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Review article

Environmental hazards and health risk of common liquid perfluoro-*n*-alkanes, potent greenhouse gases

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ABSTRACT

This article aimed at introducing the main physical properties and commercial/industrial uses of common liquid perfluoro-*n*-alkanes (including perfluoropentane, perfluorohexane, perfluoroheptane, perfluorooctane, and perfluorononane) and the environment and health hazards posed by their toxic decomposition products (especially in hydrogen fluoride and perfluoroisobutylene) because these perfluorocompounds are potent greenhouse gases, which have been blanketed into the Kyoto Protocol, but was rarely described in the National Inventory Reports by Annex I Parties. The environmental properties (including octanol–water partition coefficient, water solubility and Henry's law constant) of liquid perfluoro-*n*-alkanes were evaluated, and further discussed were its atmospheric implications according to the predicted properties and possible proposal for the formation of trifluoroacetic acid (CF_3COOH) in the atmosphere by the ionized photolysis. These predicted values revealed that liquid perfluoro-*n*-alkanes tend to be hydrophobic and partitioned into organic matter, and they have exceptionally low solubility in water and extremely high vaporization from the water bodies, suggesting that it will sink into the atmosphere if it is released into the environment.

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Contents

1. Introduction

Perfluoro-*n*-alkanes represent a class of fully fluorinated compounds (perfluorocompounds or perfluorocarbons) with unique physical and chemical properties that make them usefully suited for some specialized applications in the electronics and medical industries (Banks et al., 1994; Hall et al., 2000; Peyman et al., 1995; Tsai et al., 2002). At room temperature common perfluoro-*n*-alkanes can be grouped into gaseous and liquid compounds based on their boiling points. The former includes tetrafluoromethane (CF_4), hexafluoroethane (C_2F_6), octafluoropropane (C_3F_8), and decafluoro-*n*-butane (C_4F_{10}), but the latter are commercially available with boiling points

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from about 30 °C to 126 °C, including dodecafluoro-*n*-pentane (C_5F_{12}), tetradecafluoro-*n*-hexane (C_6F_{14}), hexadecafluoro-*n*-heptane (C_7F_{16}), octadecafluoro-*n*-octane (C_8F_{18}), and eicosafluoro-*n*-nonane (C_9F_{20}). However, all perfluoro-*n*-alkanes should be potent greenhouse gases (GHGs) because of their chemical stability and strong absorption in the longer wavelength, infrared (IR) radiation. According to the data adopted by the Intergovernmental Panel on Climate Change (IPCC, 2007), 100 year time horizon-global warming potentials (relative to CO_2) of dodecafluoro-*n*-pentane (C_5F_{12}) and tetradecafluoro-*n*-hexane (C_6F_{14}) are 9160 and 9300 (relative to CO_2), respectively. Therefore, perfluorocarbons have been considered as one of the six target GHGs under the Kyoto Protocol of the United Nations' Framework Convention on Climate Change (UNFCCC) in 1997. Annex I Parties (developed countries) that have ratified the Kyoto Protocol are required to submit information on their national inventories annually (i.e., National Inventory Report), which identify and quantify a country's primary anthropogenic sources and sinks of target GHGs. According to the National Inventory Report submitted by Annex I Parties (e.g., Japan and USA), PFCs most widely employed in estimating emissions are gaseous CF_4 and C_2F_6, although other gaseous PFCs such as C_3F_8, C_4F_{10} and octafluorocyclobutane (c-C_4F_8) are also included. It should be noted that the emissions associated with the widespread applications (e.g., cleaning solvent and heat transfer coolant) of liquid perfluoro-*n*-alkanes like C_6F_{14} will be more significant in recent years.

Common liquid perfluoro-*n*-alkanes (C_nF_{2n+2}, $n=5\sim9$) are colorless, nontoxic, nonflammable, thermally stable (inert), non-ozone-depleting and heavy compounds with high fugacity (volatility) and very low solubility in water. Following its release into the environment, these compounds almost reside in the atmosphere for a very long time. For example, the atmospheric lifetimes of dodecafluoro-*n*-pentane (C_5F_{12}) and tetradecafluoro-*n*-hexane (C_6F_{14}) are 4100 and 3200 years, respectively, based on the data adopted by the Intergovernmental Panel on Climate Change (IPCC, 2007). Furthermore, under the extreme conditions the liquid substance could yield smaller decomposition molecules which can be toxic (O'Mahony et al., 1993; Zundorf et al., 2008), although it is a virtually safe compound with very low acute and sub-chronic inhalation toxicity according to the manufacturer's brochure. As studied by O'Mahony et al. (1993), the major pyrolysis products of *n*-C_6F_{14} include tetrafluoromethane (CF_4), tetrafluoroethylene (C_2F_4), hexafluoroethane (C_2F_6), hexafluoropropene (C_3F_6), and perfluoroisobutylene (C_4F_8). Among these decomposition products, perfluoroisobutylene may be the most toxic compound with a threshold limit value-ceiling (TLV-C) of 0.01 ppm by the American Conference of Governmental Industrial Hygienists (ACGIH) (ACGIH, 2002), because it is 10 times more toxic than phosgene and can inflict severe injury on lungs (Wang et al., 2001). In the study by Zundorf et al. (2008), hydrogen fluoride (HF) was generated as a highly toxic decomposition product when hexadecafluoro-*n*-heptane (C_7F_{16}) was sterilized with gamma irradiation as it was applied on the affected dialysers. Therefore, the toxic decomposition products that are probably encountered in case of fire or industrial accidents can pose serious hazards to occupation and environment. Although these highly reactive and toxic species are recognized as water-soluble products, small quantities of these products, not completely solved in the wet scrubbing, are probably found in the vent gas. The exposure to the removed fluorides in water bodies and vented exhausts still poses a potential hazard to health.

In order to strengthen our understanding of such fully perfluorinated liquid, it is vital to investigate the environmental fate and transport between interfaces like air, water, and solid phases. However, the measured properties regarding the chemical distribution among phases are very scarce in the literature. This review paper aimed at introducing their main physical properties, commercial/industrial uses, the hazards to the environment and health caused by its toxic decomposition products and the preliminary predications of partition coefficient, water solubility, and Henry's law constant. Furthermore, the environmental implications of liquid perfluoro-*n*-alkanes were also discussed in the paper.

2. Physicochemical properties of liquid perfluoro-*n*-alkanes

It is well known that the substitution of fluorine for hydrogen in *n*-alkanes has a profound influence on the compound's chemical and physical properties because fluorine is the most electronegative element and possesses a small atomic radius. As a result, carbon-fluorine bonds in liquid perfluoro-*n*-alkanes possess a relatively low polarization as compared to carbon-hydrogen bonds in *n*-alkanes, indicating that these perfluorinated compounds boil at slightly lower temperatures than the corresponding hydrocarbon analogues even though they have considerably higher molecular weights. For example, *n*-C_6F_{14} (molecular weight 338) and *n*-C_7F_{16} (molecular weight 388), boil at 57 and 82 °C, respectively, where *n*-hexane (molecular weight 86) and *n*-heptane (molecular weight 100), boil at 69 and 98 °C, respectively (Kroschwitz and Howe-Grant, 1994).

Furthermore, the C–F bond in perfluoro-*n*-alkanes is not only considerably strong but also chemically and thermally stable. Perfluoro-*n*-alkanes are thus inert to most chemical attack, including the highly reactive element fluorine, leading to their certain applications to commerce and industry. Their physicochemical properties are different from those of hydrocarbons when they have the same carbon number. Basically, the surface tensions, refractive indices, and dielectric constants of liquid perfluoro-*n*-alkanes at room temperature are lower than those of aliphatic hydrocarbons with the same carbon skeleton, whereas their densities, viscosities, and compressibilities are higher (Kroschwitz and Howe-Grant, 1994). For example, the liquid density and kinetic viscosity of *n*-C_6F_{14} at 25 °C are 1.68 g/cm^3 and 0.7 mPa s, respectively. In contrast to the perfluorinated compound, the properties of *n*-hexane (*n*-C_6H_{14}) at 25 °C are 0.65 g/cm^3 and 0.3 mPa s, respectively. The extremely nonpolar character of liquid perfluoro-*n*-alkanes and very low attractions between the molecules contribute to their unique properties listed in Table 1. The main physicochemial properties of common liquid perfluoro-*n*-alkanes in Table 1 were mainly compiled from the available monographs or books, and references from multidisciplinary journals such as *Fluid Phase Equilibria* and *J. Chem. Eng. Data*.

3. Commercial/industrial uses of liquid perfluoro-*n*-alkanes

Like other fluorinated aliphatic hydrocarbons such as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and hydrofluorocarbons (HFCs), liquid perfluoro-*n*-alkanes possess many similar physical and chemical properties, including chemical inertness, thermal stability, low toxicity, and non-flammability coupled with its unusual physical properties (i.e., high molecular weight and liquid density, and low dielectric constant, refractive index and surface tension at room temperature as compared to the same carbon skeleton). Therefore, it was recognized that liquid perfluoro-*n*-alkanes can be potentially used as transitional or interim replacements for CFCs and HCFCs since the early 1990s. Table 2 showed the local consumptions of common liquid perfluoro-*n*-alkanes in Taiwan these years (2001–2007). The data were compiled from the annual statistics of the Directorate General of Customs (Ministry of Finance, Taiwan). Obviously, the consumption of liquid perfluoro-*n*-alkanes, which amounted to the portions of 50%–100% in response to the rapid demand in the electronic industry, was associated with the industrial/commercial uses of *n*-C_6F_{14}. The data in Table 2 also showed that the imports of *n*-C_8F_{18} have increased over 100% in volume from 5 metric tons in 2005 to 11 metric tons in 2007.

3.1. Cleaning solvent

In the past, the most common organic cleaning solvents applied to the electronic components, precision cleaning and metal finishing

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