LOW-ODP BROMINE- AND FLUORINE-CONTAINING REPLACEMENT CANDIDATES

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Halon Alternatives Technical Working Conference
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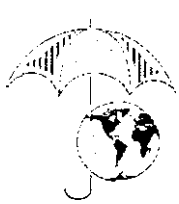

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ABSTRACT

To date, most of the work on low-ozone depletion potential (low-ODP) bromocarbon fire extinguishing candidates has emphasized hydrogen-containing monobrominated fluorocarbons (monobrominated hydrobromofluorocarbons, HBFCs). Two well-known examples are HBFC-22B1, $CHBrF_2$, and HBFC-124B1, CF_3CHBrF. The presence of one or more hydrogen atoms in the molecule allows attack by tropospheric hydroxyl free radicals, decreasing the atmospheric lifetime, and, therefore, the ODP (and greenhouse warming potential, GWP). This technique has been used extensively in the development of chlorine-containing low-ODP refrigerants, solvents, and foam blowing agents (the hydrochlorofluorocarbons, HCFCs). To date, however, such HBFCs have had ODPs higher than desired. We have been examining two additional methods to lower ODP. The first method uses two or more bromine substituents on a molecule to increase the photosensitivity. ***An*** increase in tropospheric photodecomposition will decrease the atmospheric lifetime and, therefore, the ODP. Evidence exists that geminal dibromides (molecules containing two bromine atoms on the same carbon atom) are particularly sensitive to photodegradation. Hydrogen substitution will shorten the lifetime even further. Thus, polybrominated HBFCs (particularly geminal dibromides) offer highly promising low-ODP candidates. It may be that hydrogen-substituted compounds containing geminal bromochloro groups will also prove to have acceptable ODPs. The second method of lowering ODP is to use unsaturated bromofluorocarbons containing carbon-carbon double bonds (bromofluoroalkenes). Unsaturated compounds undergo both photolysis and rapid oxidation by hydroxyl free radicals in the troposphere. In general, it has been believed that such haloalkenes are likely to be toxic; however, when the bromine atom is not adjacent to the double bond, the toxicity appears to be decreased. We have identified one such compound, which limited toxicity testing indicates may have a low toxicity.

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Overhead 1.

TROPOSPHERIC DESTRUCTION BY HYDROGEN ABSTRACTION

FE-25

$$CHF_2CF_3 + OH \rightarrow \bullet CF_2CF_3 + H_2O$$

FE-232

$$CF_3CHCl_2 + OH \rightarrow \bullet CF_3CCl + H_2O$$

FM 100

$$CHBrF_2 + OH \rightarrow \bullet CBrF_2 + H_2O$$

Overhead 2.

ALTERNATIVE TROPOSPHERIC DESTRUCTION MECHANISMS

- Hydroxyl Addition
  - Unsaturated Halocarbons
- Photolysis
  - Dibromides
  - Iodides

Overhead 3.

HYDROXYL ADDITION

$$>C = C< + OH \rightarrow >C(OH) - C<\bullet$$

Overhead **4.**

PHOTOLYSIS

$$>CBr\text{-}CBr< + h\nu \rightarrow >CBr\text{-}C<\bullet$$

$$>CBr_2 + h\nu \rightarrow \bullet>CBr + Br$$

$$\equiv CI + h\nu \rightarrow \bullet>C\text{-}$$

Overhead 5.