

A-7.2.1 Fundamental Studies on the Development of Halon Alternatives

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Abstract

This project aims at the development of perfluoroamine-type new Halon substitutes. Perfluoroamines and their derivatives are considered to be the prospective candidate for the new Halon substitute due to having some degradability at the C-F bond alpha to the nitrogen, and very low toxicity toward human body as their derivatives are being used as an artificial blood substitute. This program consists of 1) the preparation of nitrogen-containing perfluoroalkylbromides, 2) the evaluation of degradability and fire extinguishing ability for perfluoroamines containing a bromine. It was found that perfluoro(dimethylaminomethyl bromide) had less environmental impacts than that of Halon 2402 from the experiments in the liquid phase reaction with in situ generated OH radical. Furthermore, perfluoroamines, which does not contain a bromine atom as the requisite atom for imparting the sufficient fire extinguishing ability, showed unexpectedly good fire extinguishing ability. For example, perfluoro(2-dimethylaminoethyl bromide) showed better fire extinguishing ability than that of Halon 1301, and perfluorotriethylamine showed comparable one to that of Halon 1301. During this project time, regulations for the use of chlorine and bromine-containing volatile compounds were strengthened in connection with the accelerated depletion of ozone layer. So, perfluorotriethyl amine and its homologues, of which ODP is 0 due to the absence of bromine in the molecule, were found to be the most promising candidate for new Halon substitute.

Key Words Halon alternatives, Fire extinguisher, perfluoroamine, bromides

1. Introduction

The destruction of ozone layer has become the most urgent global environmental problem which should be resolved by international cooperation.¹⁾ The phase-out of CFCs and Halons by the end of 1999 has been decided at the international meeting (London, 1990). However, the fact that the ozone layer is being destroyed far faster than scientists expected has called for the development of their alternatives as well as an acceleration of the phase out time of CFCs and Halons (Copenhagen, 1992) .

2. Research Objective

This project aims at the development of perfluoroamine-type Halons (soft-Halons) as the new Halon alternatives. Halon alternatives are required to have the less environmental impacts and low toxicities yet retaining the comparable fire extinguishing ability to that of the current non-degradable Halons (hard-Halon). The incorporation of the nitrogen atom in the perfluoroalkyl group of hard-Halons is considered to clear this propositions.

3. Research Method

Halon alternatives are required to have the less environmental impacts and low toxicities yet retaining the comparable fire extinguishing ability to that of the

current non-degradable (hard Halons). The prospective Halon alternatives will be degradable Halons (soft Halons) which can be decomposed in troposphere. Consequently, the key for the design of new Halon alternatives is to provide fluorocarbons with some degradability. Methodologically, several approaches are considered for it, which involves introduction of (1) a hydrogen atom, (2) a hetero atom ²⁾ or (3) a double bond in the perfluoroalkyl chain.

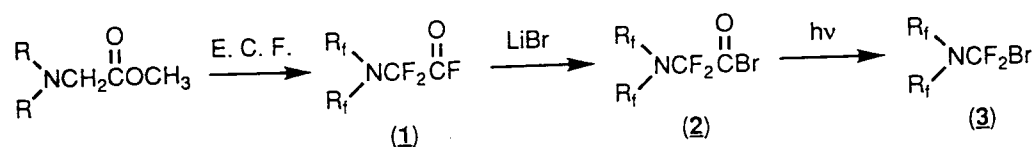
We aimed at the development of perfluoroamines and their derivatives as the new Halon alternatives. Because they are considered to have some degradability at the C-F bond alpha to the nitrogen. In addition, they are expected to have low toxicity toward human body as their derivatives are being used as an artificial blood substitute.

Our new Halon alternatives program consists of the preparation of the derivatives of perfluoroamines, and the evaluation for degradability and fire-extinguishing ability for these compounds.

4. Result

(1) Preparation of new Halon substitutes

Following successive reactions were conducted for the preparation of perfluoroamine-type new Halon substitutes; electrochemical fluorination (ECF) of nitrogen-containing carboxylic acid derivatives to give the corresponding containing perfluoroacid fluorides (1), reaction of perfluoroacid fluorides with LiBr to give corresponding acid bromides (2), decarbonylation of acid bromides to give perfluoroamines containing a bromine (3) either by a thermolysis or by a photolysis.



① Electrochemical fluorination

For the electrochemical fluorination of methyl esters of nitrogen-containing carboxylic acids, Monel cell having a capacity of 500 ml was used. In the 450 ml anhydrous hydrogen fluoride (AHF) which was purified by pre-electrolysis, about 40 g of sample was dissolved and electrolysis was achieved at an anodic current density of 3.3 A/dm², a cell voltage of 5.8 ~ 6.3V, and a cell temp of 6-8°C until calculated amounts of electricity passed. Volatile products were collected in traps cooled at -78 °C, and non-volatile compounds having bps higher than ca. 50°C were drained from the bottom of the cell after the completion of the electrolysis.

② Bromination

Nitrogen-containing perfluoroacid fluorides which was prepared by the electrochemical fluorination were purified before use by fractional distillation by adding small amounts of anhydrous NaF. The reaction was conducted by heating a cylinder fitted with a miniature valve which contained a reaction mixture of perfluoroacid fluoride and anhydrous lithium bromide. After the reaction, volatile products were separated from the residual lithium salt by using a high vacuum line and were analyzed by means of ¹⁹F-NMR.

③ Decarbonylation

Photolysis of perfluoroacid bromides were conducted using either an apparatus which was irradiated from the outside of the wall with 100W Hg lamp or the one irradiated from inner side with 400 W high pressure Hg lamp. In order to collect

volatile compounds during reaction, a trap cooled at -78°C was connected.

(2) Evaluation of degradability

A mixture of nitrogen-containing perfluoroalkylbromides (1.2 mmol) and iron (II) sulfate (1.0g) was charged in a small quartz tube (capacity: 10 ml) fitted with a cold finger, and 0.5 ml aliquot of 30% hydrogen peroxide (total addition: 5 ml) was added in it every 30 min (10 times) during the photolytic reaction with 250W high pressure Hg lamp. After the cease of an evolution of bubble and heat, photolysis was continued for the total time of 21 hr. After the reaction, the products were collected by using a vacuum line and the degree of the degradation was determined by ¹⁹F NMR.

(3) Evaluation of fire extinguishing ability

In the center of the test enclosure made of methacrylate (20 X 20 X 20 cm), was placed a 50 X 5 mm metal dish which contained fuel (n-hexane). The fuel was ignited and allowed a 7 second preburn before the introduction of the agent (perfluoroamine-type new Halon substitutes). During the preburn, air was admitted to the enclosure through the lower inlet. After 7 seconds, the air inlet was closed and the predetermined amount of agents was introduced. The extinguishing time was measured as the time between admitting the agent and extinguishment of the flame.

5. Discussion

(1) Preparation of new Halon substitute

① Electrochemical fluorination

Nitrogen-containing perfluoroacid fluorides, which are key precursors for making new Halon substitutes, were obtained by the fluorination of methyl esters of nitrogen-containing carboxylic acids in a yield of 20 ~ 30 % together with considerable amounts of cleaved and cyclized products.³⁻⁶ These by-products were also evaluated for fire-extinguishing ability.

② Bromination

The conversion of acid fluoride into acid bromides (**1**) by the reaction with LiBr was found to proceed at the temperature near 250°C quantitatively^{7,8}(Table 1). For example, perfluoromorpholinoacetyl bromide (**2**) was obtained at the reaction temperature of 120~250°C. When the temperature higher than 300°C was applied, the formation of perfluoromorpholinomethylbromide (**3**) was observed as a result of decarbonylation.

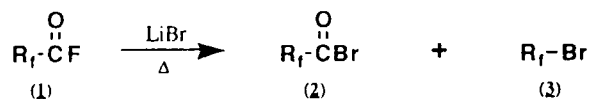
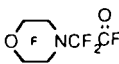


Table 1. Bromination reactions.

<u>1</u>	LiBr	Temp.	Time	Yields(%)	
				<u>2</u>	<u>3</u>
mmol	mmol	°C	hr		
	2.99	120	17.0	97	0
	3.11	200	19.0	97	0
	2.69	250	6.0	93	0
	3.19	300	2.3	88	7.8
	2.59	300	7.8	44	46

③Decarbonylation

The thermolytic reaction to give (3) from (2) in a closed system is not proper for scaling up due to the evolution of CO. So, as an alternative experiments, photolysis of (2) was investigated.^{7,9)} For example, (2) which has an absorption at 270 nm and an isoabestic point at 305 nm, was found to give (3) quantitatively.

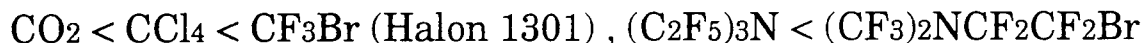
(2) Evaluation of degradability

In order to evaluate the degradability of perfluoroamine derivatives in troposphere, reactions of perfluoro(dimethylaminomethylbromide) (bp; 40.6°C) and perfluoro(dimethylaminoethylbromide) (bp; 60~61°C) with in situ generated OH radical was attempted. Halon 2402 was also investigated for a comparison. It was found that the bromine at the alpha carbon of the amine was labile than that of Halon 2402.⁷⁾



(3) Evaluation of fire extinguishing ability

Following order of fire extinguishing ability (reverse order of the extinguishing time) was observed for perfluoro(dimethylaminoethylbromide) and perfluorotriethylamine along with CO₂, Carbon tetrachloride, Halon 1301 and perfluorotriethylamine which were tested for a comparison.⁷⁾



Among agents tested, perfluoro(2-dimethylaminoethyl bromide) showed better fire extinguishing ability than that of Halon 1301, and perfluorotriethylamine showed comparable to Halon 1301 as a fire extinguisher. Perfluorotriethylamine was found to be highly effective fire extinguisher (streaming agent for fire fighting). Its good fire-extinguishing abilities considered to be based on the third body radical suppression mechanism.¹⁰⁾ The contribution of pentafluoroethyl radical which was formed as a result of the cleavage of perfluoroamine is also considered.

6. Summary

It was found that perfluoroamines and its derivatives were very good candidate for new Halon substitutes. For example, perfluoro(2-dimethylaminoethyl bromide) showed better fire extinguishing ability than that of Halon 1301, and that of perfluorotriethylamine was comparable to that of Halon 1301. However, during this project time, regulations for the use of chlorine and bromine-containing volatile compounds were strengthened in connection with the accelerated depletion of ozone layer, which was led to the total ban on the use of Halons except for the essential use from 1994. So, perfluorotriethyl amine and its homologues, of which ODP is 0 due to the absence of bromine in the molecule, were found to be the most promising candidate for new Halon substitutes.

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