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Atmospheric Chemistry of Sulfuryl Fluoride: Reaction with OH Radicals, Cl Atoms and O_3, Atmospheric Lifetime, IR Spectrum, and Global Warming Potential

M. P. SULBAEK ANDERSEN,*,[†]
D. R. BLAKE,[†] F. S. ROWLAND,[†]
M. D. HURLEY,[‡] AND
T. J. WALLINGTON*,[‡]

Department of Chemistry, 572 Rowland Hall, University of California, Irvine, Irvine, California 92697-2025, and Systems Analytics and Environmental Sciences Department, Ford Motor Company, Mail Drop SRL-3083, Dearborn, Michigan 48121-2053

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Sulfuryl fluoride (SO_2F_2) is a radiatively active industrial chemical released into the atmosphere in significant (ktonne/year) quantities. The potential for SO_2F_2 to contribute to radiative forcing of climate change needs to be assessed. Long path length FTIR/smog chamber techniques were used to investigate the kinetics of the gas-phase reactions of Cl atoms, OH radicals, and O_3 with SO_2F_2, in 700 Torr total pressure of air or N_2 at 296 ± 1 K. Upper limits of $k(Cl + SO_2F_2) < 9 \times 10^{-19}$, $k(OH + SO_2F_2) < 1.7 \times 10^{-14}$ and $k(O_3 + SO_2F_2) < 5.5 \times 10^{-24}$ cm^3 molecule^{-1} s^{-1} were determined. Reaction with Cl atoms, OH radicals, or O_3 does not provide an efficient removal mechanism for SO_2F_2. The infrared spectrum of SO_2F_2 is reported and a radiative efficiency of 0.196 W m^{-2} ppbv^{-1} was calculated. Historic production data estimates are presented which provide an upper limit for expected atmospheric concentrations. The radiative forcing of climate change associated with emissions of SO_2F_2 depends critically on the atmospheric lifetime of SO_2F_2. Further research is urgently needed to define the magnitude of potential nonatmospheric sinks.

1. Introduction

Sulfuryl fluoride, SO_2F_2, is a widely used insecticide/rodenticide for whole-structure fumigation. It is typically assumed that essentially 100% of SO_2F_2 is emitted to the atmosphere after use (*1*). Substantial production of SO_2F_2 has taken place since it was first marketed in the U.S. in the early 1960s The annual average global production since 2000 is estimated to be 2.9×10^6 kg year^{-1} (*1*). At the present time the only available data concerning atmospheric concentrations of SO_2F_2 come from the work by Mühle et al. (*2*) who reported measurements of SO_2F_2 in the remote troposphere. We are informed by these workers that their analytical procedure is being recalibrated, and the reported mixing ratios are likely to be revised (*3*). The revised data are not available at the present time and the atmospheric concentration of SO_2F_2 is unclear. With the Montreal Protocol mandated phase-out of methyl bromide, SO_2F_2 usage and associated emission rates may increase, reflecting a widening range of fumigation applications (e.g., crops and seed fumigations, soil sterilization).

The fate of SO_2F_2 in the environment is uncertain. SO_2F_2 is a gas with a vapor pressure of 16 atm at 20 °C. Upper limits to the atmospheric lifetime of 4.5 (*4*) and 14 (*2*) years have been suggested, but a laboratory study by Dillon et al. (*5*) found that the kinetics of the suggested atmospheric removal processes do not support the atmospheric lifetime estimates above. A recent experimental and theoretical study by Papadimitriou et al. (*6*) also supports an extended atmospheric lifetime for SO_2F_2.

To assess the possible contribution of SO_2F_2 to the radiative forcing of climate change, improved understanding of the atmospheric fate of SO_2F_2 is needed. This work focuses on the kinetics of the homogeneous gas-phase reactions with the title oxidants: OH radicals, Cl atoms, and ozone. The atmospheric chemistry of SO_2F_2 is discussed with respect to the atmospheric lifetime, and the global warming potential for SO_2F_2.

2. Experimental Section

Experiments were performed in a 140 L Pyrex reactor interfaced to a Mattson Sirius 100 FTIR spectrometer (*7*). The reactor was surrounded by 22 fluorescent blacklamps (GE F40T12BLB) which were used to photochemically initiate the experiments. Chlorine atoms were produced by photolysis of molecular chlorine.

$$Cl_2 + hv \rightarrow Cl + Cl \tag{1}$$

OH radicals were produced by photolysis of CH_3ONO in the presence of NO in air.

$$CH_3ONO + h\nu \rightarrow CH_3O + NO \tag{2}$$

$$CH_3O + O_2 \rightarrow HO_2 + HCHO \tag{3}$$

$$HO_2 + NO \rightarrow OH + NO_2 \tag{4}$$

Relative rate techniques were used to measure the rate constant of interest relative to a reference reaction whose rate constant has been established. The relative rate method is a well established technique for measuring the reactivity of Cl atoms and OH radicals with organic compounds (*8*). Kinetic data are derived by monitoring the loss of SO_2F_2 relative to one or more reference compounds. The decays of SO_2F_2 and the reference are then plotted using the following expression:

$$\mathrm{Ln}\left(\frac{[\text{reactant}]_0}{[\text{reactant}]_t}\right) = \frac{k_{\text{reactant}}}{k_{\text{reference}}}\mathrm{Ln}\left(\frac{[\text{reference}]_0}{[\text{reference}]_t}\right)$$

where $[\text{reactant}]_0$, $[\text{reactant}]_t$, $[\text{reference}]_0$, and $[\text{reference}]_t$ are the concentrations of SO_2F_2 and the reference compound at times "0" and "t", and k_{reactant} and $k_{\text{reference}}$ are the rate constants for reactions of Cl atoms or OH radicals with the SO_2F_2 and the reference compound. Plots of Ln($[\text{reactant}]_0/[\text{reactant}]_t$) versus Ln($[\text{reference}]_0/[\text{reference}]_t$) should be linear, pass through the origin, and have a slope of $k_{\text{reactant}}/k_{\text{reference}}$.

CH_3ONO was synthesized by the dropwise addition of concentrated sulfuric acid to a saturated solution of $NaNO_2$ in methanol. SO_2F_2 was provided by Dow AgroSciences at a purity of 99.8%. Other reagents were obtained from commercial sources. Experiments were conducted in 700 Torr

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* Address correspondence to either author. E-mail: mads@sulbaek.dk (M.P.S.A.); twalling@ford.com (T.J.W.).

[†] University of California.

[‡] Ford Motor Company.

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total pressure of air or N_2 diluent at 296 ± 2 K. Concentrations of reactants and products were monitored by FTIR spectroscopy. IR spectra were derived from 32 coadded interferograms with a spectral resolution of 0.25 cm^{-1} and an analytical path length of 27.1 m. To check for unwanted loss of reactants and reference compounds via heterogeneous reactions, reaction mixtures were left to stand in the chamber for 60 min. There was no observable (<1%) loss of any of the reactants or products in the present work.

3. Results

3.1. Kinetics of the Cl + SO_2F_2 Reaction. The rate of reaction (5) was measured relative to reaction (6):

$$Cl + SO_2F_2 \rightarrow \text{products} \qquad (5)$$

$$Cl + CH_3CF_3 \rightarrow \text{products} \qquad (6)$$

Reaction mixtures consisted of 1.76 mTorr of SO_2F_2, 1.5 − 3.2 mTorr CH_3CF_3, and 500 mTorr Cl_2 in 700 Torr of nitrogen diluent. Irradiation of the reaction mixtures for 2−50 min resulted in losses of CH_3CF_3 of 8−52%. The corresponding loss of SO_2F_2 was less than 1%. A loss of 52% CH_3CF_3 together with an upper limit of 1% for the loss of SO_2F_2 gives an upper limit for the rate constant ratio of $k_5/k_6 < 0.014$. Using $k_6 = 3.2 \times 10^{-17}$ (*9*) gives $k_5 < 4.5 \times 10^{-19}$ cm^3 $molecule^{-1}$ s^{-1}. Recognizing the factor of 2 uncertainty in k_6 (*9*) leads to $k_5 < 9 \times 10^{-19}$ cm^3 $molecule^{-1}$ s^{-1}. This upper limit is consistent with $k_7 < 5 \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1} recently reported by Papadimitriou et al. (*6*).

3.2. Kinetics of the OH + SO_2F_2 Reaction. The rate of reaction 7 was measured relative to reaction 8:

$$OH + SO_2F_2 \rightarrow \text{products} \qquad (7)$$

$$OH + C_2H_2 \rightarrow \text{products} \qquad (8)$$

Reaction mixtures consisted of 1.47−1.76 mTorr of SO_2F_2, 0.74−2.94 mTorr C_2H_2, 100 mTorr CH_3ONO, and 0−25 mTorr NO in 700 Torr of air diluent. Irradiation of the reaction mixtures for 1−45 min resulted in losses of C_2H_2 of 6−40%. The corresponding loss of SO_2F_2 was less than 1%. A loss of 40% C_2H_2 together with an upper limit of 1% for the loss of SO_2F_2 gives an upper limit for the rate constant ratio of $k_7/k_8 < 0.02$. Using $k_8 = 8.5 \times 10^{-13}$ (*10*) gives $k_7 < 1.7 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}. This result is consistent with the upper limit of $k_7 < 1 \times 10^{-15}$ reported by Dillon et al. (*5*), and $k_7 < 1 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} reported by Papadimitriou et al. (*6*).

3.3. Kinetics of the O_3 + SO_2F_2 Reaction. The kinetics of reaction 9 were studied by observing the decay of SO_2F_2 when exposed to ozone in the reaction chamber.

$$SO_2F_2 + O_3 \rightarrow \text{products} \qquad (9)$$

The reaction mixture consisted of 1.76 mTorr SO_2F_2 and 2250 mTorr O_3 in 700 Torr of air diluent. The loss of SO_2F_2 was expected to follow pseudo first order kinetics. After 7 h of exposure to ozone in the chamber, the loss of SO_2F_2 was less than 1%. A 1% loss of SO_2F_2 over 7 h corresponds to a pseudo first order rate constant of 4.0×10^{-7} s^{-1}. Combining the pseudo first order rate constant with the ozone concentration gives an upper limit of $k_9 < 5.5 \times 10^{-24}$ cm^3 $molecule^{-1}$ s^{-1}. This result is consistent with the upper limit of $k_9 < 1 \times 10^{-23}$ cm^3 $molecule^{-1}$ s^{-1} reported by Dillon et al. (*5*).

3.4. IR Spectrum of SO_2F_2. The IR spectrum of SO_2F_2 is shown in Figure 1. SO_2F_2 has IR features at 849.1, 887.0, 1270.9, and 1504.3 cm^{-1} with peak IR cross sections of 2.76×10^{-18}, 7.56×10^{-18}, 4.13×10^{-18}, and 9.28×10^{-18} cm^2 $molecule^{-1}$, respectively. The integrated cross sections for the IR absorption bands of SO_2F_2 are 5.81×10^{-17} (810−920 cm^{-1}), 2.62×10^{-17} (1220−1310 cm^{-1}), and 4.32×10^{-17} cm $molecule^{-1}$ (1455−1540 cm^{-1}). As discussed elsewhere (*11*), we estimate the uncertainty on our integrated cross-section measurements to be ±5%. The integrated cross sections are in excellent agreement with the measurements by Dillon et al. (*5*) of 5.67×10^{-17} (810−920 cm^{-1}), 2.50×10^{-17} (1220−1310 cm^{-1}), and 4.00×10^{-17} cm $molecule^{-1}$ (1455−1540 cm^{-1}). Papadimitriou et al. (*6*) have very recently reported band strengths of 5.84×10^{-17} (800.8−927.6 cm^{-1}), 2.61×10^{-17} (1211.1−1321.5 cm^{-1}), and 4.17×10^{-17} cm $molecule^{-1}$ (1448.8−1542.3 cm^{-1}) which are also consistent with the measurements presented herein.

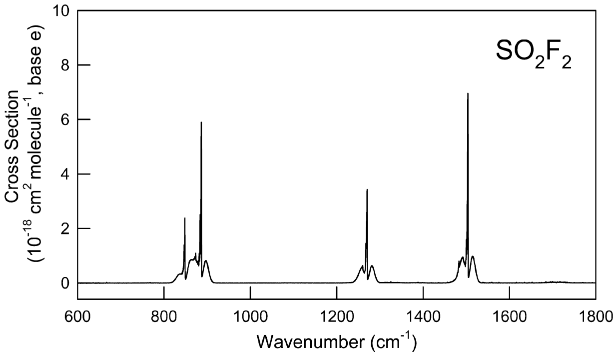

FIGURE 1. IR spectrum of SO_2F_2 in 700 Torr of air at 296 ± 1 K.

4. Environmental Implications of Atmospheric Chemistry

The motivation for the present work was to improve our understanding of the atmospheric chemistry of SO_2F_2 and to access its potential to contribute to radiative forcing of climate change. There was no discernible reaction of SO_2F_2 with OH radicals, Cl atoms,or O_3. The upper limits for the rate constants for reactions of SO_2F_2 with OH radicals, Cl atoms,and O_3 derived in the present work are listed in Table 1. Our results are consistent with the upper limits reported recently Dillon et al. (*5*) for reactions with OH and O_3, and Papadimitriou et al. (*6*) for reactions with OH and Cl. As indicated in Table 1, chlorine atoms and O_3 are not present in the atmosphere in sufficient quantities to impact the lifetime of SO_2F_2. Using the upper limit of $k(OH+SO_2F_2) < 1 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} (*6*) and a global weighted-average OH concentration of 1.0×10^6 molecules cm^{-3} (*12*) leads to a lifetime of SO_2F_2 with respect to reaction with OH radicals of >300 years.

Sulfuryl fluoride does not undergo photolysis in the actinic region of solar radiation and is not expected to undergo wet (rain-out) or dry deposition to any appreciable extent (*5*). Dissolution in ocean water followed by hydroxide ion catalyzed hydrolysis has been proposed as a dominant sink in the environment (*13, 14*). Wetted-wall flow tube experiments by Dillon et al. (*5*) suggested a negligible uptake coefficient of 6−9 × 10^{-8} (depending on pH) and no irreversible loss processes were observed. Dillon et al. (*5*) estimated that uptake/loss of SO_2F_2 to oceans accounts for only ~0.5% of annual emissions. However, a more detailed treatment of the ocean loss process, including air−sea exchange with the oceanic mixed layer indicates a more significant sink, leading to a lifetime with respect to ocean uptake of approximately 40 years (*6*).

We have not been able to discern any atmospheric loss mechanism for SO_2F_2 in the troposphere or stratosphere. SO_2F_2 does not absorb sunlight present in the troposphere or stratosphere but does absorb at 121.6 nm (Lyman-α) and is likely to be lost via photolysis and possibly reaction with electrons in the mesosphere. The absorption cross section of SO_2F_2 at 121.6 nm is similar to that of SF_5CF_3 which has an atmospheric lifetime of approximately 650−950 years with respect to photolysis and reaction with electrons in the mesosphere (*15*).

TABLE 1. Rate Constants (Units of cm^3 molecule^{-1} s^{-1}) for the reactions of Cl, OH, and O$_3$ with SO$_2$F$_2$[a]

bimolecular reaction rate constants	k_7(OH + SO$_2$F$_2$)	k_5(Cl + SO$_2$F$_2$)	k_9(O$_3$ + SO$_2$F$_2$)
Dillon et al. (*5*)	$<1 \times 10^{-15}$		$<1 \times 10^{-23}$
Papadimitriou et al. (*6*)	$<1 \times 10^{-16}$ *	$<5 \times 10^{-17}$	$<1 \times 10^{-23}$
present work	$<1.7 \times 10^{-14}$	$<9 \times 10^{-19}$ *	$<5.5 \times 10^{-24}$ *
atmospheric lifetime (years)	>300	$>10^7$	>5000

[a] Atmospheric lifetimes (years) are estimated for the individual removal processes using the rate constants marked with * and a global average oxidant concentrations of [OH]=1×10^6 molecule cm^{-3} (*12*), [Cl] = 1×10^3 molecule cm^{-3} (*20*), and [O$_3$] = 35 ppb (*20*).

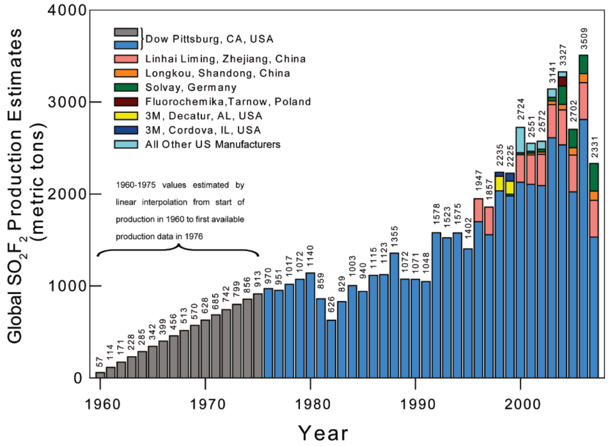

FIGURE 2. Historic production estimates for SO$_2$F$_2$. The Dow Chemical 1960−1975 production values are estimated by linear interpolation from the start of production (1960) to the first production data available (1976). Dow Chemical production values from 1975 onward have been provided by the manufacturer. Emission values for 3M locations are from the U.S. EPA Toxic Release Inventory (*21*). Production values for Linhai Liming, Longkou, Solvay, and Fluorochemika are estimates only and have not been verified by the individual companies (*1*).

Historical production data provide insight into the expected magnitude and temporal trends of atmospheric concentration, and ultimately the atmospheric lifetime of SO$_2$F$_2$. Estimated historical global production data for SO$_2$F$_2$ are given in Figure 2 (*1*). The estimated global production from 1960 to 2007 totals 61147 tons of SO$_2$F$_2$. If SO$_2$F$_2$ had no loss mechanism and assuming that all SO$_2$F$_2$ produced has been emitted into the atmosphere and remained there indefinitely, one would expect an atmospheric concentration of the order of 3.5 ppt. By comparison, if we assume an atmospheric lifetime of approximately 10 years, one would expect the atmospheric abundance to be on the order of 1 ppt. As mentioned in the introduction, the analytical procedure used by Mühle et al. (*2*) is being recalibrated and there is considerable uncertainty in the atmospheric mixing ratio of SO$_2$F$_2$ (*3*). It is interesting that while neither we, nor Dillon et al. (*5*), have been able to observe any significant atmospheric loss mechanism for SO$_2$F$_2$ in our laboratory experiments, the preliminary field measurements by Mühle et al. (*2*) do suggest that there is a significant loss mechanism. It is worth noting that the laboratory experiments have focused on abiotic loss mechanisms. SO$_2$F$_2$ is a biologically active compound and is used as insecticide/rodenticide. It seems reasonable to speculate that there may be one or more biotic processes (e.g., removal by biota in soils or vegetation) which serve as sinks for SO$_2$F$_2$ (*16*). Further research in this area is needed but is beyond the scope of the present work.

As great uncertainty remains in the atmospheric lifetime for SO$_2$F$_2$, it is informative at this point to estimate the global warming potential of SO$_2$F$_2$ for a range of potential atmospheric lifetimes. Using the method outlined by Pinnock et al. (*11*), the IR spectrum of SO$_2$F$_2$ shown in Figure 1 and the IR spectrum of CFC-11 (*17*) we calculate instantaneous forcings for SO$_2$F$_2$ and CFC-11 of 0.196 and 0.26 W m^{-2} ppb^{-1}, respectively. Values of the halocarbon global warming potential, HGWP (*18*), for SO$_2$F$_2$ (relative to CFC-11) can then be estimated using expression II:

$$\mathrm{HGWP}_{\mathrm{SO_2F_2}} = \left(\frac{\mathrm{IF}_{\mathrm{SO_2F_2}}}{\mathrm{IF}_{\mathrm{CFC-11}}}\right)\left(\frac{\tau_{\mathrm{SO_2F_2}}\mathrm{M}_{\mathrm{CFC-11}}}{\tau_{\mathrm{CFC-11}}\mathrm{M}_{\mathrm{SO_2F_2}}}\right)\left(\frac{1-\exp(-t/\tau_{\mathrm{SO_2F_2}})}{1-\exp(-t/\tau_{\mathrm{CFC-11}})}\right) \quad \text{(II)}$$

where IF$_{\mathrm{SO2F2}}$, IF$_{\mathrm{CFC-11}}$, M$_{\mathrm{SO_2F_2}}$, M$_{\mathrm{CFC-11}}$, $\tau_{\mathrm{SO_2F_2}}$, and $\tau_{\mathrm{CFC-11}}$ are the instantaneous forcings, molecular weights, and atmospheric lifetimes of SO$_2$F$_2$ and CFC-11, and *t* is the time horizon over which the forcing is integrated. We assume $\tau_{\mathrm{CFC-11}}$ = 45 years (*19*). For the purposes of illustrating the potential *order of magnitude* contribution of SO$_2$F$_2$ to radiative forcing of climate change we have considered a range of atmospheric lifetimes for SO$_2$F$_2$ of 1−100 years (centered on the value of 10 years discussed above and varied by an order of magnitude). The GWP for SO$_2$F$_2$ relative to CO$_2$ is estimated by multiplying the HGWP values for 20, 100, and 500 year time horizons by factors of 6730, 4750, and 1620, respectively (*19*). Figure 3 shows the GWP of SO$_2$F$_2$ for 20, 100, and 500 year time horizons plotted as a function of the atmospheric lifetime of SO$_2$F$_2$. As illustrated in Figure 3, the uncertainty in the atmospheric lifetime of SO$_2$F$_2$ leads to considerable uncertainty in its GWP (120−7600 for a 100 year time horizon). The fact that we, Dillon et al. (*5*), and Papadimitriou et al. (*6*) have been not able to identify any significant atmospheric

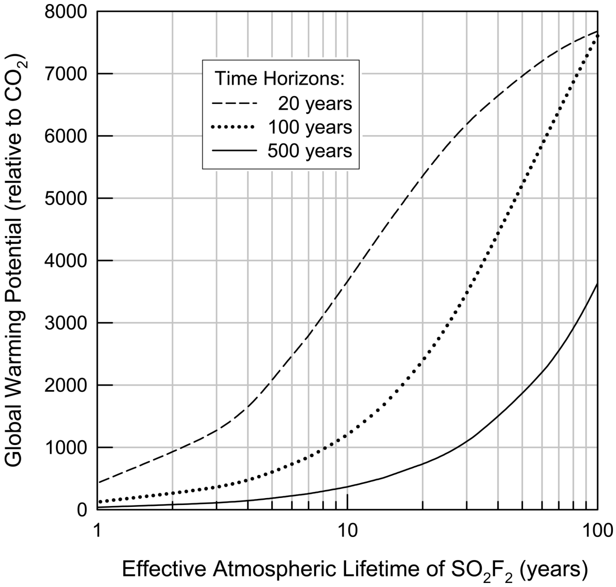

FIGURE 3. Global warming potential for SO$_2$F$_2$ as a function of atmospheric lifetime.

sink for SO_2F_2 underscores the need for improved documentation of emission rates, atmospheric abundance trends, and potential oceanic or terrestrial sinks for this compound. While SO_2F_2 appears to be long-lived in the atmosphere, further work is needed to better define the atmospheric lifetime of SO_2F_2.

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Literature Cited

(1) Krieger, M. S. Dow AgroSciences, personal communication, 2008.

(2) Mühle, J.; Harth, C. M.; Salameh, P.; Miller, B. R.; Weiss, R. F.; Porter, L. W.; Fraser, P. J.; Greally, B. R.; O'Doherty, S. Global measurements of atmospheric sulfuryl fluoride *Eos Trans. AGU* **2006**, *87*, 52, Fall Meet. Suppl., Abstract A53B-0191.

(3) Mühle J. and Weiss, R. F. University of California, San Diego, personal communication, 2008.

(4) Competent Authority Report, Sulfuryl Fluoride/Vikane (PT8), Doc. III-B7, May 2005; European Union, 2005.

(5) Dillon, T. J.; Horowitz, A.; Crowley, J. N. The atmospheric chemistry of sulphuryl fluoride, SO_2F_2. *Atmos. Chem. Phys.* **2008**, *8*, 1547–1557.

(6) Papadimitriou, V. C.; Portmann, R. W.; Fahey, D. W.; Mühle, J.; Weiss, R. F.; Burkholder, J. B. Experimental and theoretical study of the atmospheric chemistry and global warming potential of SO_2F_2. *J. Phys. Chem. A* **2008**, *112*, 12657−12666.

(7) Wallington, T. J.; Japar, S. M. Fourier transform infrared kinetic studies of the reaction of HONO with HNO_3, NO_3 and N_2O_5 at 295 K. *J. Atmos. Chem.* **1989**, *9*, 399–409.

(8) Atkinson, R. *J. Phys. Chem. Ref. Data* **1989**, Monograph 1.

(9) Ammann, M.; Atkinson, R.; Cox, R. A.; Crowley, J. N.; Hynes, R. G.; Jenkin, M. E.; Rossi, M. J.; Troe, J.; Wallington, T. J. IUPAC datasheet oClOx27, http://www.iupac-kinetic.ch.cam.ac.uk/ (accessed November 2008).

(10) Sørensen, M.; Kaiser, E. W.; Hurley, M. D.; Wallington, T. J.; Nielsen, O. J. Kinetics of the reaction of OH radicals with acetylene in 25−8000 torr of air at 296 K. *Int. J. Chem. Kinet* **2003**, *35*, 191–197.

(11) Pinnock, S.; Hurley, M. D.; Shine, K. P.; Wallington, T. J.; Smyth, T. J. Radiative forcing of climate by hydrochlorofluorocarbons and hydrofluorocarbons. *J. Geophys. Res.* **1995**, *100* (D11), 23227–23238.

(12) Prinn, R. G.; Huang, J.; Weiss, R. F.; Cunnold, D. M.; Fraser, P. J.; Simmonds, P. G.; McCulloch, A.; Salameh, P.; O'Doherty, S.; Wang, R. H. J.; Porter, L.; Miller, B. R. Evidence for substantial variations of atmospheric hydroxyl radicals in the past two decades. *Science* **2001**, *292*, 1882–1888.

(13) Kollman, W. S. *Sulfuryl Fluoride (Vikane) Risk Characterization Document, Volume III, Environmental Fate*; California Environmental Protection Agency, Environmental Monitoring Branch, Department of Pesticide Regulation: Sacramento, CA, 2006.

(14) Cady, G. H.; Misra, S. Hydrolysis of sulfuryl fluoride. *Inorg. Chem.* **1974**, *13*, 837–841.

(15) Takahashi, K.; Nakayama, T.; Matsumi, Y.; Solomon, S.; Gejo, T.; Shigemasa, E.; Wallington, T. J. Atmospheric lifetime of SF_5CF_3 Geophys. Res. Lett. 2002, *29*, 15, 1712, doi: 10.1029/2002GL015356.

(16) Jeffers, P. M.; Wolfe, N. L.; Nzengung, V. Green plants: A terrestrial sink for atmospheric CH_3Br. *Geophys. Res. Lett.* **1998**, *25*, 43–46.

(17) Ninomiya, Y.; Kawasaki, M.; Gushin, A.; Molina, L. T.; Molina, M.; Wallington, T. J. Atmospheric Chemistry of n-$C_3F_7OCH_3$: Reaction with OH radicals and Cl atoms and atmospheric fate of n-$C_3F_7OCH_2O$ radicals. *Environ. Sci. Technol.* **2000**, *34*, 2973–2978.

(18) Fisher, D. A.; Hales, C. H.; Wang, W.; Ko, M. K. W.; Sze, N. D. Model calculations of the relative effects of CFCs and their replacements on global warming. *Nature* **1990**, *344*, 513–516.

(19) Forster, P.; Ramaswamy, V.; Artaxo, P.; Berntsen, T.; Betts, R.; Fahey, D. W.; Haywood, J.; Lean, J.; Lowe, D. C.; Myhre, G.; Nganga, J.; Prinn, R.; Raga, G.; Schulz M.; Van Dorland, R. 2007: Changes in atmospheric constituents and in radiative forcing In *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*; Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., Miller, H. L., Eds.; Cambridge University Press: New York, 2007.

(20) Finlayson-Pitts, B. J.; Pitts, J. N., Jr. *Chemistry of the Upper and Lower Atmosphere*; Academic Press: London, 2000.

(21) U.S. Environmental Protection Agency. *Toxics Release Inventory (TRI)*. Available at http://www.epa.gov/triexplorer/ (accessed February 2008).

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