Update on Advanced Agent Candidates

Robert E. Tapscott, Garth Gobeli, Everett W. Heinonen,
Jacob A. Kaizerman, Joseph L. Lifke, and Roger A. Patterson
Center for Global Environmental Technologies
University of New Mexico
901 University Boulevard S.E.
Albuquerque, NM 87106-4339
Phone: (505) 272-7250, Fax: (505) 272-7203

INTRODUCTION

To date, no environmentally acceptable halon substitute equivalent to the existing halons in toxicity, effectiveness, and dimensionality has been identified. Halocarbons **as** replacements for halons have been well studied, and it is unlikely that new, highly effective, halon replacements will be identified among the typical non-iodinated haloalkanes. The hydrocblorofluorocarbons (HCFCs), perfluorocarbons (PFCs or FCs), and hydrofluorocarbons (HFCs) are all less effective than the present halons in most scenarios. Moreover, all of these have some adverse global environmental impact (ozone depletion, global warming, and/or long atmospheric lifetime). PFCs and HCFCs are already subject to some restrictions, and such restrictions may eventually extend to HFCs. There is, therefore, an increasing incentive to look at compounds other than typical haloalkanes, i.e., “advanced agents”. These compounds **are** non-halocarbon candidates and a special class of halocarbons, the “tropodegradable” halocarbons. Promising non-halocarbon agents are phosphorus compounds (particularly, the phosphorus nitrides, which include phosphazenes, phosphonitriles, and phosphazanes), metal compounds, and silicon compounds. Based on considerations of physical properties only, the tropodegradable halocarbons have the greatest potential **as** Halon 1301 replacements.

TROPODEGRADABLE HALOCARBONS

The rationale is to use bromocarbons with extremely short atmospheric lifetimes (tropodegradable halocarbons). The term “tropodegradable” is used here for any halocarbon with an atmospheric lifetime on the order of days or weeks. Tropodegradable halocarbons help solve three environmental problems — ozone depletion, global warming, and atmospheric lifetime. If the atmospheric lifetimes **are** similar to those of the iodides (which appear to have received environmental acceptance), and the market potential is small (halon replacement only), such compounds may be environmentally acceptable. The tropodegradable halocarbon families that exhibit halon replacement potential, and that are being emphasized in this effort *are* hydrobromofluoroethers (HBFEs), hydrobromofluoroamines (HBFAs), fluorobromo unsaturated compounds (alkenes and aromatics), and bromofluorocarbonyl compounds. Most of the materials *are* highly fluorinated (to decrease flammability and hepatotoxicity), but in many cases are not completely fluorinated.

Assessment of tropospheric sinks indicates four mechanisms of importance for the compounds of interest here—(1) reaction with atmospheric hydroxyl free radicals, (2) photolysis, (3) physical removal, and (4) reaction with tropospheric ozone. An overall pseudo first-order rate constant k_1 can be written, where $k_1 = k_{OH}[\bullet OH] + k_{physical} + k_{photo} + k_{O3}[O_3]$. $[\bullet OH]$ and $[O_3]$ are globally averaged tropospheric hydroxyl and ozone concentrations. We have calculated (in agreement with some experimental data) that rate constants for reaction with hydroxyl free radicals increase by a factor of approximately 200 for addition of an ether linkage adjacent to a hydrogen atom. This gives atmospheric lifetimes as short as 0.3 years for some hydrofluoroethers (HFEs). Replacement of a fluorine with a bromine will reduce the atmospheric lifetime by about a factor of 10. Thus brominated HFEs should have atmospheric lifetimes as short as 11 days. Similar results hold for brominated hydrofluoroamines. Carbonyl compounds comprise the only family among those being investigated where there is significant absorption and photodissociation in the troposphere (*i.e.*, absorption for $\lambda = 299$ nm ***to*** 700 nm). Excluded in this statement is the photodissociation inherent in all of these materials due to the presence of bromine. Unsaturated compounds (primarily alkenes and aromatics) have very short lifetimes (on the order of days or less) due to interaction with tropospheric *OH and O_3.

PHOSPHORUS-BASED COMPOUNDS

Although all phosphorus compounds are under consideration, the emphasis has been on phosphorus nitrides. Volatile phosphorus nitrides (a term used here to include materials such as phosphazenes, phosphonitriles, phosphazanes, etc.) have been shown to be highly effective extinguishing agents. These materials exist as two groups — cyclic compounds containing a ring backbone (usually with alternating phosphorus and nitrogen atoms) and linear compounds, which have a linear chain backbone (but which also may contain cyclic substituents along the chain). The latter are often polymers whose exact structures have not been fully characterized. Cup-burner extinguishment concentrations **of** 1.08%, 0.91%, and 0.96% have been found for $P_3N_3F_6$, $P_3N_3ClF_5$, and $P_3N_3Cl_2F_4$. These can be compared with concentrations of approximately 3% determined for Halon 1301. As expected, however, these initially studied compounds have an unacceptable toxicity, apparently owing to hydrolysis of the P-X bonds ($X = F$ and Cl). Recent evaluations have focused on PN compounds containing no phosphorus-halogen bonds — primarily, alkoxy-substituted and aryl-substituted phosphazenes, $P_3N_3(OR)_6$ and $P_3N_3(R)_6$. Some of these materials are known to have relatively low toxicities, although a large amount of toxicological work remains to be done. Blends of $P_3N_3(OCH_2CF_3)_3[OCH_2(CF_2)_2CF_3]_3$ and $P_3N_3(OCH_2CF_3)_3[CH_2(CF_2)_3CHF_2]_3$ with hydrofluoroether (HFE) and other carriers have now been shown to be remarkably effective as streaming agents. Although these compounds have a low volatility, many low-volatility compounds exhibit remarkably good performance as total-flood agents. Nevertheless, we have proceeded on to include evaluations of lower molecular weight materials. The synthesis of $P_3N_3(OCH_2CF_3)_6$, which testing now indicates to be a better extinguishant than the higher molecular weight alkoxyphosphoranes tested earlier (see above), has been completed, and $P_3N_3(CH_3)_6$ and $P_3N_3(CF_3)_6$ are now being considered. Another class **of** compounds being investigated are perfluoroalkylphosphines and their derivatives. **Heptafluoropropyliodophosphines** and **heptafluoropropylchlorophosphines** have been prepared and tested in the NMERI cup burner apparatus with extinguishment concentrations of 0.88% and 0.87%, respectively. Evidence obtained in studies on the analogous arsines indicates that these compounds decompose thermally by homolytic cleavage of the phosphorus-carbon bond to generate free radicals. Although the iodo- and chlorophosphines tested so far are impractical extinguishants due to their high reactivity and toxicity, it is believed that these can be significantly reduced by replacing the halogen atoms with Lewis bases such as amines or alcohols. Work in this area is currently underway.

SILICON-BASED COMPOUNDS

Many organosilicon compounds are relatively stable, inert, and have a low toxicity. Of particular importance is that silicon compounds have lower atmospheric lifetimes than do the closely related carbon compounds. Thus, all other things being equal, Global Warming Potentials (GWPs) and Ozone Depletion Potentials (ODPs) are lower. In fact, it is not unlikely that one can incorporate bromine in silanes and siloxanes without having unacceptably large ODPs, and this approach is being evaluated. Silicon compounds that do not contain bromine or an other group providing chemical fire suppression, do not appear to have a significant inherent fire suppression activity other than that provided by heat absorption and related physical processes. Two groups of silicon compounds are of interest — silanes (analogous to the carbon-containing alkanes) and siloxanes (which contain one or more Si-0-Si groups). Based on some experimental data and calculated properties, atmospheric lifetimes as short as 3 days and ODPs as low as 0.002 for bromofluorosilicon compounds have been estimated in this work.

The following characteristics are targets for the compounds being evaluated: (1) To avoid toxicity and stability problems, halogen atoms (fluorine, chlorine, bromine, and iodine) should not be attached directly to the silicon atom. Molecules containing direct silicon-halogen bonds are highly susceptible to hydrolysis with the formation of hydrogen halides. (2) To provide a chemically active fire suppressant, bromine is needed. This is incorporated in groups such as $-CF_2Br$, where halogen atoms are attached only to carbon and are kinetically resistant to hydrolysis. (3) Volatility, usually a desirable property, increases with the hydrogen content. Increased hydrogen content, however, also leads to increased flammability and decreased effectiveness as a fire extinguishing agent. Thus, it is important to keep the number of hydrogen atoms as low as possible (there are exceptions). (4) In general, fluorine substitution leads to a lower toxicity than does chlorine substitution. In addition, fluorine substitution often provides increased volatility.

METAL COMPOUNDS

Alkali metal salts have long been known to be as effective as halons in many scenarios. Transition metal compounds are even better. For example, iron pentacarbonyl, $Fe(CO)_5$, may very well be one of the most effective extinguishing agents ever found. Moreover, chromyl chloride, CrO_2Cl_2, appears to be as much as two orders of magnitude more effective than the halons in inhibiting hydrocarbon flames.

Four mechanisms have been proposed for flame suppression by metals: (1) Metal-containing particulates formed during flame interaction may allow heterogeneous free-radical recombination on the surface. Some work in the Former Soviet Union (FSU) indicates free-radical recombination on metal oxide particles. (2) The extinguishing ability of transition metal compounds may be due to incomplete electronic shells (multiple oxidation states), which could provide catalytic pathways for oxidation/reduction reactions. Such reactions could eliminate combustion precursors and intermediates. **(3)** Metal-oxygen monomers (or low molecular weight polymers) may participate in homogeneous catalytic free radical removal and/or recombination. **(4)** Heat absorption due to agent decomposition may aid in extinguishment. This could be an important mechanism for alkali metal extinguishants, but does not explain the unusually large extinguishing abilities **of** some transition metal compounds.

Unfortunately, most transition metal compounds are either highly toxic (such as iron pentacarbonyl and chromyl chloride) or are solids, with an effective method for delivery and three-dimensional dispersion yet to be developed. However, one large group of transition metal compounds may have the properties needed for effective use as fire extinguishants and, at the same time, may have low toxicities. Organic ligands containing negative charges whose sum is equal to the positive charge on the central ion allow preparation of neutral transition metal compounds. That the compounds are non-ionic gives two important characteristics: (1) Some neutral-charged complexes are known to have a relatively high volatility, a property that helps in multidimensional fire and explosion suppression. (2) All or nearly all of these compounds are soluble in organic liquids, providing a means for dispersion. Note, however, that some of the work under way is exploring aerosol applications of ionic and other low-volatility metal compounds.

Extinguishment mechanisms are now being examined by introducing metal compounds into flames as aerosols **or** as vapors. Using the “Sapphire” apparatuses (heated, flat-flame burners with optical ports), the heat removed during extinguishment by metal compounds is being determined as functions of agent concentration and stoichiometric fuel/air ratio. The curves obtained vary with the extinguishment mechanism and permit both qualitative and quantitative estimations of the contributions from physical and chemical processes. In addition, a Fraunhofer particle analyzer is being used to characterize particulate formation and injected aerosols in the flame.

CONCLUSIONS

Several different families have been identified which may provide effective fire suppression while still being environmentally acceptable. Hydrofluoroethers are believed to have atmospheric lifetimes as low as **0.3** years. Phosphorus-based compounds have been synthesized with demonstrated cup-burner extinguishments less than 1/3 that of Halon 1301. Silicon-based compounds have low atmospheric lifetimes and may be promising if methods of attaching bromine or fluorine atoms on the backbone can be developed. Metal complexes have extremely low extinguishment concentrations, approximately 2 orders of magnitude lower than Halon 1301, but toxicity and deliver issues have yet to be resolved. Work is being proposed to synthesize and test members of these chemical families.