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Atmospheric chemistry of cyc-$CF_2CF_2CF_2CH=CH$–: Kinetics, products, and mechanism of gas-phase reaction with OH radicals, and atmospheric implications

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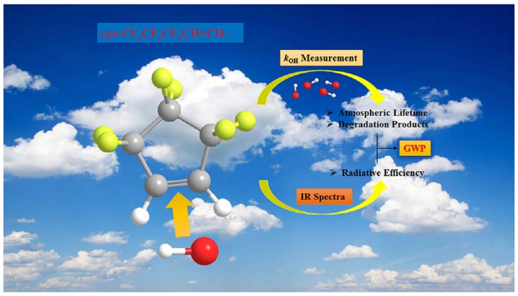
GRAPHICAL ABSTRACT



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ABSTRACT

The rate constants for the gas-phase reactions of cyc-$CF_2CF_2CF_2CH=CH$– with OH radicals were determined by a relative rate method between 253 and 328 K. The rate constant k_1 at 298 K was measured to be $(1.08 \pm 0.04) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}, and the Arrhenius expression was $k_1 = (3.72 \pm 0.14) \times 10^{-13}$ exp $[(-370 \pm 12)/T]$. The atmospheric lifetime of cyc-$CF_2CF_2CF_2CH=CH$– was calculated to be 107 d. The products and mechanism for the reaction of cyc-$CF_2CF_2CF_2CH=CH$– with OH radicals were also investigated. CO, CO_2, and COF_2 were identified as the main carbon-containing products following the OH-initiated reaction. Moreover, the radiative efficiency (RE) was determined to be 0.143 $W\,m^{-2}\,ppb^{-1}$, and the global warming potentials (GWPs) for 20, 100, and 500 yr were 54, 15, and 4, respectively. The photochemical ozone creation potential of the title compound was estimated to be 1.3.

1. Introduction

Chlorofluorocarbons (CFCs) have been used in various fields, in products such as refrigerants, solvents, foam blowing agents, and electronic detergents (Midgley and Henne, 1930). In accordance with the Montreal Protocol and subsequent amendments, chlorofluorocarbons have been phased out due to their strong ability to deplete ozone and significantly contribute to climate change as greenhouse gases (Molina and Rowland, 1974; Farman et al., 1985; Rowland, 1990). Hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs), which have shorter atmospheric lifetimes due to the presence of hydrogen atoms, were introduced as replacements for phased-out CFCs. Starting around 2007, HCFCs were also designated for a phasedown in an effort to eliminate ozone depletion deriving from the release of CFCs and their replacements. As a result, the use of HFCs has increased rapidly. HFCs do not contain Cl atoms and, hence, do not

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contribute to ozone depletion. However, the presence of C-F bonds in HFCs leads to strong absorption in an "atmospheric window" (800–1200 cm^{-1}), causing them to act as potent greenhouse gases. As such, persistent efforts are underway to exploit shorter-lived compounds, reducing the global warming potential (GWP) by substituting for the high-GWP HFCs.

Hydrofluoro-olefins (HFOs) are the new generation replacements with lifetimes of days or weeks (Burkholder et al., 2015a). The introduction of the carbon double bond significantly enhances the reactivity of HFCs towards the OH radical (Burkholder et al., 2015b), which is the most prevalent oxidant in the troposphere. The compound cyc-$CF_2CF_2CF_2CH=CH$–, a kind of HFO, has been proposed as a useful refrigerant or heat transfer fluid in the process of producing cooling or heat (Sievert et al., 2007; Clodic et al., 2016).

As an HFO, cyc-$CF_2CF_2CF_2CH=CH$– is expected to have a short tropospheric lifetime, and a study of the atmospheric chemistry of cyc-$CF_2CF_2CF_2CH=CH$– is necessary prior to commercial application. However, cyc-$CF_2CF_2CF_2CH=CH$– has not been previously studied. Therefore, this work provides the first study of the atmospheric implications of cyc-$CF_2CF_2CF_2CH=CH$–.

In the atmosphere, cyc-$CF_2CF_2CF_2CH=CH$– is primarily removed by reaction with OH radicals:

$$\text{cyc-}CF_2CF_2CF_2CH=CH\text{–} + OH \rightarrow \text{Products } k_1 \quad (1)$$

In this work, the following studies were performed: (i) rate constants for the reaction of cyc-$CF_2CF_2CF_2CH=CH$– with OH radicals at 253–328 K; (ii) IR absorption cross section spectrum between 400 and 2500 cm^{-1}; (iii) radiative efficiency (RE) and global warming potential (GWP); (iv) photochemical ozone creation potential (POCP); and (v) the products and mechanism of OH-initiated oxidation of cyc-$CF_2CF_2CF_2CH=CH$–.

2. Experimental

2.1. Reagents

A sample of cyc-$CF_2CF_2CF_2CH=CH$– was synthesized in our laboratory by eliminating the HF molecule from cyc-$CF_2CF_2CF_2CH_2CHF$– (Qing et al., 2016), where DMF was used as a solvent and catalyst. Its purity was identified as 99.2% by GC-FID. C_3H_8 (99.5% purity, GL Sciences Inc., Japan) and CH_3CHFCH_3 (99.0% purity, SynQuest Labs, Inc., USA) were used as reference compounds in the measurement of rate constants. Helium (99.995% purity) and O_2 (99.99% purity) were purchased from Iwatani International Corp. (Osaka, Japan).

2.2. Apparatus and OH generation

The apparatus has been described in detail in our previous studies (Chen et al., 2003). All experiments were conducted in an 11.5-dm^3 cylindrical quartz chamber (diameter: 10 cm, length: 146 cm) with an external jacket, where heated/cooled water or a coolant (PF-5070, Sumitomo 3M, Tokyo, Japan) was circulated to control the temperature in reaction chamber. A thermocouple was attached to both sides to monitor the temperature with an accuracy of ± 1 K. Ten low-pressure Hg lamps surrounded the reaction chamber and were used as a UV light source. A GC-FID (GC-2014A; Shimadzu, Tokyo, Japan) and a FT-IR spectrometer (Nicolet iS50, Thermo Scientific, US) were connected with the chamber. A greaseless vacuum line was established for the preparation of the reaction gas mixture.

In the presence of water vapor, O_3 underwent UV photolysis to generate OH radicals:

$$O_3 + h\nu \rightarrow O\,(^1D) + O_2 \quad (2)$$

$$O\,(^1D) + H_2O \rightarrow 2OH \quad (3)$$

An O_3/O_2 (3%, O_3) gas mixture was generated from pure O_2 through a silent-discharge ozone generator (ECEA-1000, Ebara Jitsugyo Co., Japan).

2.3. Relative rate method

The rate constant k_1 was measured by monitoring the loss rate of cyc-$CF_2CF_2CF_2CH=CH$– relative to that of the reference compounds in the presence of OH radicals:

$$\text{cyc-}CF_2CF_2CF_2CH=CH\text{–} + OH \rightarrow \text{Products } k_1 \quad (1)$$

$$\text{Reference} + OH \rightarrow \text{Products } k_r \quad (4)$$

In the relative rate measurements, cyc-$CF_2CF_2CF_2CH=CH-$, a reference compound (C_3H_8 or CH_3CHFCH_3), and H_2O were introduced into the reaction chamber, and He gas was used to dilute the gas mixture to a total pressure of 200 Torr. Four UV lamps were used for irradiation, and an O_3/O_2 gas mixture was continuously introduced into the chamber at a flow rate of 1.0–4.0 $cm^3\,min^{-1}$ at STP, resulting in a pressure increase of 3–15 Torr. During the measurements, the concentrations of cyc-$CF_2CF_2CF_2CH=CH-$ and the reference compounds were monitored by GC-FID at 7-min intervals. The capillary column was TC-Bond Q metal (length: 30 m, diameter: 0.53 mm, GL Sciences Inc., Japan). The column temperature was set to 443 K. For each sampling cycle, the gas mixture in the line between the sampling loop and the chamber was withdrawn and discarded, which led to a 0.17% loss of gas mixture (Zhang et al., 2015).

The following equation was adopted to evaluate k_1/k_r:

$$\ln\left(\frac{[\text{Sample}]_0}{[\text{Sample}]_t}\right) + D_n = \frac{k_1}{k_r}\left[\ln\left(\frac{[\text{Reference}]_0}{[\text{Reference}]_t}\right) + D_n\right] \quad (5)$$

where $[\text{Sample}]_{0(t)}$ and $[\text{Reference}]_{0(t)}$ are the concentrations of cyc-$CF_2CF_2CF_2CH=CH-$ and the reference compound (C_3H_8 or CH_3CHFCH_3), respectively, at time $t = 0$. $D_n = n\ \ln\ (0.9983)$ is a parameter correcting for the loss deriving from GC-FID sampling, where n is the number of sampling analyses.

In the reaction chamber, the initial concentrations of the reactants were 3.64–7.27 × 10^{14} (cyc-$CF_2CF_2CF_2CH=CH-$), 2.10–3.06 × 10^{14} (C_3H_8), 1.39–4.36 × 10^{14} (CH_3CHFCH_3), and 0.36–1.19 × 10^{18} (H_2O) molecules cm^{-3}, respectively. After 40–70 min, the loss of cyc-$CF_2CF_2CF_2CH=CH$–, C_3H_8, and CH_3CHFCH_3 were 17–30%, 84–85%, and 82–85%, respectively.

2.4. IR absorption cross section measurements

The IR spectrum of cyc-$CF_2CF_2CF_2CH=CH$– was measured at room temperature with a FT-IR spectrometer (Nicolet iS50, Thermo Scientific, US; resolution: 0.5 cm^{-1}; detector: DTGS) and a glass cell (optical path length: 10 cm, KBr windows). The background was collected after the glass cell was vacuumed. Then, 1.6–2.8 Torr of cyc-$CF_2CF_2CF_2CH=CH$– was introduced into the cell, and the IR spectra was obtained. The absorption cross section (σ) of the title compound at wavenumber ν (cm^{-1}) was obtained according to the Beer–Lambert law:

$$A = \sigma(\nu,\ T)nL, \quad (6)$$

where A is the infrared absorbance, $\sigma\ (\nu,\ T)$ is the wavenumber- and temperature-dependent absorption cross section, n is the molecular concentration (molecules cm^{-3}), and L is the optical path length (cm). Furthermore, the integrated absorption cross section $S(T)$ (cm^2 $molecule^{-1}$ cm^{-1}), between ν_1 and ν_2, was calculated through the following expression:

$$S(T) = \int_{\nu_1}^{\nu_2} \sigma(\nu,\ T)d\nu. \quad (7)$$

The concentrations of cyc-$CF_2CF_2CF_2CH=CH$– were monitored through the pressure in the glass cell by two pressure meters (MKS