A-2.4 Human Impact of Halon Alternatives

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Abstract The following halon alternatives including halon 1301 and halon 1211 were used for toxicity test and pyrolysis experiments: 2H-heptafluoropropane, trifluoroiodomethane, perfluorotriethylamine, N,N-bis(trifluoromethyl)-2H-tetrafluoroethylamine, N,N-bis(trifluoromethyl)-2-bromotetrafluoroethylamine, perfluorodimethylvinylamine, and perfluoro-N-ethylpyrrolidine. All halon alternatives except for perfluorodimethylvinylamine did not show prominent genotoxicity and cytotoxicity. Toxicities of whole pyrolysis products from 2H-heptafluoropropane and perfluorotriethylamine were also examined. Pyrolysis products of perfluorotriethylamine showed weak cytotoxicity and no genotoxicity, although those of 2H-heptafluoropropane did not show any toxic effects. Pyrolysis of halon alternatives produced large amounts of hydrogen fluoride. Organic pyrolysis products from halon alternatives were a few and a little. Starting temperatures of pyrolysis depended on molecular structures and element composition.

Key Words Halon alternatives, Genotoxicity, Cytotoxicity, Culture cells, Pyrolysis

1. Introduction

Special halons such as halon 1211 or halon 1301 have been forbidden to be manufactured and to be used by Montreal Treaty in order to minimize the stratospheric ozone depletion. However, some chemicals for fire-fighting or for fire prevention are essential for modern society. Several trials for manufacturing effective halon alternatives are being performed all over the world. Several kinds of halon alternatives have already been developed in the world, but their toxicity and potential formation of toxic substances by pyrolysis are not known. Recently a new type of halon alternatives, perfluorinated trialkylamines, have been developed by Dr. Abe et al. Toxicities of the new halon alternatives have not been examined. It is unknown what kinds of chemical substances are formed from halon alternatives under thermal decomposition whose situation is similar to that of actual fire. There are little information about pyrolysis or thermal decomposition of halon alternatives. It is an urgent work to investigate the toxicities of these halon alternatives and to clarify the behavior of these halon alternatives under high temperatures.

2. Research Objective

This research has two aims: One is an investigation of genotoxicity and cytotoxicity of halon alternatives and their pyrolysis products and the other is an analysis of pyrolysis products from halon alternatives. Toxicity tests are focused on chronic toxicity, particularly genotoxicity and cytotoxicity, since many people working in computer rooms, modern chemical factories, museums, and airplanes using halon or halon alternatives are exposed for long term with halon or halon alternatives. Pyrolysis is performed to examine what kinds of products are generated in fire or under high temperature from halon alternatives.

3. Experimental

Halon alternatives and related compounds used for toxicity tests and pyrolysis are listed with abbreviations in Table 1. Fluorinated amines were supplied by Dr. Abe and other chemicals were purchased commercially in Japan.

Table 1. Halon alternatives and related compounds used for toxicity tests and pyrolysis

Name (Abbreviation)	Boiling point (°C)	Toxicity test	Pyrolysis test
2H-Heptafluoropropane (HFP)	-15.2	○	○
Trifluoroiodomethane (Halon 13001)	-22.5	○	○
Trifluorobromomethane (Halon 1301)	-57.8	○	○
Difluorobromochloromethane (Halon 1211)	-3.9	○	
Bromochloromethane (BCM)	68	○	
Perfluorotriethylamine (PFTEA)	70.3	○	○
N,N-Bis(trifluoromethyl)-2H-tetrafluoroethylamine (DFDMEA)	32.0	○	○
N,N-Bis(trifluoromethyl)-2-bromotetrafluoroethylamine (PFDMBEA)	59.5~60.5	○	○
Perfluorodimethylvinylamine (PFDMVA)	13.7	○	○
Perfluoro-N-ethylpyrrolidine (PFEP)	61.5~62.0		○

○: Used for toxicity test or pyrolysis experiment.

Genotoxicity and cytotoxicity as toxicity tests were performed by using Chinese Hamster Lung (CHL) cells. Induction of sister-chromatid exchange (SCE) and the rate of growth inhibition in cell culture were measured in genotoxicity tests and cytotoxicity tests, respectively. The CHL cultured cells were exposed to the air containing several %(v/v) of target compound for one day in the special gas exposure system for a rapid and convenient *in vitro* toxicity screening method, which has been newly developed for halon alternatives which are insoluble in water and highly volatile. After 1-day exposure the number of cells were counted with a Coulter counter and the rate of growth inhibition was calculated as an index of cytotoxicity. The remaining cells were used for analysis of SCE as an index of genotoxicity. Details of toxic tests using CHL cells have been reported by Shiraishi *et al.*[1)]

Pyrolysis of halon alternatives was performed by passing 5% (v/v) halon alternative in air into quartz tube heated stepwisely from 300 to 800°C. Amounts of halon alternatives and pyrolysis products were determined by gas chromatography. The exhaust gas during pyrolysis was passed through aqueous solution of potassium hydroxide in order to remove reactive and toxic substances such as hydrogen fluoride and an aliquot of the gas was analyzed. Pyrolysis products were identified by gas chromatography-mass spectrometry and library search system of mass spectra. Fluoride ion was measured by ion chromatography.

Whole pyrolysis gas from 2H-heptafluoropropane or perfluorotriethylamine was also submitted to the toxicity tests described above. In pyrolysis of HFP, the exhaust gas was washed with aqueous solution of potassium hydroxide for an elimination of hydrogen fluoride and in pyrolysis of PFTEA, aqueous solution of potassium hydroxide and an aqueous solution of N-(1-naphthyl)ethylenediamine with sulfanilic acid and acetic acid was used for elimination of hydrogen fluoride and nitrogen dioxide, because hydrogen fluoride and nitrogen dioxide kill the cultured cells.

4. Results and Discussion

The results of toxicity tests are shown in Table 2. All halon alternatives except for

Table 2. The results of toxic tests about halon alternatives

Compound (Abbreviation)	Concentration % (v/v)	Growth inhibition %	Ratio of SCEs induced (Exposed/Control)
Halon 1301	2	10	1.69
	5	22	2.09
	8	27	2.33
Halon 1211	2	14	1.32
	5	21	1.42
	8	24	1.48
HEP	2	4	1.02
	5	8	1.07
	8	36	1.66
Halon 13001	2	9	1.42
	5	26	1.49
	8	52	1.69
PFTEA	2	-8	0.95
	5	-13	1.06
DFDMEA	2	4	1.05
	5	15	1.51
PFDMBEA	2	2	1.17
	4	7	1.34
PFDMVA	1	22	1.38
	2	56	1.63
	5	87	1.85
BCM	0.5	16	2.52
	1	37	3.71
	2	55	5.54
Propane	2	13	1.27
	5	15	1.29
	8	16	1.42

Propane was used as a representative of non-toxic compounds in this research.

perfluorodimethylvinylamine did not have prominent genotoxicity and cytotoxicity. However, perfluorodimethylvinylamine had strong cytotoxicity and weak genotoxicity. Toxic levels of halon alternatives were fairly weak compared with those of specific halons. Therefore, toxic properties of halon alternatives were not important. Whole pyrolysis products from 2H-heptafluoropropane and perfluorotriethylamine showed weak cytotoxicity and no toxicity, respectively.

Pyrolysis behavior of halon alternatives is shown in Figure 1. Pyrolysis of fluorinated organics produced lots of hydrogen fluoride which is strongly toxic. Moreover, lots of hydrogen fluoride and nitrogen dioxides were evolved in pyrolysis of fluorinated alkylamines. Organic products from halon alternatives by pyrolysis are shown in Table 3. Generally the numbers and the amounts of organic products from halon alternatives by pyrolysis were a few and a little. Main product from 2H-heptafluoropropane was perfluoroisobutane. Its formation mechanism is assumed to be a combination of heptafluoropropyl radical and trifluoromethyl radical, which are generated from 2H-heptafluoropropane. The mechanism is consistent with the hypothesis[2] that trifluoromethyl radical is responsible greatly to fire extinguishing ability of fluorinated compounds. In most cases, identification of pyrolysis products were not successful, because of small amounts of products and of lack of reference mass spectra. Starting temperatures of pyrolysis are dependent on molecular structure and

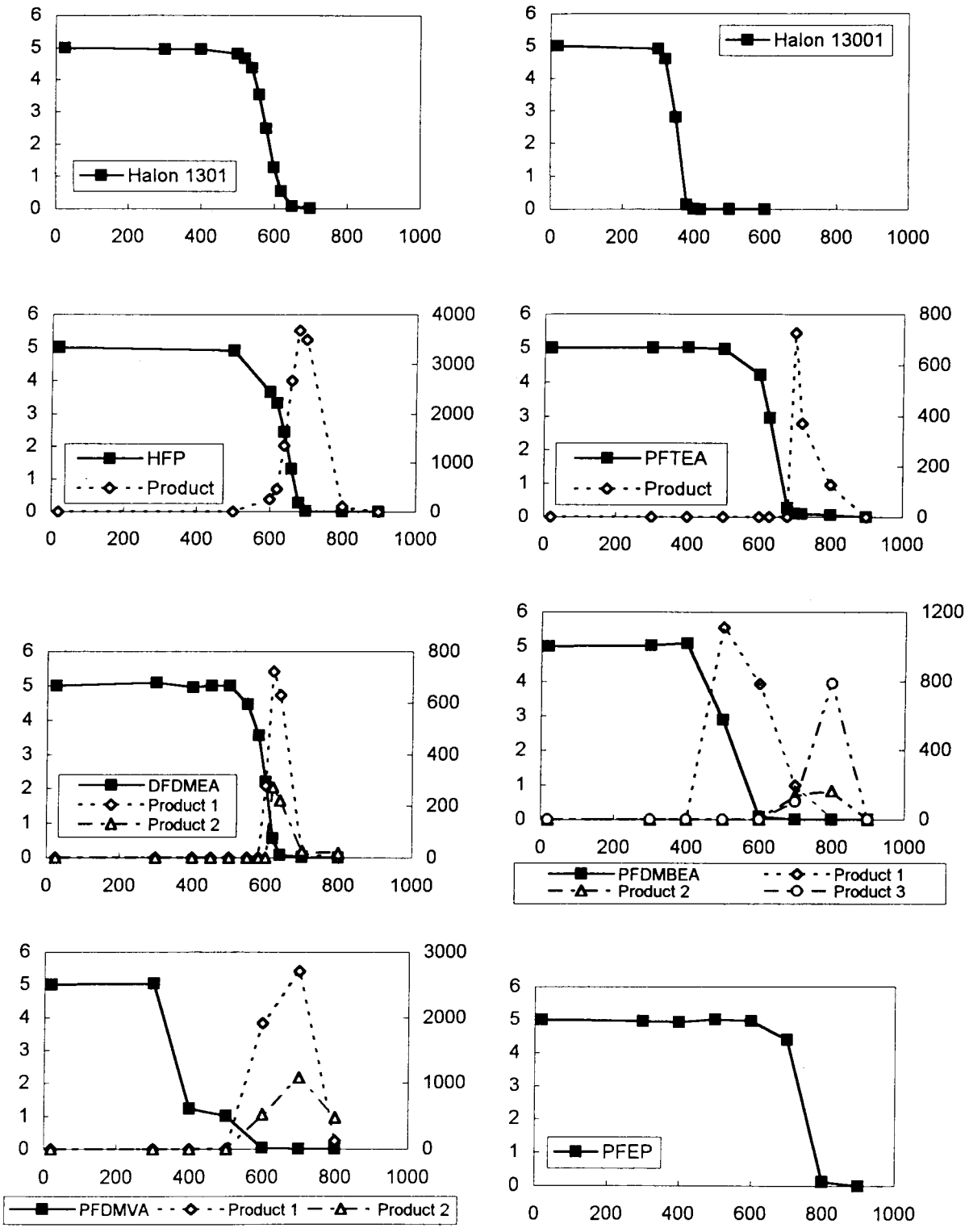

Figure 1 Decomposition of halon and halon alternatives and formation of organic products in pyrolysis

The axis of abscissas, the axis of ordinates on the left, and the axis of ordinates on the right show pyrolysis temperature(°C), concentration (%,v/v) of halon or halon alternative in exhaust gas, and concentrations (ppm,v/v) of pyrolysis products, respectively.

kinds of elements involved in molecule. Namely, halon alternatives bearing bromine atoms or iodine atoms or double bonds in their molecules showed easier thermal decomposition than other halon alternatives. Perfluorinated alkylamines act in pyrolysis in the same manner as fluorinated hydrocarbons. Half of fluorine atoms in halon alternatives changed to inorganic compounds such as hydrogen fluoride and the residual fluorine atoms were trapped with silica in quartz or glass wall of pyrolysis apparatus.

Table 3. Organic products from halon alternatives by pyrolysis

Compounds	Pyrolysis products
2H-Heptafluoropropane	Perfluoroisobutane, Perfluoropropane, Perfluoroethane
Trifluoroiodomethane	No products
Trifluorobromomethane	No products
Perfluorotriethylamine	Perfluoro-N-ethylpyrrolidine
N,N-Bis(trifluoromethyl)-2H-tetrafluoroethylamine	Perfluorotrimethylamine, One unknown
N,N-Bis(trifluoromethyl)-2-bromotetrafluoroethylamine	Three unknown
Perfluorodimethylvinylamine	Two unknown
Perfluoro-N-ethylpyrrolidine	No products

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