CHEMISTRY LETTERS, pp. 57-60, 1993.

Decomposition of Chlorinated Hydrocarbons in Aqueous Solutions by Ultrasonic Irradiation

Koji INAZU, Yoshio NAGATA,*† and Yasuaki MAEDA
Laboratory of Environmental Chemistry, College of Engineering,
University of Osaka Prefecture, Gakuen-cho 1-1, Sakai, Osaka 591
† Research Institute for Advanced Science and Technology,
University of Osaka Prefecture, Gakuen-cho 1-2, Sakai, Osaka 593

Trichloroethylene, tetrachloroethylene, 1,1,1-trichloroethane, chloroform and carbon tetrachloride in dilute aqueous solutions were rapidly decomposed to chloride anions, hydrogen, carbon monoxide and carbon dioxide by ultrasonic irradiation.

It has been known that high intensity ultrasonic irradiation provides various chemical and physical effects.1) These effects are known to arise from cavitation which brings about instantaneous local high temperature and high pressure in liquid.2) When water is irradiated, thermal dissociation of water occurs and reactive species such as OH radicals or H atoms are formed.3) Therefore, ultrasonic irradiation of aqueous solutions can be a usefull method to investigate the reactivity of OH radicals which play important roles in environmental chemistry, as well as to investigate the thermal effects caused by ultrasound.

Chlorinated hydrocarbons such as trichloroethylene are widely used as solvents. But they are persistent in environment due to their undecomposable properties and have attracted public attention in that ground water and river water were often found polluted by them.4)

Sonolyses of dichloromethane and some chlororinated hydrocarbons have been studied, although decomposition products and reaction mechanism have not been elucidated.[5)]

Now we report the results of the sonolysis of five chlorinated hydrocarbons in aqueous solutuon.

Ultrasonic irradiation was carried out with a high intensity ultrasound generator and a barium titanate oscillator (frequency, 200 kHz; intensity, 6 W/cm^2). An aqueous solution (65 cm^3) of 10 ppm of a chlorinated hydrocarbon was sonicated in a 200 cm^3 of cylindrical glass vessel under argon, oxygen or air atomosphere. The vessel had a side arm with a silicon rubber septum for gas bubbling, solute injection or sample extraction without opening the vessel. The bottom of the vessel was planar and 1 mm in thickness. After the solute reaching equilibrium between gas phase and aqueous phase, the the irradiated solution was withdrawn at desired time intervals, and was extracted with decane. The decane layer and aqueous one were submitted to analysis by a gas chromatograph equipped with ECD and an ion chromatograph, respectively. The gaseous products were determined by gas chromatography using TCD and FID.

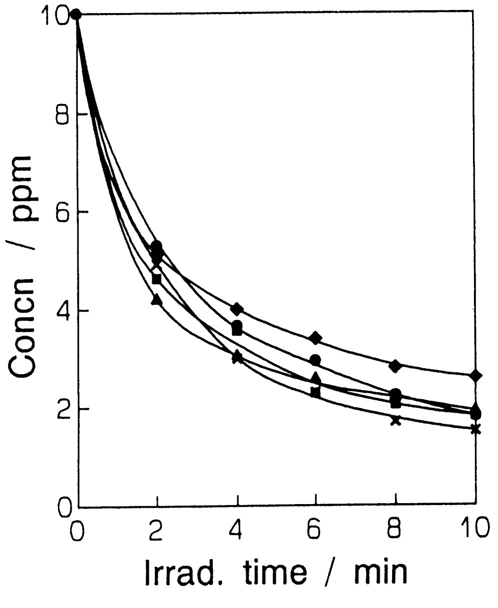

Fig.1. Time-profiles of five chlorinated hydrocarbons by ultrasonic irradiation.

●: $Cl_2C=CCl_2$, ■: $ClHC=CCl_2$,
▲: CH_3CCl_3, under Ar,
×: CCl_4, ◆: $CHCl_3$, under air.

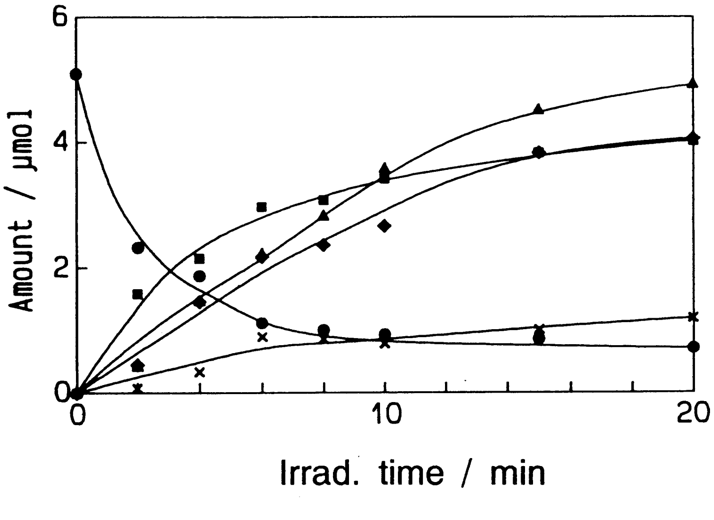

Fig.2. Time-profiles of degradation of trichloroethylene and formation of products under argon.

●: $ClHC=CCl_2$, ■: Cl^-(x 1/3),
▲: H_2, ◆: CO(x 1/2), ×: CO_2

The time-profiles of degradation of five chlorinated hydrocarbons upon irradiation are shown in Fig. 1. Over 75% of their initial amounts were decomposed within 10 min. The order of the degradation rates was : trichloroethylene ≒ 1,1,1-trichloroethane > tetrachloroethylene in argon, and carbon tetrachloride > chloroform in air although the differences among them were small.

It can be suggested by the following observations that the main reactions are thermal decomposition or combustion in cavitation bubbles and not reactions by OH radicls or H atoms. 1) The decomposition of trichloroethylene was not suppressed by the addition of tert-BuOH which is known as a scavenger of OH radicals. 2) Sonolytic decomposition of 1,1,1-trichloroethane was about 5 times faster than γ -induced decomposition under N_2O (in which OH radicals are main reactive species) when compared with per OH radical basis. 3) The degradation rates in argon and oxygen were not much varied, although H atoms would be quenched by oxygen and no hydrogen was formed in air or oxygen atmosphere, $\cdot H + O_2 \rightarrow HO_2\cdot$.

This reactivity of the chlorinated hydrocarbons is attributed to their high volatility and their low solubility in water, properties which facilitate them to concentrate in cavitation bubbles and to decompose rapidly by high temperature and high pressure.$^{6)}$

The time-profiles of degradation of trichloroethylene and formation of products under argon are shown in Fig. 2. The major products were chloride anions, carbon monoxide and hydrogen. The reactions may proceed *via* pyrolysis of trichloroethylene in water as shown in Eq. 1. The amounts of hydrogen in Fig. 2 were calculated by

$$ClHC{=}CCl_2 + 2H_2O \xrightarrow[\triangle]{} 2CO + 3Cl^- + 3H^+ + H_2 \qquad (1)$$

deducting the amounts of hydrogen formed in pure water from those formed in trichloroethylene solution. The minor products were carbon dioxide, methane and ethylene. A trace amount of dichloroethylene was detected by GC-MS.

In the case of the sonication under oxygen or air, we observed no carbon monoxide but considerable amount of carbon dioxide. We can propose two routes for the production of carbon dioxide. Carbon monoxide once formed *via* Eq. 1 may be efficiently oxidized or the combustion of the chlorinated hydrocarbon may produce

Table 1. Yield (%) of Chloride Anions and Carbon Monoxide

Reactants	Atmosphere			
	Argon		Oxygen	Air
	Cl^-	CO	Cl^-	Cl^-
$ClHC=CCl_2$	91	81	85	83
$Cl_2C=CCl_2$	82	82	80	82
CH_3CCl_3	87	73	81	82

carbon dioxide directly (Eq. 2).

$$ClHC=CCl_2 \xrightarrow[\triangle]{O_2} CO_2 + Cl^- + H^+ \qquad (2)$$

The yields of carbon monoxide and chloride anions based on the amount of decomposition of chlorinated hyrdocarbons are shown in Table 1. It is clear that all of the compounds were efficiently decomposed to inorganic carbons and chloride anions, and therefore, ultrasonic irradiation is effective for the decomposition of chlorinated hydrocarbons in aqueous solutions.

Now we are investigating the decomposition of various water pollutants by ultrasonic irradiation.

References

1) D. Bremner, "Advances in Sonochemistry," ed by T. J. Mason, JAI Press, London (1990), Vol. 1, pp. 1–37.
2) E. B. Flint and K. S. Suslick, Science, **253**, 1397 (1991).
3) K. Makino, M. M. Mossoba, and P. Riesz, J. Am. Chem. Soc., **104**, 3537 (1982); K. Makino, M. M. Mossoba, and P. Riesz, J. Phys. Chem., **87**, 1396 (1983).
4) H. B. Kerfoot, Environ. Sci. Technol., **21**, 1022 (1987).
5) H. M. Cheung, A. Bhatnagar, and G. Jansen, Environ. Sci. Tecnol., **25**, 1510 (1991).
6) E. J. Hart and A. Henglein, J. Phys. Chem., **90**, 5992 (1986).

(Received September 14, 1992)