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Effects of pH and Temperature on the Degradation of Chloroacetones That are Mutagenic

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Recently, several reports on the mutagenicity of the mill effluents from paper and pulp industries have been published (Ander et al 1977; Eriksson et al 1979; Kamra et al 1983; Nestmann and Lee 1985; Douglas et al 1985). The compounds such as halo-*p*-cymenes (Bjørseth et al 1979), neoabietic acid (Nestmann et al 1980), chloroacetones (McKague et al 1981), 2-chloropropenal (Kringstad et al 1981; Kringstad et al 1983), chlorofuranone (Holmbom et al 1981), and trichlorocyclohexanone (McKague et al 1981) were isolated and identified as mutagens from the spent chlorination liquors at the bleaching stage in the industries. Some of them might be released through a drainage-pipe into the river and/or the coastal sea water. But the fate of these compounds in the aquatic environment is little known in the literature.

In this paper, we report the degradation efficiency of three mutagenic chloroacetones: 1,3-dichloroacetone, pentachloroacetone and hexachloroacetone, in a buffer solution. We also describe their degradation efficiency in the environmental waters at different pH and temperatures with and without sun-light.

MATERIALS AND METHODS

Two chemicals, 1,3-dichloroacetone (DCA) and hexachloroacetone (HCA), were purchased from Tokyo-Kasei Co. Tokyo of Japan. Pentachloroacetone (PCA) was purchased from Aldrich Chemical Co. Inc. Milwaukee, Wisconsin of U.S.A.

In the first experiment, 4 kinds of buffer solutions which had pH 4.0 (0.2 M, acetate), pH 6.0 and 7.0 (0.2 M, phosphate), and pH 8.0 (0.2 M, Tris-HCl) were used as test solutions.

In the second experiment, sea water (pH 8.0, COD = 1.0 mg/L), effluents A (pH 4.3, COD = 148.3 mg/L) and B (pH 6.1, COD = 49.4 mg/L) from a kraft pulp mill were employed for test solutions.

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The effluent B was discharged into the sea after treatment of an effluent A with agglutant.

Fifty µL of a 10 ppm acetone solution of DCA and PCA, or a dioxane solution of HCA was mixed with a 5 mL of test solution in each test tube and kept for 0 - 48 h. After an appropriate time, 5 mL of n-hexane for PCA and HCA, or 5 mL of ethylacetate for DCA followed by 2 g of NaCl were added and the residual chloroacetone was extracted by repeating 8 times of 30 sec shaking. An extract was diluted with the same solvent to an appropriate concentration and was analyzed by a gas-liquid chromatograph equipped with a electron capture detector. The running conditions were as follows: instrument, Shimadzu GC-4CM; column, 2% silicone OV-17 (id 2mm x 2m); column temperature, 100°C (DCA and PCA), 120°C (HCA); injection and detector temperature,210°C; carrier gas, N_2, 40 mL/min. The retention times of DCA, PCA and HCA were 2.9 min, 5.4 min and 4.0 min, respectively. The content of each chloroacetone was calculated from the calibration curve.

These experiments were done in the dark (shielding light with an aluminum foil) or under the sun-lamp (270-440 nm, max 320 nm) at different temperatures (0°C, 15°C, 40°C). The extraction efficiency of each organic solvent to three chloroacetones was 95 ±2% in the preliminary experiment.

RESULTS AND DISCUSSION

The changes of the content of DCA, PCA and HCA in each buffer solution were shown in Figures 1, 2 and 3, respectively. Among them, DCA was the most stable chemical with and without irradiation of the light. At 15°C more than 80% of the original content of DCA remained after 48 h in the acidic or neutral buffer solutions in the dark (Figure 1a). But the remainder of the compound was only 3.3% in the basic solution. Another degradation experiment of DCA was carried out at pH 8.0 under three different temperatures (Figure 1b). The degradation proceeded with the increase of irradiation time of the light except the reaction at 0°C, and it disappeared within 48 h. The exposure of sun-lamp slightly accelerated the degradation rate. From these experiments, it was suggested that DCA is relatively stable compound in acidic conditions, and it becomes labile as the increase of pH. The exposure temperature was also a determinant for the degradation of DCA, but the light was not necessarily. In the case of PCA it disappeared within 6 h at higher pH than 7.0 (Figure 2a and b). On the other hand, HCA was extremely unstable compound even in the acidic conditions. It entirely disappeared within 6 h except the reaction at pH 4.0 (0°C) as shown in Figures 3a and b. The residual ratio of HCA in the solution (pH 4.0, 0°C) was 70% after 24 h. The photo-irradiation also accelerated the degradation ratio of HCA. In this experiment, dioxane was used as a solvent because of the lability of HCA in an acetone solution. The similar solvent interaction of HCA was also observed by other investigators (Zochlinski and Mower 1981; Nestmann et al 1985).

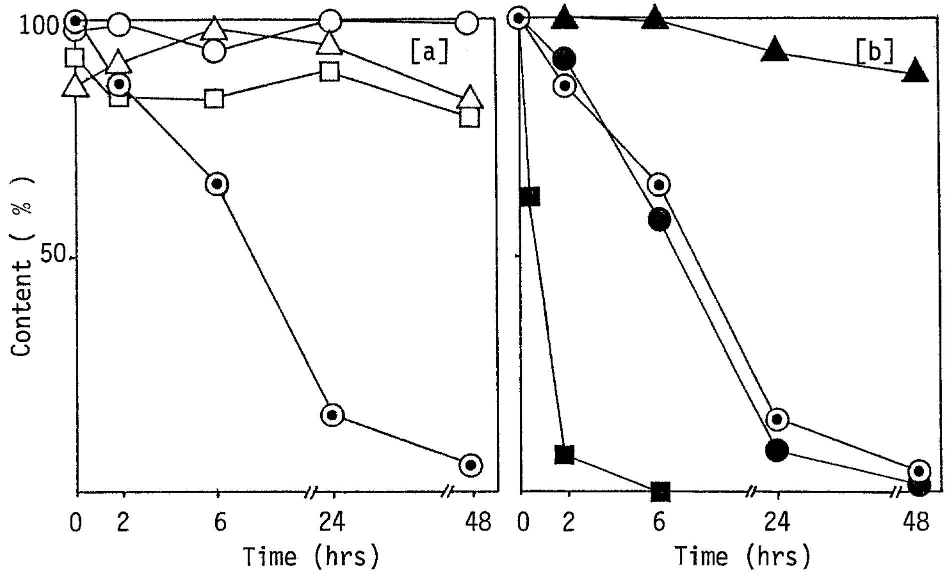

Figure 1. Degradation of 1,3-dichloroacetone in several buffer solutions.

In the dark: -○- pH4.0, 15°C -△- pH6.0, 15°C -□- pH7.0, 15°C
-⊙- pH8.0, 15°C -▲- pH8.0, 0°C -■- pH8.0, 40°C
Under the sun-lamp: -●- pH8.0, 15°C

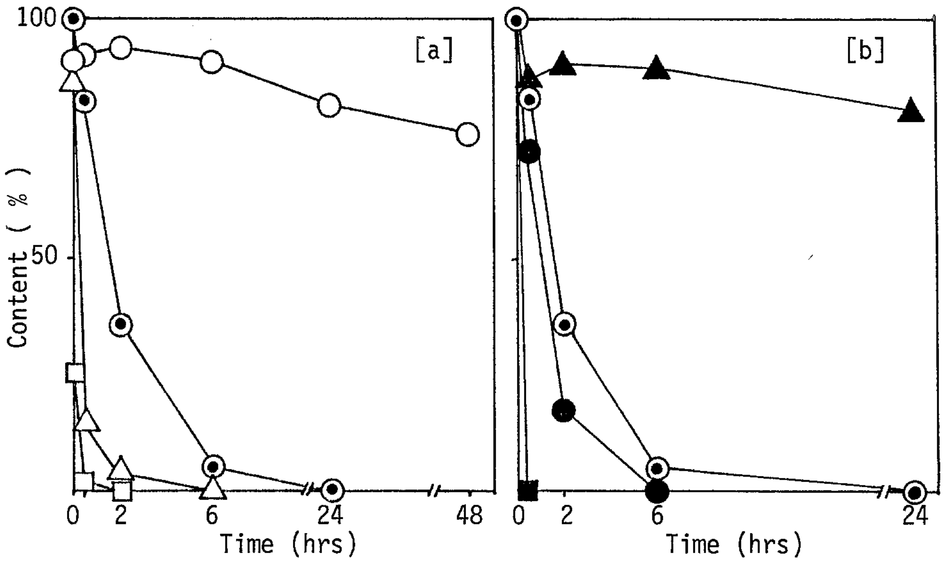

Figure 2. Degradation of pentachloroacetone in several buffer solutions.

In the dark: -○- pH4.0, 15°C -⊙- pH6.0, 15°C -△- pH7.0, 15°C
-□- pH8.0, 15°C -▲- pH6.0, 0°C -■- pH6.0, 40°C
Under the sun-lamp: -●- pH6.0, 15°C

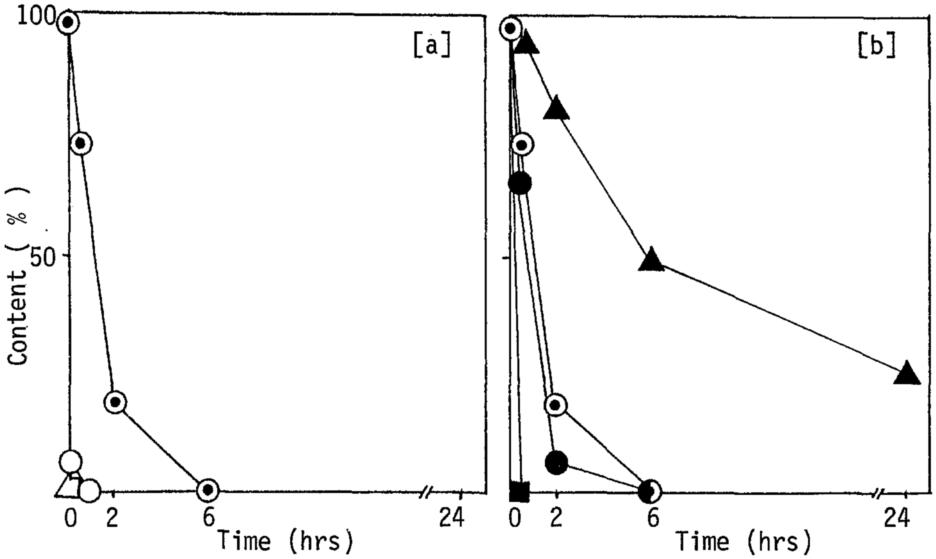

Figure 3. Degradation of hexachloroacetone in several buffer solutions.

In the dark: -⊙- pH4.0, 15°C -○- pH6.0, 15°C -△- pH7.0, 15°C
-□- pH8.0, 15°C -▲- pH4.0, 0°C -■- pH4.0, 40°C
Under the sun-lamp: -●- pH4.0, 15°C

From the above fundamental examination by using several buffer solutions, it was found that the degradation ratio of three chloroacetones which show mutagenic activity was depend upon the reaction pH and temperature, but not so much on the light. We also found that the increase of the number of chlorine atoms in the molecule cause the decrease of the stability of these chloroacetones and the order of the degradation rate was HCA > PCA > DCA.

In the second experiment, the degradation efficiency of three chloroacetones was examined in the environmental samples such as coastal sea water (pH 8.0), kraft pulp mill effluents A (pH 4.3) and B (pH 6.1) in the dark. The changes of the content of DCA, PCA and HCA under several conditions were shown in Figures 4a, b and c, respectively. PCA and HCA disappeared immediately during the incubation in sea water. The residual ratio of DCA incubated for 24 h in sea water was 8%. DCA and PCA were relatively stable in effluent A which had pH 4.3. On the contrary, HCA was very fragile and it disappeared within 2 h in three water samples. The degradation of chloroacetones in the environmental samples was consistent with that observed in buffer solutions. These results are compatible with a report in which 2-chloropropenal in acidic solution is more stable than in a basic solution (Kringstad et al 1983). In our previous experiment, PCA was isolated as a potent mutagen from a paper mill effluent A (Kinae et al 1986). But the correlation of the mutagen and the fish disease has not been demonstrated so far.

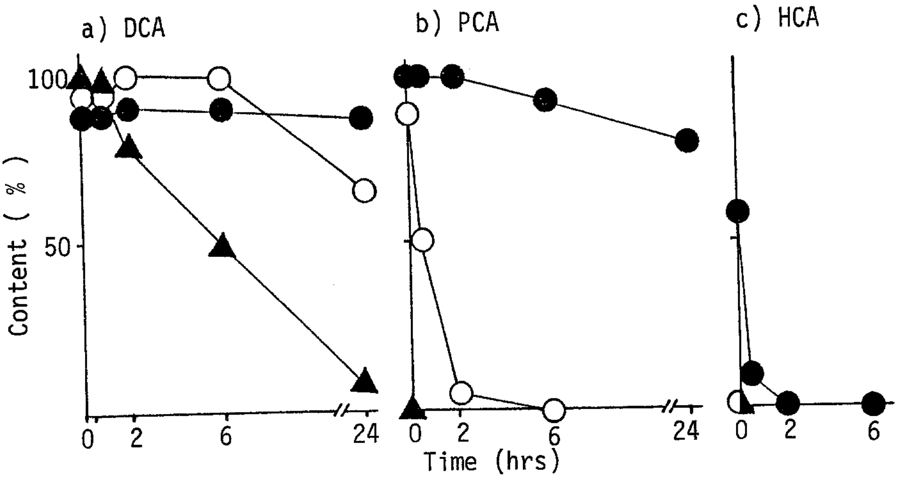

Figure 4. Degradation of chlorinated acetones in the kraft pulp mill effluents and in the coastal sea water.

-●- Effluent A -○- Effluent B -▲- Sea water

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