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Kinetics and Mechanism of the Photodecomposition of Trifluorobromomethane and Tetrafluorodibromoethane under the Action of Light with a Wavelength of 253.7 nm

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Abstract—The kinetics of photodecomposition of Halons CF_3Br and $C_2F_4Br_2$ was studied at different times of the irradiation of a mixture of these substances with oxygen at the wavelength $\lambda = 253.7$ nm. Kinetic data were obtained from changes in the absorption spectra in the region of Halon absorption and at a wavelength of 416 nm, which corresponds to the absorption maximum of molecular bromine. Kinetic schemes were proposed for the photodecomposition of CF_3Br and $C_2F_4Br_2$ at $\lambda = 253.7$ nm, and the quantum yields of their photodecomposition at this wavelength were determined.

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INTRODUCTION

Trifluorobrominemethane (CF_3Br, Halon 13B1) and tetrafluorodibromoethane ($C_2F_4Br_2$ Halon 114B2) are widely used in fire extinguishing, especially, in large fires in power engineering and industry, as well as on submarines and in airliners. Halon 13B1 is most widespread in the West as a result of its small toxicity, whereas Halon 114B2 is most commonly used in Russia because of its higher efficiency in fire extinguishing. However, Halon 114B2 is more toxic by a factor of 30. The fractions of $C_2F_4Br_2$ and CF_3Br in the lower atmosphere are 0.45 and 2.3 ppt, respectively [1, 2].

In 1987 in Montreal, the industrial countries signed a protocol on the gradual reduction and then the total cessation of the release of Halons because of their danger for the ozone layer of the Earth [3].

In Russia, the production of CF_3Br and $C_2F_4Br_2$ was ceased since January 1994 and December 2000, respectively. However, the use of currently available substances is permitted, and Halons remain the main fire extinguishing agents. When these substances arrive at the stratosphere, they are decomposed under the action of ultraviolet radiation with the formation of bromine atoms, which destroy stratospheric ozone as a result of chain processes [4, 5].

Bromine-containing Freons are much more dangerous for the ozone layer than Freons that contain chlorine. Chang and Duewer [6] found that the effectiveness of the bromine cycle of ozone depletion is higher than that of the chlorine cycle by a factor of 45. The difference in the effectiveness of chlorine and bromine compounds was evaluated in the range from 40 to 400 times [7, 8]. Different effectiveness of chlorine and bromine cycles in the decomposition of stratospheric ozone is related to different rates chain termination processes in them and, therefore, to different chain lengths [9].

It is the practice to evaluate the effectiveness of organic bromine compounds in the decomposition of ozone—Ozone Depletion Potential (ODP)—with respect to $CFCl_3$.

The reported values of ODP for CF_3Br and $C_2F_4Br_2$ are 16 and 7 [10] and the lifetimes in the atmosphere are 65 and 20 years, respectively [11]. These lifetimes ensure the presence of CF_3Br and $C_2F_4Br_2$ at the heights of the average and upper stratosphere, where the intensity of emission at $\lambda = 253.7$ nm is sufficiently high for their photodissociation. This fact explains the formulation of the problem that was solved in this work: to study the kinetics of photodecomposition of Halons CF_3Br and $C_2F_4Br_2$ in a mixture with oxygen at various irradiation times at $\lambda = 253.7$ nm.

EXPERIMENTAL

The system for the photolysis of $C_2F_4Br_2$ and CF_3Br at $\lambda = 253.7$ nm consisted of a quartz cell with a diameter of 4 cm and a length of 14 cm; a 8-W low-pressure mercury lamp, which served as a radiation source with $\lambda = 253.7$ nm; and an M-40 spectrophotometer, which was used for the recording of spectra and the measurement of the adsorption of test substances in the ultraviolet and visible ranges.

In the experiments on the photolysis of Halons, Halon mixtures with helium, which served as a buffer gas, and oxygen, which served for the removal of primary radicals, were irradiated. The presence of oxygen led to the formation of passive peroxide radicals,

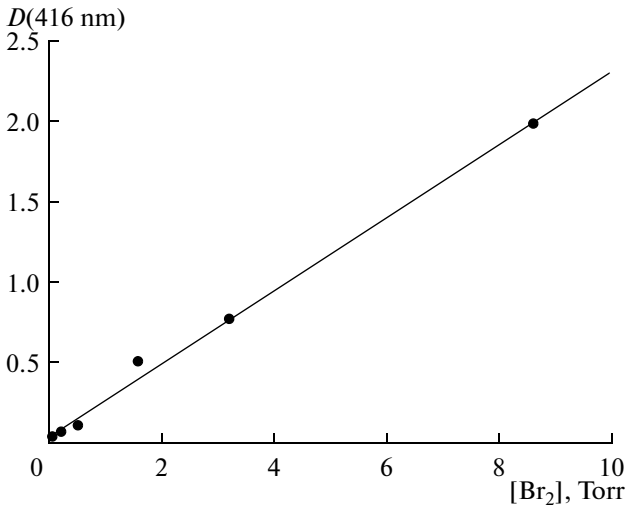

Fig. 1. Dependence of absorbance at λ = 416 nm on the pressure of molecular bromine.

which stopped the further chemical transformations of photolysis products. The reagent mixtures were prepared in a vacuum system of molybdenum glass, in which shutoff valves of only glass and Teflon components were used. Gases were stored in glass bulbs, and $C_2F_4Br_2$ as a liquid was kept in ampoules away from light. Helium of high-purity grade and oxygen of pure grade were used in the experiments. All of the substances used in the experiments were purified by low-temperature distillation. Vacuum gages and a Sapfir manometer, which was calibrated based on the pressure of water vapor at 273 K, were used for pressure measurements. Pressures in the ranges of 0–30 and 30–760 Torr were measured to within 0.05 and 3 Torr, respectively.

For determining the spectral composition of radiation, the spectrum of the lamp was recorded in the wavelength range of 200–900 nm. The kinetics of photodecomposition of Halons was studied by measuring the absorbance of the test mixture at different irradiation times in the region of Halon absorption and at a wavelength of 416 nm, which corresponds to the absorption maximum of molecular bromine.

For determining the emission intensity of the lamp (**I**) under the given conditions, we carried out experiments with the following three actinometers: HBr, CH_3Br, and phosgene. These substances are widely used as actinometers in the range of 180–280 nm. The found lamp emission intensities were $(2.1 \pm 0.2) \times 10^{15}$, $(1.7 \pm 0.2) \times 10^{15}$, and $(1.63 \pm 0.2) \times 10^{15}$ photon $cm^{-2}\,s^{-1}$ with the use of HBr, CH_3Br, and phosgene actinometers, respectively. The averaged value based on these three calibrations was $(1.8 \pm 0.2) \times 10^{15}$ photon $cm^{-2}\,s^{-1}$.

Before the experiments, were carried out calibration to determine the relationship between absorbance at λ = 416 nm and the vapor pressure of molecular bromine. Figure 1 shows these data.

The absorption cross section of molecular bromine at λ = 416 nm and 295 K was determined from the slope of the straight line in Fig. 1. It was 6.3×10^{-19} cm^2. Forster et al. [12] reported a value of 6.5×10^{-19} cm^2 for this quantity at λ = 415 nm and a temperature of 298 K.

Before the onset of the measurements, the optical cell was evacuated to a pressure of 3×10^{-3} Torr using a fore pump and washed several times with helium. Then, the spectrum of the evacuated cell was measured and the cell was filled with a mixture of the test substances. The mixture of the substances was irradiated during specified time intervals and the spectra of the contents of the cell were measured in the wavelength range of 200–900 nm. A scanning beam passed along the entire cell, and the absorbance of the cell was subtracted from the general spectrum. Changes in the absorbance of the mixture in the region of Halon absorption and at 416 nm, which corresponds to the absorption maximum of molecular bromine, made it possible to study the kinetics of Halon photodecomposition and molecular bromine accumulation. In accordance with the Lambert–Beer law, the absorbance $D(\lambda)$, which is determined from spectrophotometer readings, is related to the concentration of the substance present in the optical cell by the following equation:

$$D(\lambda) = n\sigma(\lambda)l, \qquad (1)$$

where n is the substance concentration, molecule/cm^3; $\sigma(\lambda)$ is the absorption cross section of the substance at λ = 253.7 nm, cm^2; l is the cell length, cm.

According to our estimations, the absorbance of the mixtures depended on the presence of Halons because the contribution of oxygen to absorption (at λ < 242 nm) under conditions of our experiments could be ignored.

THEORETICAL

The kinetics of photodecomposition and the quantum yields of bromine-containing Halons were determined from the absorption spectra of Halons and molecular bromine, which was formed as a result of the combination of bromine atoms released upon the photodissociation of Halons.

The absorption of a photon by a bromine-containing Halon results in the following reaction sequence (Scheme I):

(I)

(1) $R{-}Br + h\nu \longrightarrow R{-}Br^{\bullet}$,

(2) $R{-}Br^{\bullet} \longrightarrow R^{\bullet} + Br$,

(3) $R{-}Br^{\bullet} + M \longrightarrow R{-}Br + M$,

(4) $R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet}$,

(5) $R^{\bullet} + Br_2 \longrightarrow R{-}Br + Br$,

(6) $R^{\bullet} + R^{\bullet} \longrightarrow R_2$,

(7) $Br + Br + M \longrightarrow Br_2 + M$,

(8) $Br + wall \longrightarrow 1/2Br_2$.

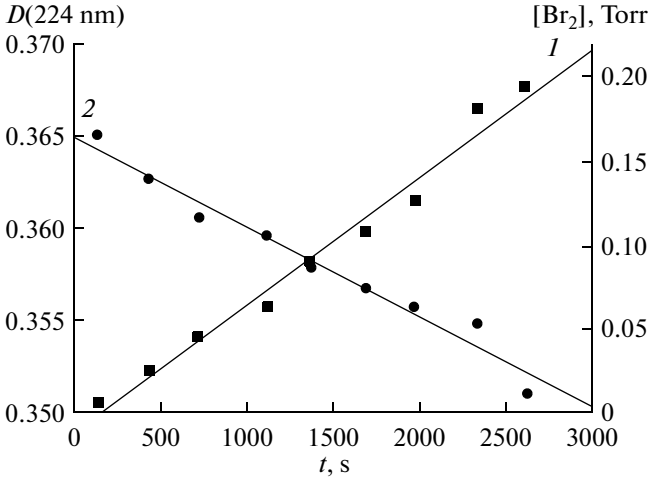

Fig. 2. Dependence of (*1*) the concentration of molecular bromine and (*2*) absorbance at $\lambda = 224$ nm on irradiation time for a mixture containing $C_2F_4Br_2$ (3.36 Torr) and oxygen (3.2 Torr).

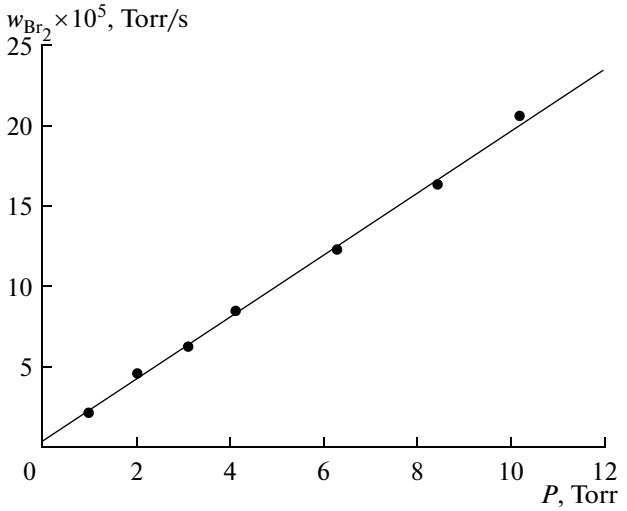

Fig. 3. Dependence of the rate of formation of molecular bromine on the pressure of $C_2F_4Br_2$.

If the pressure of oxygen is higher than 1 Torr, the following condition is fulfilled: $k_4[O_2] \gg k_6[R]$. This conclusion follows from a comparison between the rate constants k_4 [13] and k_6 [14], the ration between which is close to 1, and the ratio $[O_2]/[R]$, which was ~10^4 under conditions of our experiments. As a result, the expression for the rate of Halon consumption and molecular bromine accumulation takes the following form:

$$-d[RBr]/dt = 2d[Br_2]/dt = \sigma_d I[RBr]\alpha\beta, \qquad (2)$$

where σ_d is the dissociation cross section, cm^2, at $\lambda = 253.7$ nm; I is the light flux, photon cm^{-2} s^{-1}, at the same wavelength; $\alpha = k_2/(k_2 + k_3[M])$ is the fraction of molecules that avoided deactivation and formed bromine atoms; $\beta = k_4[O_2]/(k_4[O_2] + k_5[Br_2])$ is the term that takes into account the regeneration of Halon in a reaction of radical R* with molecular bromine.

The following differential equation describes the shape of a accumulation curve of molecular bromine in time:

$$2d[Br_2]/dt = \sigma_d I[RBr]\alpha k_4[O_2]/(k_4[O_2] + k_5[Br_2]). \qquad (3)$$

At the initial portion corresponding to the condition $k_5[Br_2] \ll k_4[O_2]$, the concentration of molecular bromine linearly increases with time, and the slope is $1/2\sigma_d I\alpha[RBr]$.

RESULTS AND DISCUSSION

Tetrafluorodibromoethane

The photolysis of $C_2F_4Br_2$ was carried out at a temperature of 295 K. Filters were not used in the main experiments because it was found previously that the emission of the lamp at $\lambda = 185$ nm does not contribute to the photolysis. (Preliminary experiments were carried out under the irradiation of a mixture with and without a filter with the cut-off region at $\lambda = 185$ nm.) The difference in the rates of formation of bromine precisely corresponded to a decrease in the radiation intensity at $\lambda = 253.7$ nm.

Figure 2 shows changes in absorbance at the absorption maximum of $C_2F_4Br_2$ and in the concentration of molecular bromine. The experimental data were obtained without the use of a filter.

The dependence of the rate of accumulation of molecular bromine on the concentration of $C_2F_4Br_2$ was obtained in experiments at a fixed oxygen content, which corresponded to 2 Torr. Figure 3 shows the experimental data. It can be seen that the dependence is linear and corresponds to Eq. (2).

We studied the effect of oxygen pressure on the accumulation of bromine under the irradiation of mixtures containing $C_2F_4Br_2$ at a fixed pressure. The consumption of Halon and the formation of bromine did not occur in the experiments without the addition of oxygen. This fact suggests that, in the absence of oxygen, an equilibrium between the reaction of $C_2F_4Br_2$ decomposition and the reverse recombination reaction was established. However, upon the addition of oxygen to only 1 Torr, the concentration of $C_2F_4Br_2$ decreased and the concentration of bromine increased as a result of the irradiation of the mixture. Figure 4 shows the dependence of the rate of bromine formation on the pressure of oxygen.

It can be seen that the rate of bromine formation did not depend on the pressure of oxygen over a range from 1 to 330 Torr. The dependence of the rate of bromine formation on the pressure of helium was also not observed over a range from 2 to 600 Torr. This suggests that the coefficient α in Eq. (2) is 1.

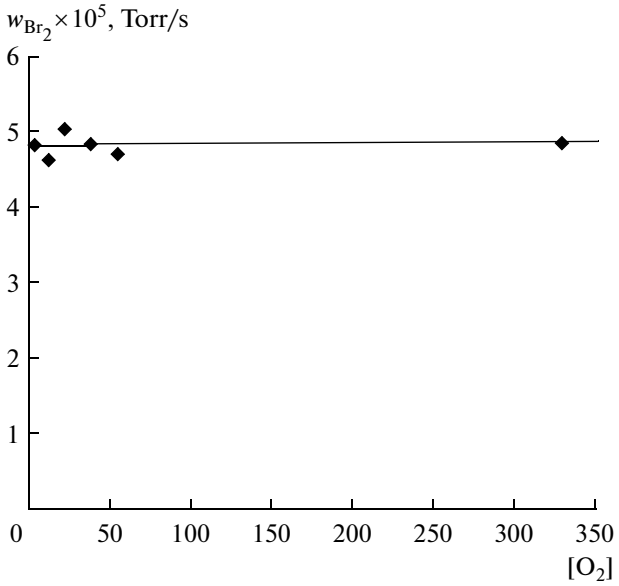

Fig. 4. Dependence of the rate of formation of molecular bromine on the concentration of oxygen at a $C_2F_4Br_2$ pressure of 2 Torr.

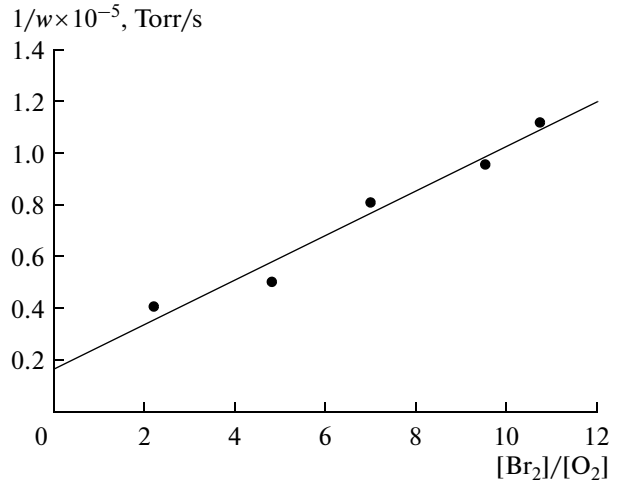

Fig. 5. Dependence of $1/w_{Br_2}$ on the $[Br_2]/[O_2]$ ratio.

To determine the coefficient β in Eq. (2), that is, the ratio between the rates of steps (4) and (5) in Scheme (I), we performed experiments with the addition of molecular bromine to the mixture. Let us denote the rate of accumulation of molecular bromine by *w*. From Eq. (2), it follows that, at a constant pressure of $C_2F_4Br_2$,

$$1/w = A(1 + k_5[Br_2]/k_4[O_2]), \quad (4)$$

where $A = 1/\sigma_d I[C_2F_4Br_2]$.

Figure 5 shows the experimental data. The ratio k_5/k_4 was found to be 0.47.

Our experimental data allowed us to state that the processes occurring on the photolysis of $C_2F_4Br_2$ in the presence of oxygen are described by the following reaction scheme:

(II)
(1) $C_2F_4Br_2 + h\nu \longrightarrow C_2F_4Br^{\bullet} + Br$,
(2) $C_2F_4Br^{\bullet} + O_2 \longrightarrow C_2F_4BrO_2$,
(3) $Br + Br + M \longrightarrow Br_2 + M$,
(4) $Br + wall \longrightarrow 1/2Br_2$.

The rate of accumulation of molecular bromine is related to the photodissociation cross section σ_d by the simple equation

$$w_{Br_2} = 1/2\,\sigma_d I[C_2F_4Br_2]. \quad (5)$$

The quantum yield (φ) is determined from the ratio of the dissociation cross section (σ_d) at a corresponding wavelength to the absorption cross section (σ) at the same wavelength:

$$\varphi = \sigma_d/\sigma. \quad (6)$$

The absorption cross section for $C_2F_4Br_2$ at λ = 253.7 nm was taken from [15].

The quantum yield of $C_2F_4Br_2$ at λ = 253.7 nm was φ = 1.08 ± 0.16, as found from Eq. (6). The found quantum yield of $C_2F_4Br_2$ is close to unity; this is different from data published by Zou et al. [16], who obtained the values of 1.9 ± 0.1, 1.9 ± 0.1, and 1.4 ± 0.1 at wavelengths of 193, 233, and 266 nm, respectively. We explain this by the fact that, under the conditions for our experiments, reaction (2) in Scheme (II) predominated over the decomposition reaction of the radical $C_2F_4Br^*$ with the formation of a bromine atom and C_2F_4, which was an additional source of atomic bromine in the work of Zou et al. [16], in the entire range of oxygen pressures. Unfortunately, we failed to find published data on the absorption spectrum of $C_2F_4BrO_2$; however, our experimental data suggest that, under the conditions of our experiments, the further decomposition of $C_2F_4BrO_2$ did not occur.

Trifluorobromomethane

Analogous experiments were also performed with CF_3Br. The mixtures were also irradiated in the absence of a filter. As in the case of the experiments with tetrafluorodibromoethane in the absence of oxygen, the irradiation of a mixture did not lead to the formation of molecular bromine and the consumption of CF_3Br. In the range of oxygen pressures from 2 to 400 Torr, the rate of accumulation of molecular bromine was constant.

Figure 6 shows the time dependence of the rate of accumulation of molecular bromine at a CF_3Br pressure of 207 Torr and an oxygen pressure of 15 Torr. It can be seen that the dependence was linear over the entire range of irradiation times.

Based on the experimental data, we can conclude that the photodecomposition of CF_3Br is also described by the following simple reaction scheme:

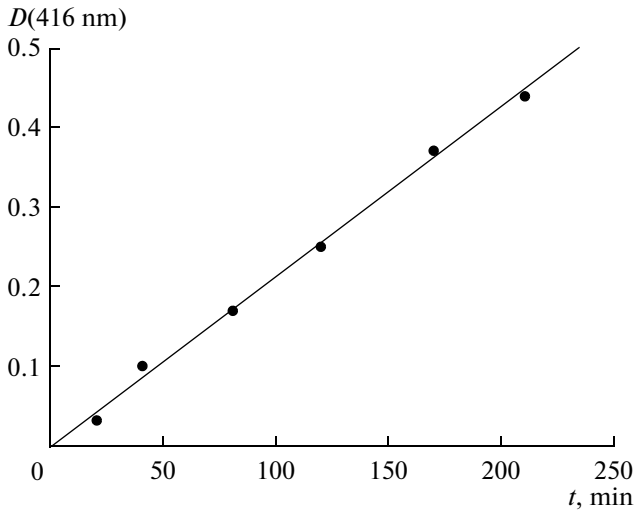

Fig. 6. Dependence of absorbance at λ = 416 nm on irradiation time for a mixture containing CF_3Br (207 Torr) and oxygen (15 Torr).

$$\begin{aligned}
&(1)\ CF_3Br + h\nu \longrightarrow CF_3^{\bullet} + Br,\\
&(2)\ CF_3^{\bullet} + O_2 \longrightarrow CF_3O_2,\\
&(3)\ Br + Br + M \longrightarrow Br_2 + M,\\
&(4)\ Br + \text{wall} \longrightarrow 1/2Br_2.
\end{aligned} \qquad \text{(III)}$$

The rate of formation of molecular bromine is related to the photodissociation cross section σ_d by the equation

$$w_{Br_2} = 1/2\,\sigma_d I[CF_3Br]. \qquad (7)$$

The absorption cross section for CF_3Br at λ = 253.7 nm was taken from [7].

The quantum yield of CF_3Br calculated from Eq. (6) was found to be

$$\varphi = 0.9 \pm 0.15.$$

The found quantum yield of CF_3Br is consistent with a decrease in the quantum yield with wavelength, which was observed by Talukdar et al. [18], who found the quantum yields of 1.12 ± 0.16 and 0.92 ± 0.15 upon the irradiation of CF_3Br at λ = 193 and 222 nm, respectively.

Thus, in this work, we obtained the following results:

(1) We determined the absorption cross section of molecular bromine at λ = 416 nm and a temperature of 295 K. It was 6.3×10^{-19} cm^2, which is consistent with published data [12].

(2) We determined the quantum yield of the photodecomposition of trifluorobromomethane at λ = 253.7 nm and proposed a kinetic scheme for its photodecomposition.

(3) We determined the quantum yield of the photodecomposition of tetrafluorodibromoethane at λ = 253.7 nm and also proposed a kinetic scheme for its photodecomposition.

(4) We were the first to directly determine experimentally the ratio between constants k_5/k_4 for tetrafluorodibromoethane, that is, the ratio between the rate constants k_5 and k_4 of the reactions of the C_2F_4Br radical with bromine and oxygen, respectively. This ratio was found to be 0.47.

REFERENCES

1. Gillotay, D., Simon, P., and Dierickx, L., *Aeronomica Acta A*, 1988, vol. 335, p. 1.
2. Burkholder, J.B., Wilson, R.R., Gierczak, T., Talukdar, R.K., McKeen, S.A., Orlando, J.J., Vaghjiani, G.L., and Ravishankara, A.R., *J. Geophys. Res.*, 1991, vol. 96, p. 5925.
3. *Montreal Protocol on Substances that Deplete the Ozone Layer: 2006 Assessment Report of the Halons Technical Options Committee*, Nairobi, 2006.
4. Schauffler, M., Atlas, E.L., Blake, D.R., Flocke, F., Lueb, R.A., Lee-Taylor, J.M., Stroud, V., and Travnicek, W., *J. Geophys. Res.*, 1999, vol. 104, p. 21513.
5. Wuebbles, D.J., *J. Geophys. Res.*, 1983, vol. 88, p. 1433.
6. Chang, J.S. and Duewer, W.H., *Ann. Rev. Phys. Chem.*, 1979, vol. 30, p. 443.
7. Daniel, J.S., Solomon, S., Portmann, R.W., and Garcia, R.R., *J. Geophys. Res.*, 1999, vol. 104, p. 23871.
8. Solomon, S., Mills, M., Heidt, L.E., Pollock, W.H., and Tuck, A.F., *J. Geophys. Res.*, 1992, vol. 97, p. 825.
9. Daniel, J.S., Solomon, S., and Albritton, D.L., *J. Geophys. Res.*, 1995, vol. 100, p. 1271.
10. Platt, U. and Honniger, G., *Chemosphere*, 2003, vol. 52, p. 325.
11. Sander, S.P., Kurilo, L.M., Orkin, V.L., Golden, D.M., Huie, R.E., Finlayson-Pitts, B.J., Kolb, C.T., Molina, M.J., Friedl, R.R., Ravishankara, A.R., and Moortgat, G.K., *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation no. 15*, Pasadena, Calif.: NASA Jet Propulsion Laboratory, California Institute of Technology, 2006.
12. Forster, P., Ramaswamy, V., Artaxo, P., Berntsen, T., Betts, R., Fahey, D.W.., Haywood, J., and Lean, J., *Climate Change*, Cambridge: Cambridge Univ. Press, 2007, ch. 2.
13. Vagin, N.P., Zolotarev, V.A., Kryukov, P.G., Pazyuk, V.S., Podmar'kov, Yu.P., Frolov, M.P., and Yuryshev, N.N., *Sov. J. Quantum Electron.*, 1991, vol. 21, p. 28.
14. Caralp, F., Lesclaux, R., and Dognon, A.M., *Chem. Phys. Lett.*, 1986, vol. 129, p. 433.
15. Orkin, V.L. and Kasimovskaya, E.E., *J. Atmos. Chem.*, 1995, vol. 21, p. 1.
16. Zou, P., McGivern, W.S., Sokhabi, O., Suits, A.G., and North, S.W., *J. Chem. Phys.*, 2000, vol. 113, p. 7149.
17. Molina, L.T., Molina, M.J., and Rowland, F.S., *J. Phys. Chem.*, 1982, vol. 86, p. 2672.
18. Talukdar, R.K., Vashjiani, G.L., and Ravishankara, A.R., *J. Chem. Phys.*, 1992, vol. 96, p. 8194.