

IR metrics allowed EPA to take into consideration the ozone forming potential of other reactions of the compound in addition to the initial reaction with the hydroxyl radical. Volatile methyl siloxanes proved to be less reactive than ethane both on a per mole and per gram basis. In 1995, EPA considered another compound, acetone, using IR metrics. After considering the IR metrics, EPA exempted acetone based on the fact that acetone was less reactive on the basis of grams of ozone formed per grams of VOC emitted (60 FR 31635, June 16, 1995). Prior to 1994, all exemptions had been based on k_{OH} values. Since 1995, EPA has exempted

one additional compound, methyl acetate, based on comparisons of IR metrics. The reactivity of methyl acetate was found to be comparable to or less than that for ethane both under a per gram basis and under a per mole basis.

On February 5, 1999, the Performance Chemicals and Fluid Division of the 3M Company submitted to EPA a petition requesting that the compound 1,1,1,2,2,3,3-heptafluoro-3-methoxypropane be added to the list of compounds which are considered to be negligibly reactive in the definition of VOC at 40 CFR 51.100(s). The next year on August 21, 2000, the Performance Chemicals and Fluid Division of the 3M

Company submitted to EPA a petition requesting that the compound 3-ethoxy-1,1,1,2,3,4,4,5,5,6,6,6-dodecafluoro-2-(trifluoromethyl) hexane be added to the same list.

Potential uses for these two compounds (and other compounds for consideration under this proposal) are shown in Table 1. In its petition, 3M points out that it has requested the compound 1,1,1,2,2,3,3-heptafluoro-3-methoxypropane be listed as an acceptable substitute for CFCs and hydrochlorofluorocarbons (HCFCs) in certain uses and; as such, use of this substance may mitigate depletion of stratospheric ozone.

TABLE 1.—POTENTIAL USES OF COMPOUNDS ADDRESSED IN THIS PROPOSAL

Compound	Potential use
1,1,1,2,2,3,3-heptafluoro-3-methoxypropane	—refrigerant —aerosol propellant
3-ethoxy-1,1,1,2,3,4,4,5,5,6,6,6-dodecafluoro-2-(trifluoromethyl)hexane	—refrigerant
1,1,1,2,3,3,3-heptafluoropropane	—fire suppressant —aerosol propellant
methyl formate	—blowing agent

Although 3-ethoxy-1,1,1,2,3,4,4,5,5,6,6,6-dodecafluoro-2-(trifluoromethyl)hexane has not been identified as a substitute, specifically, the SNAP program has identified hydrofluoroethers (HFEs), as a class, as replacement substitutes for CFCs.

In support of the 1,1,1,2,2,3,3-heptafluoro-3-methoxypropane and the 3-ethoxy-1,1,1,2,3,4,4,5,5,6,6,6-dodecafluoro-2-(trifluoromethyl)hexane petitions, 3M Company supplied information on their respective photochemical reactivities. The 3M Company stated that, as hydrofluoroethers, these compounds are very similar in structure, toxicity, and atmospheric properties to other compounds such as $C_4F_9OCH_3$, $(CH_3)_2CFCF_2OCH_3$, $C_4F_9OC_2H_5$, $(CH_3)_2CFCF_2OC_2H_5$ which are exempt from the VOC definition.

Other information submitted by 3M Company consists mainly of a peer reviewed article entitled "Atmospheric Chemistry of Some Fluoroethers," Guschin, Molina, Molina: Massachusetts Institute of Technology, May 1998, which has been submitted to the docket. This article discusses a study in which the rate constant for the reaction of the compounds with the hydroxyl (OH) radical is shown to be less than that for ethane and slightly more than for methane. This rate constant (k_{OH} value) is commonly used as one measure of the photochemical reactivity of compounds. The petitioner compared the rate constants with that of ethane which has

already been listed as photochemically negligibly reactive (ethane is the compound with the highest k_{OH} value which is currently regarded as negligibly reactive). The compounds under consideration are listed with their reported k_{OH} rate constants in Table 2 along with that of ethane. The scientific information which the petitioner has submitted in support of the petition has been added to the docket for this rulemaking. This information includes references for the journal articles where the rate constant values are published.

TABLE 2.—REACTION RATE CONSTANTS (AT 25 °C) WITH OH RADICAL

Compound	cm ³ /molecule/sec
ethane	2.4×10^{-13}
n-C ₃ F ₇ OCH ₃	1.2×10^{-14}
HFE-7500	2.2×10^{-14}
HFC-227ea	1.09×10^{-15}
methyl formate	2.27×10^{-13}

Together with 5-day and 28-day inhalation toxicity studies, 3M Company also has included Material Safety Data Sheets indicating both their compounds as having very low toxicity. This information has been placed in the docket.

On February 18, 1998, the Great Lakes Chemical Corporation ("Great Lakes") petitioned EPA for the exclusion of 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea) from the definition of VOC. The rate constant for the reaction of HFC-

227ea with the OH radical was based on studies performed at the laboratories of Aerodyne Research, Inc. and reported by Nelson, Zahniser, and Kolb in the *Geophysical Research Letters*, Vol. 20, No. 2, pages 197–200. The rate constant for HFC-227ea as reported in this paper (Table 2) is 1.09×10^{-15} cm³/molecule/sec at 277K (0 °C) which places it well under two orders of magnitude below ethane's reactivity.

Great Lakes also claims that HFC-227ea is not an ozone depleting substance. This compound has been approved under EPA's SNAP program as an acceptable substitute for Halon 1301 and Halon 1211 in various fire suppression applications. Also, EPA has determined HFC-227ea to have a GWP at 3800 times that of carbon dioxide, making it a probable substitute for its competitor fire suppressants which have even higher GWPs.

On February 12, 2002, Foam Supplies, Inc. submitted a petition to exclude methyl formate from the definition of VOC. Foam Supplies, Inc. submitted journal articles showing three separate studies measuring methyl formate's rate constant with hydroxyl radicals and compared this to ethane measured in a like manner as a rate constant (cm³/molecule/sec). The highest value tested for methyl formate was that of 2.27×10^{-13} cm³/molecule/sec which is slightly below that of ethane at 2.4×10^{-13} cm³/molecule/sec (shown in Table 2).