated in Fig. 2, the yields of Br^- and H_2CO from the sealed and the aerated systems are initially the same (that is, $G(Br^-) = 5.7$ and $G(H_2CO) \simeq 4$), but on further irradiation, the yields from the sealed system rise very sharply at doses over 10^{22} eV l^{-1}. This might be due to a progressive depletion of the oxygen content in solutions, because the yields after the break are very close to those in deaerated solutions, that is, $G(Br^-) = 54$ and $G(H_2CO) = 50$, indicating that the dissolved oxygen inhibits the chain reaction.

The species initially produced by the irradiation of methanol are usually presented as follows:

$CH_3OH \rightsquigarrow e_{sol}^-$, H, CH_2OH, $CH_3OH_2^+$ and molecular products (0)

The solvated electrons and H atoms are likely to react with dihalogeno methane as follows:

$$e^-_{sol} + CH_2X_2 \longrightarrow CH_2X + X^- \qquad (1)$$

$$H + CH_2X_2 \longrightarrow CH_2X + HX \qquad (2)$$

$$\searrow CHX_2 + H_2 \qquad (2')$$

X is Cl or Br depending on the solute. In deaerated methanol solutions of CH_2X_2 above 0.05 M, the observed $G(H_2)$ is almost equal to the molecular yield of hydrogen, $G_{H_2}=1.7$, so Reaction (2′) may be excluded in the present system.[14] Our finding that, in a deaerated CH_2Cl_2 solution, $G(Cl^-)$ is 3.6 and very close to $Ge^-_{sol}+G_H$, taking $Ge^-_{sol}=2.0$ and $G_H=1.7$, indicates that all the Cl^- results from Reactions (1) and (2), while CH_2OH dose not contribute to Cl^- formation in this system. Otherwise, $G(Cl^-)$ would have to be equal to the total radical yield, $G(R)=Ge^-_{sol}+G_H+G_{CH_2OH}=6.5$. The high yields of Br^- and H_2CO from deaerated CH_2Br_2 solutions suggest that these products are formed by the following chain mechanism, similar to that proposed for the radiolysis of carbon tetrachloride in alcohols:[15]

$$CH_2OH + CH_2Br_2 \longrightarrow CH_2Br + H_2CO + HBr \qquad (3)$$

$$CH_3OH + CH_2Br \longrightarrow CH_2OH + CH_3Br \qquad (4)$$

Since $G(Br^-)$ and $G(H_2CO)$ are very close to each other, as is shown in Fig. 2, these products are likely to be formed by the same reactions. Although the yield of CH_3Br in Reaction (4) has been determined only qualitatively at the present time, its presence may support this view. On a thermochemical basis, Reaction (4) is exothermic ($\Delta H=-2$ kcal mol^{-1}), while it is endothermic ($\Delta H=4$ kcal mol^{-1}) when $X=Cl^-$. Moreover, in the 0.07 M CH_2Cl_2 solution, the observed $G(H_2CO)$ was only about 2,[14] close to the molecular yield of H_2CO in pure methanol, so the chain dehalogenation of CH_2Cl_2 is unlikely to occur. These considerations can explain the marked difference between $G(Cl^-)$ and $G(Br^-)$. In an aerated system, the chain breaking may be due to the reaction of dissolved oxygen with CH_2OH and CH_2Br.

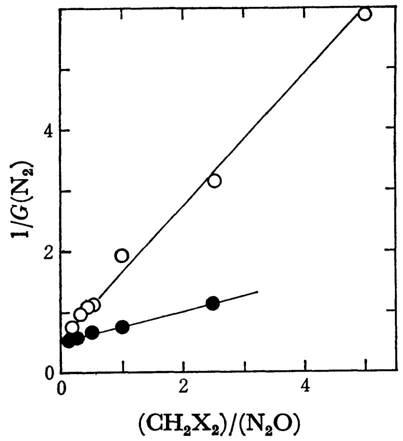

Fig. 3. $1/G(N_2)$ *vs.* $(CH_2X_2)/(N_2O)$ plotted according to Eq. (1). ●: CH_2Cl_2, ○: CH_2Br_2

When nitrous oxide is present in a deaerated system, Reaction (5) will compete with Reaction (1) for the solvated electron:

$$e^-_{sol} + N_2O \longrightarrow N_2 + O^- \qquad (5)$$

On the basis of simple competition kinetics, one can formulate:

$$\frac{1}{G(N_2)} = \frac{1}{G_{e^-_{sol}}}\left[1+\frac{k_1(CH_2X_2)}{k_5(N_2O)}\right] \qquad (I)$$

where k_1 and k_5 represent the rate constants of Reactions (1) and (5) respectively. Plots of $1/G(N_2)$ *vs.* $(CH_2X_2)/(N_2O)$ are seen to give straight lines in Fig. 3. From the slopes of the lines and the intercept, one can obtain $k_1/k_5=0.50$ for CH_2Cl_2 and $k_1/k_5=2.15$ for CH_2Br_2. Taking 1.3×10^{10} M^{-1} s^{-1} for k_5,[16] k_1 is estimated to be 6.5×10^{9} M^{-1} s^{-1} for CH_2Cl_2 and 2.9×10^{10} M^{-1} s^{-1} for CH_2Br_2.

References

1) J. W. T. Spinks and R. J. Woods, "An Introduction to Radiation Chemistry," John Wiley & Sons, New York (1964).
2) M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isotopes* **18**, 493 (1967).
3) W. V. Sherman, *J. Phys. Chem.*, **70**, 2872 (1966).
4) W. V. Sherman, *J. Amer. Chem. Soc.*, **88**, 1567 (1966).
5) W. V. Sherman, *J. Phys. Chem.*, **72**, 2287 (1968).
6) C. Radlowski and W. V. Sherman, *ibid.*, **74**, 3043 (1970).
7) R. Evans, E. Neyto, C. Radlowski, and W. V. Sherman *ibid.*, **75**, 2762 (1971).
8) T. Sawai and Y. Shinozaki, *Chem. Lett.*, **1972**, 865.
9) T. Sawai, T. Shimokawa, and Y. Shinozaki, This Bulletin, **47**, 1889 (1974).
10) H. Matsuoka, K. Sato, T. Masuda, and M. Kondo, *Nippon Kagaku Zasshi*, **87**, 1520 (1966).
11) H. Matsuoka, *J. Nucl. Sci. Technol.*, **8**, 23 (1971).
12) H. Matsuoka, K. Sato, Y. Asahi, T. Masuda, and M Kondo, *ibid.*, **9**, 7 (1972).
13) M. Imamura, S. U. Choi, and N. N. Lichtin, *J. Amer Chem. Soc.*, **85**, 3565 (1963).
14) H. Ogura, T. Unnai, and M. Kondo, unpublished data.
15) p. 337 in Ref. (1).
16) H. Seki and M. Imamura, *J. Phys. Chem.*, **71**, 870 (1967).