

DESTRUCTION OF CFC113 IN SUPERCRITICAL AND SUBCRITICAL WATER

Sang-Woo Park*, Ji-Ho Yoon and Huen Lee[†]

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology,
373-1 Kusung-dong, Yusung-gu, Taejon 305-701, South Korea

(Received 2 July 1996 • accepted 31 October 1996)

Abstract – Destruction of 1,1,2-trichlorotrifluoroethane (CFC113) in supercritical and subcritical water was performed over a wide range of pressure at 673 K. The hydrolysis reaction of CFC113 in the supercritical water could lead to complete destruction of CFC113, while the CFC113 destruction below the critical pressure of water was quite low. The Cl destruction yields were higher than those of F over the whole pressure range including both supercritical and subcritical regions, which implies that the bonding energy of F on the backbone of CFC113 is stronger than that of Cl. The destruction yields represented by two ions were found to have the linear dependency on the reduced water density.

Key words: Supercritical Water, CFC113, Reaction

INTRODUCTION

Supercritical water (SCW) has been of considerable interest as a reaction medium for the destruction of hazardous organic compounds such as phenol, 2-chlorophenol, and carbon monoxide [Thornton and Savage, 1992; Li et al., 1993; Helling and Tester, 1988]. Moreover, it has been recognized that the SCW can be used as a suitable medium for control of reaction rates and pathways since its physical and chemical properties drastically change by small variations of temperature and pressure.

Recently, many studies on the SCW reaction with or without oxygen supply have been reported in the literature. Lee and Gloyna [1992] developed the reaction kinetics of acetamide in the SCW at the reaction conditions of temperatures between 673 and 798 K and pressures between 230 and 340 bar. They insisted that the hydrolysis reaction in the SCW proceed more rapidly than the oxidation emphasizing the role of the SCW as an active reactant. Huppert et al. [1989] and Townsend et al. [1988] have studied decomposition in the SCW of cyclic organic compounds such as dibenzyl ether, guaiacol, and benzyl phenyl amine and found that the reaction followed the parallel hydrolysis and pyrolysis pathways, and the density of the SCW affected the rate constants of decomposition reaction. The oxidation kinetics of ammonia, methanol, and ammonia-methanol mixtures by using the SCW were determined in a packed and unpacked tubular plug flow reactors by Webley et al. [1991] and Tester et al. [1993]. Furthermore, the SCW reaction of high-molecular weight species such as cellulose and poly(vinyl chloride) have been also carefully examined by several workers [Adschiri et al., 1993; Kocher et al., 1993].

In this study, we examined the SCW destruction of 1,1,2-trichlorotrifluoroethane (CFC113), which its discharge has been regulated for protection of ozone layer in the stratosphere. The

hydrolysis reaction of CFC113 was carried out at both supercritical and subcritical conditions of water.

EXPERIMENTAL

A tubular-type batch reactor having a small volume of about 15 ml was used to investigate the hydrolysis of CFC113 by the supercritical and subcritical water. The reactor was manufactured with stainless steel 316, and it was operated successfully up to pressures of 700 bar and temperatures of 873 K. The temperature of the reactor was measured by a K-type thermocouple with a digital thermometer (Cole-Parmer, 104957) having the resolution of ± 0.1 K. The thermocouple was calibrated against a mercury thermometer certified by NIST and was found to be accurate within ± 0.2 K.

The system was initially evacuated to remove the residual gas substances, among which oxygen is the most important because of its great effect on the hydrolysis reaction. The tubular reactor was loaded with an aqueous solution prepared by mixing the distilled water and CFC113 with a weight ratio of 1 to 20. The reactor was heated with a 3 kW electric furnace at the specified temperature of 673 K. The system pressure could be more accurately adjusted to the desired value by controlling the amount of water loaded in the tubular reactor. Directly after termination of the reaction, the reactor was removed from the furnace and immersed quickly into an ice bath to suppress the reaction. The reactor was then opened and the liquid products in the reactor were collected for analysis.

The concentrations of chloride ion (Cl^-) and fluoride ion (F^-) in the product stream were measured by an ion analyzer (Orion, EA940) using a combination chloride electrode (Orion, 96-17B) and a combination fluoride electrode (Orion, 96-09). The standard solutions with a concentration of 100 ± 0.5 ppm for both Cl^- and F^- were used for calibration. The destruction products after the hydrolysis reaction in the SCW were diluted to the range of the constructed calibration curves and were analyzed at least twice for each sample. The destruction yields of CFC

[†]To whom all correspondences should be addressed.

*Present address: Process Engineering Dept., Samsung Engineering Co., LTD., Seoul, South Korea.

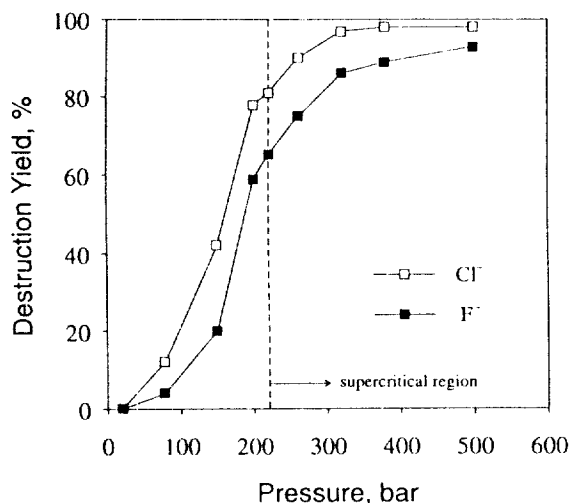


Fig. 1. Destruction yield of CFC113 by supercritical and subcritical water as a function of pressure at 673 K.

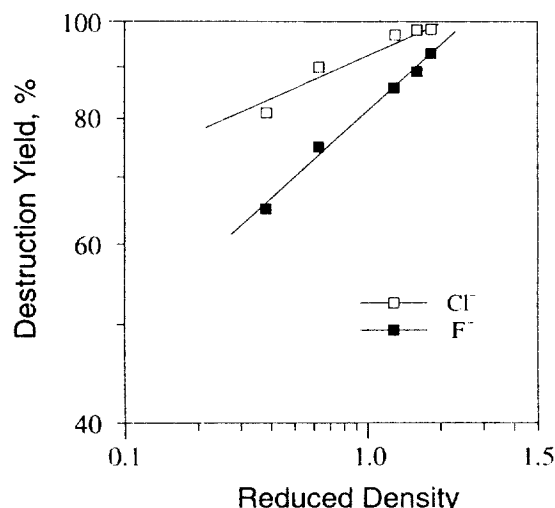


Fig. 2. Typical semi-logarithmic plot of destruction yield of CFC 113 as a function of reduced water density at 673 K.

113 to Cl^- and F^- were reproducible to within a 2% error range. The distilled water and CFC113 having a purity of 99.9% supplied by Aldrich were used without further purification.

RESULTS AND DISCUSSION

All reactions were carried out during the reaction time of 100 min at constant temperature of 673 K. The destruction yields of CFC113 to Cl^- and F^- were depicted in Fig. 1. Both Cl^- and F^- yields increase substantially near the critical pressure of water as expected. It should be noted from this figure that the Cl^- destruction yields were higher than those of F^- over the whole pressure range including both supercritical and subcritical regions. This result implies that the bonding energy of F^- on the backbone of CFC113 is stronger than that of Cl^- . The hydrolysis reaction of CFC113 in the SCW could lead to complete destruction of CFC113, while the CFC113 destruction

was quite low below the critical pressure of water. A plot of destruction yield vs. reduced water density is shown in Fig. 2 by the semi-logarithmic scale. The destruction yields represented by two ions were found to have the linear dependency on the SCW density. As shown from Fig. 2, the dependency of F^- was also slightly higher than that of Cl^- . Therefore, it can be said that the kinetic constants of the hydrolysis of CFC113 in the SCW will be affected by the variations of the SCW density. Furthermore, as mentioned earlier, it was necessary to recognize the role of the SCW as a reaction medium.

This work didn't cover the complete analysis of the liquid and gas products resulting in the lack of the overall CFC113 destruction kinetic data. It becomes thus necessary to accumulate and test the kinetic data at a variety of temperature and pressure conditions, also considering reaction times.

ACKNOWLEDGMENT

This work was supported by the Korea Science and Engineering Foundation and University Awards Program of the Korea Advanced Institute of Science and Technology.

REFERENCES

- Adschiri, T., Hirose, S., Malaluan, R. and Arai, K., "Noncatalytic Conversion of Cellulose in Supercritical and Subcritical Water", *J. Chem. Eng. Jpn.*, **26**, 676 (1993).
- Helling, R. K. and Tester, J. W., "Oxidation of Simple Compounds and Mixtures in Supercritical Water: Carbon Monoxide, Ammonia, and Ethanol", *Environ. Sci. Technol.*, **22**, 1319 (1988).
- Huppert, G. L., Wu, B. C., Townsend, S. H., Klein, M. T. and Paspek, S. C., "Hydrolysis in Supercritical Water: Identification and Implication of a Polar Transition State", *Ind. Eng. Chem. Res.*, **28**, 161 (1989).
- Kocher, B. S., Azzam, F. O. and Lee, S., "Oxidative Depolymerization of Poly(vinyl chloride) in Supercritical Water", presented paper at the AIChE Annual Meeting, St. Louis, Missouri, November (1993).
- Lee, D. S. and Gloyna, E. F., "Hydrolysis and Oxidation Acetamide in Supercritical Water", *Environ. Sci. Technol.*, **26**, 1587 (1992).
- Li, R., Savage, P. E. and Szmukler, D., "2-Chlorophenol Oxidation in Supercritical Water: Global Kinetics and Reaction Products", *AIChE J.*, **39**, 178 (1993).
- Tester, J. W., Webley, P. A. and Holgate, H. R., "Revised Global Kinetic Measurements of Methanol Oxidation in Supercritical Water", *Ind. Eng. Chem. Res.*, **32**, 236 (1993).
- Thornton, T. D. and Savage, P. E., "Kinetics of Phenol Oxidation in Supercritical Water", *AIChE J.*, **38**, 321 (1992).
- Townsend, S. H., Abraham, M. A., Huppert, G. L., Klein, M. T. and Paspek, S. C., "Solvent Effects during Reactions in Supercritical Water", *Ind. Eng. Chem. Res.*, **27**, 143 (1988).
- Webley, P. A., Tester, J. W. and Holgate, H. R., "Oxidation Kinetics of Ammonia and Ammonia-Methanol Mixtures in Supercritical Water in the Temperature Range 530-700°C at 246 bar", *Ind. Eng. Chem. Res.*, **30**, 1745 (1991).