Gasphase hydrolysis of SOF2 and SOF4

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Gas-phase hydrolysis of SOF_2 and SOF_4

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The rates for gas-phase hydrolysis of SOF_2 (thionylfluoride) and SOF_4 (thionyl tetrafluoride) have been measured at a temperature of 298 K. The second order rate constant for SOF_2 hydrolysis in SF_6 buffer gas was found to have the value $(1.2 \pm 0.3) \times 10^{-23}$ cm^3/s which agrees with previous estimates of Sauers *et al.*, but is three orders of magnitude lower than the value obtained by Rüegsegger *et al.* at 340 K. The rate constant for SOF_4 hydrolysis has not previously been measured and its value in both SF_6 and N_2 buffer gases was found here to be $(1.0 \pm 0.3) \times 10^{-21}$ cm^3/s.

I. INTRODUCTION

The oxyfluorides SOF_2 (thionylfluoride) and SOF_4 (thionyl tetrafluoride) are known[1-3] to hydrolyze according to the reactions:

$$SOF_2 + H_2O \xrightarrow{k_1} SO_2 + 2HF, \quad \Delta H^{\circ}_{298} = +54 \text{ kJ/mol} \tag{1}$$

and

$$SOF_4 + H_2O \xrightarrow{k_2} SO_2F_2 + 2HF, \quad \Delta H^{\circ}_{298} = -2 \text{ kJ/mol.} \tag{2}$$

The indicated reaction enthalpies that apply at 298 K were estimated from available thermochemical data.[4-6] The hydrolysis rate for SOF_2 is known to be relatively slow compared to that of other thionylhalogens,[1] and this can be expected on the basis of its endothermicity.[5] Because hydrolysis of SOF_4 appears to be only slightly exothermic, the rate for reaction (2) might also be relatively slow.

Rüegsegger *et al.*[7] have recently reported a gas-phase rate constant for reaction (1) of $(4.0 \pm 1.5) \times 10^{-20}$ cm^3/s at 340 K. This rate is about two to three orders of magnitude greater than the rate estimated by Sauers *et al.*[8] at a comparable temperature, and is also greater than that expected from measurements of oxyfluoride and SO_2 yields from electrical discharges in SF_6 reported by Van Brunt[9] and Latour-Slowikowska *et al.*[10] There has been no previously reported information on the SOF_4 gas-phase hydrolysis rate k_2.

The species SOF_2, SOF_4, SO_2F_2, SO_2, and HF are known to be the major long-lived stable gaseous by-products from decomposition of SF_6 in the presence of oxygen and water vapor.[6-15] A knowledge of the rates for reactions (1) and (2) is needed to understand the mechanisms of thermal and electrical decomposition of SF_6 and for the design of chemical diagnostics for high-voltage systems in which SF_6 serves as an insulating or dielectric medium.[16,17] In the present work, the rate constants k_1 and k_2 have been measured for SOF_2 and SOF_4 in either N_2 or SF_6 buffer gas at a total pressure of 200 kPa (~2 atm) and at a room temperature of 298 K.

II. MEASUREMENT METHOD

The measurements of hydrolysis rates were performed by preparing gas mixtures of either SOF_2 or SOF_4 with water vapor and either N_2 or SF_6 buffer gas in a 3.7 ℓ cell from which small, 0.85 ml samples were periodically extracted and injected into a gas chromatograph–mass spectrometer (GC/MS) used to determine the time dependences of the gaseous reactant and product concentrations. The method of gas mixture preparation is similar to that previously described.[9,18] Between 10–30 $\mu\ell$ of liquid H_2O were injected into the cell under vacuum followed by injection of the desired quantity of oxyfluoride gas and then introduction of the buffer gas to a total pressure of 200 kPa. The oxyfluoride and water vapor partial pressures were much less than that of the buffer gas.

The configuration and operating conditions of the chromatograph were identical to those used[9] for observing decomposition of SF_6. The chromatographic technique was similar to that employed by others[14,15] to measure oxyfluorides and SO_2 concentrations in high-pressure gases. The mass spectrometer was programmed to sequentially detect ions with mass-to-charge ratios (m/e) characteristic of the species monitored, i.e., $m/e = 18$ for H_2O, $m/e = 64$ for SO_2, $m/e = 83$ for SO_2F_2, and $m/e = 86$ for both SOF_2 and SOF_4.

The GC/MS was calibrated for quantitative measurement of SO_2, SOF_2, SO_2F_2, and SOF_4 by direct comparison with reference mixtures containing known quantities of these gases in the appropriate buffer gas which produced approximately the same GC/MS response as the unknown gas from the reaction vessel. The calibration for water vapor involved comparisons of the GC/MS response at $m/e = 18$ with the response from a reference water vapor–buffer gas mixture in which the water vapor content was determined using a precalibrated aluminum oxide hygrometer probe.[19] In preparing the water vapor containing reference sample, sufficient time was allowed to ensure equilibrium between the probe and gas within the cell. Calibrations of the GC/MS were performed immediately after each measurement of reaction rates. To within the uncertainties of measurement and

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gas sample preparation, the response of the GC/MS was found to be linearly proportional to concentration in the relevant range for all species detected.

III. RESULTS

Examples of measured concentrations vs time from which the rate constants for reactions (1) and (2) were determined are shown in Figs. 1–3. Measurements were made for different initial concentrations of H_2O and either SOF_2 or SOF_4 in the reaction vessel. Because of the relatively long times required for these measurements, the concentration of H_2O at any given time was influenced not only by the hydrolysis reaction, but also by exchange with H_2O absorbed on surfaces within the vessel. The rapid drop off in $[H_2O]$ evident in the early stages of most experiments (see Figs. 1 and 3) could also be observed under conditions where neither SOF_2 or SOF_4 were present, and is therefore attributed to absorption of water vapor on the walls.

The second order rate constants were derived from data such as shown in Figs. 1–3 by assuming that the time dependences of the observed species are governed by the following set of rate equations:

$$\frac{d[X]}{dt} = k_i [Y][H_2O], \tag{3}$$

$$\frac{d[Y]}{dt} = -k_i [Y][H_2O], \tag{4}$$

$$\frac{d[H_2O]}{dt} = -k_i [Y][H_2O] + k'\Delta[H_2O], \tag{5}$$

where $[Y]$ and $[X]$ are the reactant and product concentrations, i.e., SOF_2 or SOF_4 and SO_2 or SO_2F_2 for $i = 1$ or 2, respectively. The term $k'\Delta[H_2O]$ is included to account for absorption or evaporation of water vapor from surfaces. This rate is assumed to be proportional to the deviation, $\Delta[H_2O] = [H_2O]_e - [H_2O]$, of the water vapor concentration from equilibrium with the walls, where $[H_2O]_e$ is the normal equilibrium level. The rate factor $k_i[Y]$ in the first term on the right-hand side in Eq. (5) was sufficiently small compared to k' in the second term that decreases in water vapor concentrations due to the hydrolysis reactions were

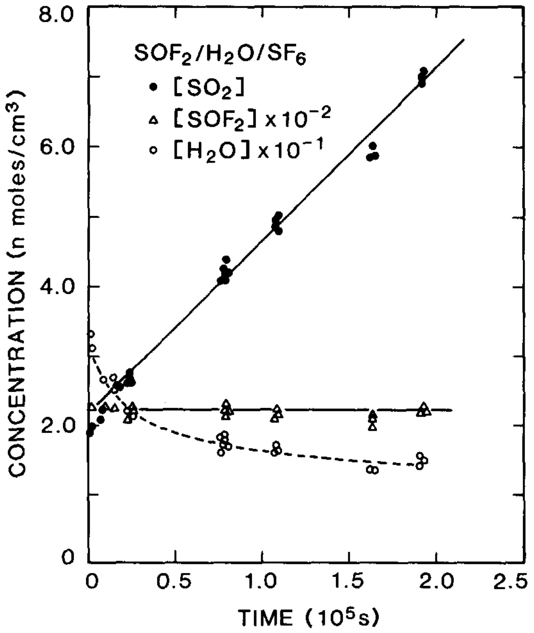

FIG. 1. Measured SO_2, SOF_2, and H_2O concentrations vs time in SF_6 buffer gas.

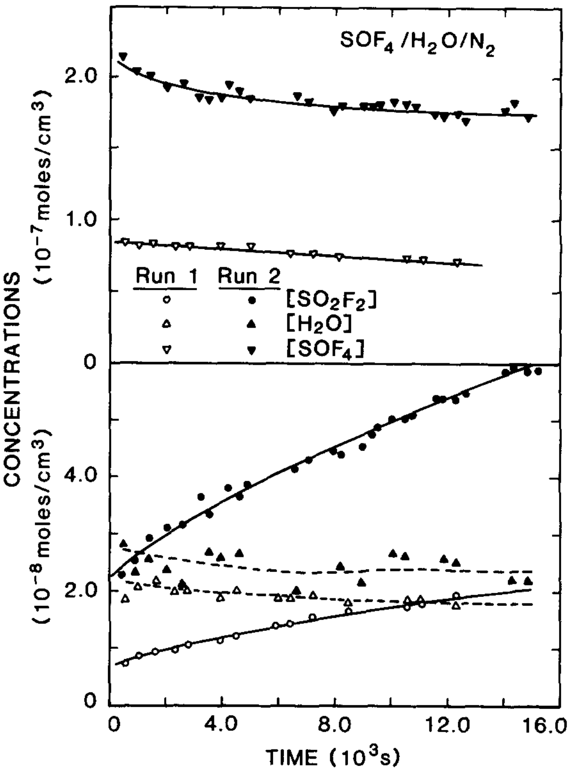

FIG. 2. Measured SO_2F_2, SOF_4, and H_2O concentrations vs time in N_2 buffer gas for two runs corresponding to different initial conditions.

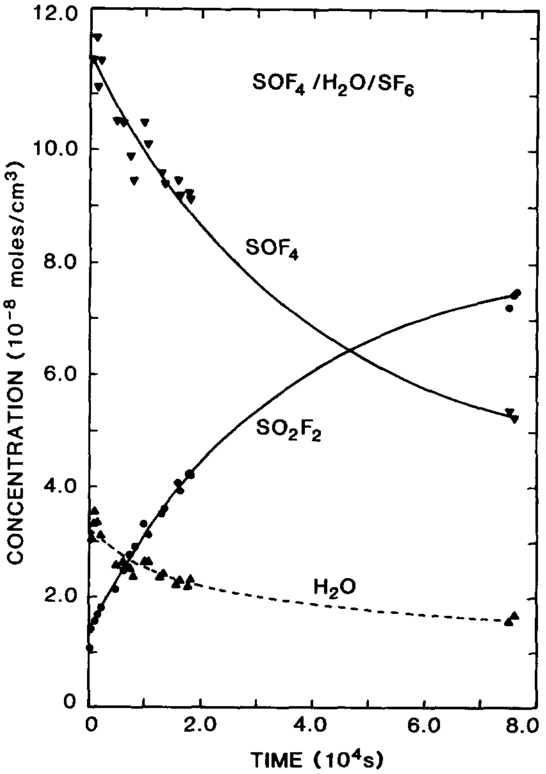

FIG. 3. Measured SO_2F_2, SOF_4, and H_2O concentrations vs time in SF_6 buffer gas.

TABLE I. Rate constants determined from data as shown in Figs. 1–3 for different buffer gases and initial water vapor and oxyfluoride concentrations.

Reactant oxyfluoride	Buffer gas	Initial concentrations $[H_2O]_0$ (mol/cm^3)	$[SOF_2]_0$ or $[SOF_4]_0$ (mol/cm^3)	Rate constant (cm^3/s)
SOF_2	SF_6	1.1×10^{-8}	1.1×10^{-7}	$k_1 = (1.4\pm0.3)\times10^{-23}$
SOF_2	SF_6	3.3×10^{-8}	2.2×10^{-7}	$k_1 = (1.2\pm0.2)\times10^{-23}$
SOF_4	SF_6	3.4×10^{-8}	1.17×10^{-7}	$k_2 = (1.06\pm0.27)\times10^{-21}$
SOF_4	N_2	2.2×10^{-8}	0.82×10^{-7}	$k_2 = (1.06\pm0.30)\times10^{-21}$
SOF_4	N_2	2.4×10^{-8}	2.11×10^{-7}	$k_2 = (0.95\pm0.28)\times10^{-21}$

not discernible. However, at the highest $[Y] = [SOF_4]$ concentration used, a condition was evidently reached under which the rate of H_2O consumption by hydrolysis was sufficient to cause noticeable fluctuations in the H_2O level (compare the two data sets shown in Fig. 2).

The rate for reaction (1) was too slow to permit observation of a statistically significant decrease in $[SOF_2]$ due to reaction (1) within the time intervals used (see Fig. 1). As can be seen from Fig. 3, the decrease in $[SOF_4]$ from reaction (2) could be observed after a sufficiently long time, and this decrease was found to agree with the corresponding increase in $[SO_2F_2]$.

The rate constants were computed using Eq. (3) and the averages of the slopes of the $[X]$-vs-time production curves. Values for the rate constants calculated in this manner from the data shown in the figures are listed in Table I. The indicated uncertainties primarily reflect the dominant source of error associated with the determination of $[H_2O]$. At any given time, the calculated rate constants k_1 and k_2 were found to be independent of $[H_2O]$ and $[SOF_2]$ (or $[SOF_4]$) to within the estimated measurement uncertainties.

IV. DISCUSSION

Based on an analysis of the results discussed above, the second-order rate constants for gas-phase hydrolysis of SOF_2 and SOF_4 are assigned the values $(1.2\pm0.3)\times10^{-23}$ and $(1.0\pm0.3)\times10^{-21}$ cm^3/s, respectively. The fact that the rate constants for these reactions were found to be independent of water vapor and oxyfluoride concentrations implies that reactions (1) and (2) are indeed second order and occur predominantly in the gas phase. Because of the relatively high gas pressure and the large volume-to-surface ratio of the reaction vessel used, it can be expected that contributions to SO_2 or SO_2F_2 production from surface reactions would be insignificant provided that the rates for these reactions do not greatly exceed the gas-phase rates. To within the measurement uncertainties, there were no indications of major contributions from surface reactions for either of the two hydrolysis processes investigated.

The relative magnitudes of the rate constants for reactions (1) and (2) are consistent with expectations based upon the known heats of reaction, i.e.,

$$k_1 < k_2 \ll k_c,$$

where k_c corresponds to the reactant bimolecular collision rate in the gas. The rate constant k_1 was previously estimated by Sauers[8] *et al.* to be about three to four orders of magnitude lower than their measured rate of $(0.9 \text{ to } 2.6)\times10^{-19}$ cm^3/s for hydrolysis of SF_4. As noted above, Rüegsegger *et al.*[7] have reported a value of $(4.0\pm1.5)\times10^{-20}$ cm^3/s for k_1, which differs significantly from the value obtained here and the estimates by Sauers *et al.*[8] In both of these earlier works, the hydrolysis rate for SOF_2 was determined indirectly from mass spectrometric observations of SO_2 formation during hydrolysis of SF_4 at relatively low pressures from which the hydrolyzable SOF_2 is produced by the reaction

$$SF_4 + H_2O \xrightarrow{k_3} SOF_2 + 2HF, \quad \Delta H^\circ_{298} = -84 \text{ kJ/mol.} \tag{6}$$

Rüegsegger *et al.*[7] obtained a value of $k_3 = (2.0\pm0.6)\times10^{-19}$ cm^3/s which agrees favorably with the above indicated value from the work of Sauers *et al.*[8] Because reaction

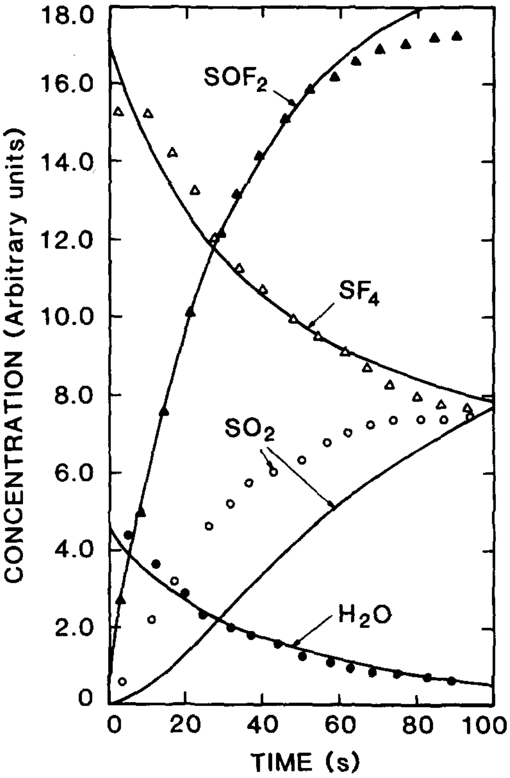

FIG. 4. Computer simulation of the mass spectral data from Ref. (7) for hydrolysis of SF_4 as indicated by the solid lines. The symbols ▲,△,○,●, correspond, respectively, to the data from Ref. (7) for SOF_2, SF_4, SO_2, and H_2O. The simulation was performed using the computer code described in Ref. (20) with the assumptions given in the text.

(6) is much more energetically favorable than reaction (1), it should be expected that $k_3 \gg k_1$.

In order to reconcile the large discrepancy between the present value for k_1 and that reported by Rüegsegger *et al.*,[7] an attempt was made to reanalyze the mass spectral data given in this earlier work from which the rate constants k_1 and k_3 were apparently derived. This analysis was performed using a chemical kinetics computer code developed by Brown.[20] It was assumed that only the gas-phase reactions (1) and (6) occur isothermally in a fixed volume initially containing only an SF_4–water vapor mixture. The rate constants k_1 and k_3 were assigned the values indicated above from the work of Rüegsegger *et al.*,[7] and the initial partial pressures of SF_4 and H_2O were adjusted to approximate the observed decreases in relative concentrations for those gases that appeared to occur during the time span of the measurement. As suggested by Herron,[21] the reactions (1) and (6) were assumed to proceed in two steps involving unstable intermediates SOFOH and SF_3OH, respectively, that undergo rapid unimolecular decomposition into $SO_2 + HF$ and $SOF_2 + HF$, respectively.

The predictions derived from this model calculation are compared with the experimental results of Rüegsegger *et al.*[7] in Fig. 4. It is obvious that although the model calculation agrees with the measured relative concentrations for SOF_2, SF_4, and H_2O, it fails to predict the observed behavior for SO_2 production. In contrast to the predicted behavior, the observed SO_2 production rate is highest at the lowest SOF_2 concentration. This trend is clearly inconsistent with the assumption that SO_2 is formed only by reactions (1) and (6). The present analysis suggests that the observed SO_2 production in the experiments of Rüegsegger *et al.* was predominately from mechanisms other than reaction (1). It is conceivable that SO_2 can be formed directly from SF_4 by a reaction mechanism on a surface where the effective density of H_2O approaches that in the liquid phase. There is evidence[8,22] that hydrolysis of SF_4 in liquid H_2O need not involve SOF_2 as an intermediate. Although the behavior of SO_2 production exhibited in Fig. 4 suggests direct formation from SF_4, more information is needed to confirm this possibility.

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