of 6, within experimental error, for all three metal ions as seen from some typical results in Table I. The majority of the Ga^{3+} and In^{3+} C_{TMP} determinations were made at 0 and −30°, respectively as broadening of the doublet components consistent with an increase in the rate of solvent exchange was observed at higher temperatures. Exchange broadening of the doublet signals from the Al^{3+}–TMP system was not marked at 35°. In acetone–TMP solvent the C_{TMP} remained close to 6 for the three metal ions, and no coordinated acetone signal was observed, which is consistent with acetone acting solely as an inert diluent as has been observed in acetone–water solvent.[11] This is an important observation as it was found that the use of acetone as a diluent for the TMP–water system first increased the miscibility of the solvents and second reduced the rate of proton exchange between coordinated and bulk water[11] thereby facilitating the observation of well-resolved coordinated and bulk water signals for the Al^{3+} and Ga^{3+} systems.

The data for a number of solutions, in which the mole ratios metal ion:TMP:water:acetone were varied, are listed in Table I. The total coordination number ($C_{TMP} + C_{H_2O}$) for both Al^{3+} and Ga^{3+} is seen to remain close to 6. The spectra were recorded at temperatures at which the best signal resolution was obtained, the upper temperature limit being determined by exchange broadening and the lower by viscosity broadening. A trend in which water competes more favorably than TMP for sites in the first coordination sphere is seen in both the Al^{3+} and Ga^{3+} data. Steric hindrance probably reduces the ability of TMP to compete with water as has been observed for other bulky solvent molecules.[12]

A spectrum of a solution of Al^{3+} in TMP–water–acetone solvent is shown in Figure 2. The coordinated water signal has a multiplet character which is consistent with the superimposition of several singlets exhibiting different chemical shifts. Similarly the coordinated TMP signal consists of superimposed doublets. This spectrum suggests the existence of several species in equilibrium, possessing the formula $[Al(TMP)_{6-n}(H_2O)_n]^{3+}$, where n may vary from zero to 6, but it is not practicable to assign the various coordinated water and TMP signals to specific species at this time. In some cases the coordinated signals, although broadened, did not exhibit a multiplet character, as indicated in Table I. At −80°, the lowest temperature studied, coalescence of coordinated and bulk TMP signals and coordinated and bulk water signals, consistent with rapid solvent exchange induced relaxation, precluded a determination of the composition of the first solvation sphere of In^{3+}.

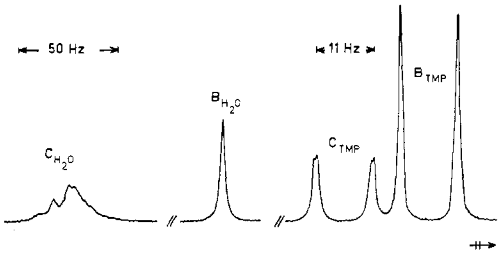

Figure 2.—Pmr spectrum of $Al(ClO_4)_3$ in TMP–H_2O–acetone solvent at −10°. Coordinated TMP and H_2O and bulk TMP and H_2O signals are labeled C_{TMP}, C_{H_2O}, B_{TMP}, and B_{H_2O}, respectively. Both H_2O signals were recorded at the same sweep width and at a gain 5 times that at which the TMP signals were recorded. The TMP signals were recorded over a smaller sweep width than were the H_2O signals. The acetone signal is not shown. The Al:TMP:H_2O:acetone mole ratios were 1.00:6.00:5.60:30.5.

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Contribution from the Department of Chemistry,
University of Washington, Seattle, Washington 98195

Kinetics of Hydrolysis of Oxygen Difluoride

By Sudhindra N. Misra and George H. Cady*

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The basic hydrolysis of oxygen difluoride has previously been studied, but under such conditions that the rate-controlling step was the rate of dissolving of the gas rather than the rate of hydrolysis when in solution.[1] In the present study, the rate of disappearance of dissolved OF_2 was measured. Substantially no gaseous phase was present in the system. The total reaction was

$$OF_2 + 2OH^- = O_2 + 2F^- + H_2O \qquad (1)$$

Oxygen difluoride does not behave as the anhydride of an acid. It has only a low solubility in water[2] or even in cold 40% KOH.[3] None of its reactions are known to produce the recently discovered molecule HOF.[4]

Experimental Section

Oxygen difluoride used in this study was a commercial product obtained from the Allied Chemical Co. When a sample of that gas was taken directly from the cylinder, its infrared spectrum showed no evidence for impurities. Fractional codistillation of a sample also gave indication of the presence of only one substance. In spite of this evidence for purity, the gas, before use in studies of its hydrolysis, was bubbled through 0.1 M NaOH to remove SiF_4 and other acidic gases which might have been present. The base would have caused the introduction of some oxygen into the OF_2. This oxygen impurity should not have been harmful. Before making a run, a solution of OF_2 was prepared by shaking a sample of the gas with water held in a 2-l. flask.

Apparatus.—The reactor was a vessel of polypropylene having a volume of 1245 ml. The vessel was 18 cm in diameter and had a tight but removable lid equipped with polypropylene fittings to hold the following items: (1) a fluoride ion sensitive electrode made by Orion Research, Inc., Model 94-09, (2) a reference electrode for use with the fluoride electrode, (3) and (4) a glass electrode and reference electrode for use in measuring pH, (5) a thermometer. A Teflon-covered magnetic stir bar was placed in the vessel and was rotated during a run by a magnetic stirrer placed under the thermostat bath. Measurement of pH was made with a Leeds and Northrup 7400 A2 series meter. The

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emf of the cell involving the F^--sensitive electrode was measured with an Orion Research Specific Ion Meter, Model 401.

Procedure.—A measured amount of solution of OF_2 was transferred to the reactor. Other reagents as desired were also added, and the reactor, before use in a run, was caused to be completely filled with solution and closed with a loosely fitting plug. The vessel was placed in water held at constant temperature to within 0.1°. After the solution reached constant temperature, readings were made from time to time of the pH and F^- concentration. Many runs were made in buffered solutions containing sodium carbonate, sodium bicarbonate, and enough sodium nitrate to give a total ionic strength of 0.25 *M*. In other runs the solution was made alkaline with sodium hydroxide, and the pH was allowed to change as the reaction occurred. A comparison of rate constants obtained by the two methods indicates that the presence of ions other than OH^- in the buffered solutions had little or no influence upon the rate of hydrolysis of OF_2. Some of the runs were made with solutions more alkaline than pH 11. Since the fluoride-sensitive electrode could not be used in this range, the concentration of dissolved OF_2 was measured by withdrawing a 25-ml sample of solution and adding it to a solution of potassium iodide. After adding dilute sulfuric acid in excess, the iodine was titrated with sodium thiosulfate solution. To keep the reactor filled so that OF_2 would not escape from solution, glass beads were added immediately after removal of the sample of solution. In runs involving use of the fluoride ion sensitive electrode the concentration of OF_2 was not observed directly. Along the course of a run, the concentration of F^- ion was measured at intervals. At the termination of a run the solution was allowed to stand until substantially all of the OF_2 had reacted. The molar concentration of dissolved OF_2 at any stage of the run could then be calculated by considering it to be half as great as the increase in molarity of F^- from that time until all of the gas had reacted.

During the course of the work the pH meter was tested frequently with buffer solutions. The fluoride-sensitive electrode was also checked frequently using solutions containing F^- of known molarity, pH, and ionic strength. Because of this method of calibration, the electrode as used gave F^- concentrations in moles per liter. From readings of the pH meter, the corresponding activities of OH^- in moles per liter were calculated. The fluoride ion sensitive electrode behaved in the manner reported by the manufacturer toward F^- concentration and influence of ionic strength. Because of interference by OH^- ion, the electrode was not used at pH in excess of 11.

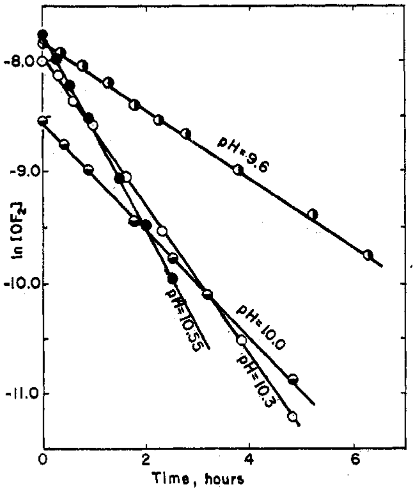

Figure 1.—Rate of hydrolysis at 20.0° in buffered solutions.

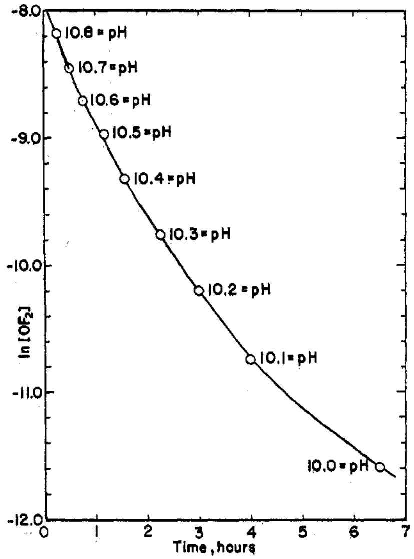

Figure 2.—Rate of hydrolysis of OF_2 in a solution of sodium hydroxide at 20.0°. Concentrations of OF_2 and OH^- decreased as time passed.

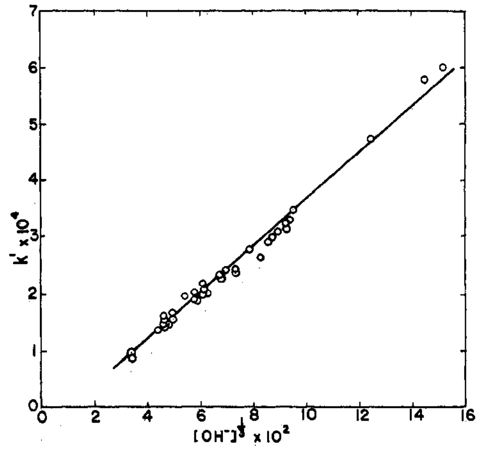

Figure 3.—Relationship between k' and $[OH^-]^{1/3}$ at 20.0°.

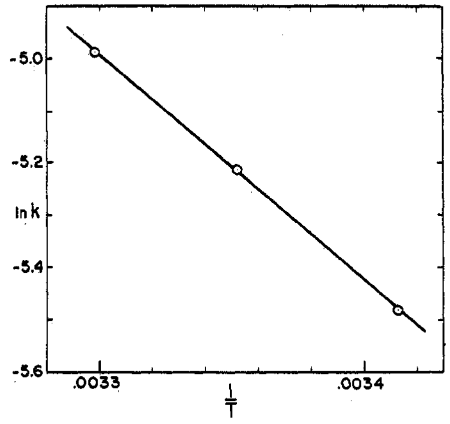

Figure 4.—Relationship between ln k and $1/T$ where k is the rate constant in the equation $d[OF_2]/dt = -k[OF_2]\{[OH^-]^{1/3} - 0.0105\}$.

Results

Observed data are represented within the limits of experimental accuracy in Figures 1–4. Figure 1 represents four runs at 20.0° using solutions buffered at different values of pH. These runs together with others not shown indicate that at constant pH and temperature the rate is directly proportional to the concentration of OF_2. Figure 2 represents a run at 20.0° in which OF_2 reacted with a solution of sodium hydroxide while the pH was allowed to change as hydrolysis occurred. From the shape of the curve it is apparent that a decrease in the concentration of OH^- ions causes a decrease in the rate of reaction. If one draws a tangent to the curve at a selected value of pH, the slope is the same (within experimental accuracy) as a straight line in Figure 1 for the same pH. Numerous runs of this type were made, some at pH values greater than 11. At constant pH, the rate follows the equation $d[OF_2]/dt = -k'[OF_2]$.

To evaluate k' as a function of $[OH^-]$, graphs were drawn in which k' was plotted *vs.* various powers of the molarity of OH^-. Figure 3 shows that at 20° in the pH range 9.6–11.5 the value of k' is directly proportional to $\{[OH^-]^{1/3} - 0.0105\}$. The rate equation may, therefore, be written as

$$d[OF_2]/dt = -k[OF_2]\{[OH^-]^{1/3} - 0.0105\}$$

In the evaluation of k' and k, time was measured in seconds. The straight line in Figure 3 corresponds to k having a numerical value at 20° of 4.1×10^{-3} when time is in seconds and concentrations are in moles per liter.

The three highest points in Figure 3 were obtained using iodometric titration of dissolved OF_2 as it was reacting with a solution of NaOH. The other points were obtained using the fluoride ion sensitive electrode as the dissolved OF_2 reacted either with a solution of NaOH or with a buffered solution containing Na_2CO_3, $NaHCO_3$, and $NaNO_3$. Most of these points were obtained for buffered solutions.

Runs were made using buffered solutions at pH 10.0 at 25.0 and 30.0°. From these runs, values of k were calculated. Figure 4 shows the relationship between ln k and the reciprocal of absolute temperature. The slope of the line in this figure corresponds to an energy of activation of 8.5 kcal/mol.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WASHINGTON, SEATTLE, WASHINGTON 98195

Synthesis and Characterization of Oxotetrakis(fluorosulfato)tungsten(VI)

BY RAJENDAR DEV AND GEORGE H. CADY*

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Peroxydisulfuryl difluoride is known to react with molybdenum hexacarbonyl to give dioxobis(fluorosulfato)molybdenum(VI).[1] The transition metal chlorides and oxychlorides, niobium pentachloride,[2] tantalum pentachloride,[2] vanadyl chloride,[2] and chromyl chloride[3] give the corresponding oxyfluorosulfates with peroxydisulfuryl difluoride. Tungsten hexacarbonyl, tungsten oxytetrachloride, and tungsten hexachloride have been found to react with peroxydisulfuryl difluoride to form the new compound oxotetrakis(fluorosulfato)tungsten(VI).

Experimental Section

Materials.—Peroxydisulfuryl difluoride was prepared by the reaction of fluorine with sulfur trioxide[4] and purified by prolonged pumping of the crude product held at −78°. Infrared analysis and vapor density measurements indicated that the product was substantially pure.

Tungsten hexachloride and oxytetrachloride were used as received from Alfa Inorganics Inc. Tungsten hexacarbonyl was purified by sublimation before use. The materials were handled in a drybox in an atmosphere of dry nitrogen.

Reaction of Peroxydisulfuryl Difluoride with Tungsten Hexacarbonyl.—A 0.2548-g (0.72-mmol) sample of resublimed tungsten hexacarbonyl was placed in a glass reaction vessel. Peroxydisulfuryl difluoride, 2.783 g (14.06 mmol), was condensed at the surface of the $W(CO)_6$, while the vessel was held at −183°. The reaction vessel was then kept at −78° for a time and was later allowed to come slowly to room temperature while held behind a safety shield. On one occasion when the vessel was warmed rapidly, an explosion occurred. The volatile products were separated by codistillation[5] and identified by their infrared spectra. Carbon dioxide, pyrosulfuryl fluoride, and peroxydisulfuryl difluoride and a trace of silicon tetrafluoride were present. The nonvolatile product, a colorless viscous liquid, was pumped to a constant weight, 0.4362 g. The theoretical weight for $WO(SO_3F)_4$ was 0.4314 g. The nature of the volatile by-products, the weight of the compound, and the elemental analysis all indicated the formation of oxotetrakis(fluorosulfato)tungsten(VI), $WO(SO_3F)_4$, by the reaction.

Reaction of Peroxydisulfuryl Difluoride with Tungsten Oxytetrachloride.—Tungsten oxytetrachloride, 0.2337 g (0.638 mmol), was placed in a glass reaction vessel. An excess of peroxydisulfuryl difluoride was distilled into the reaction vessel at −183°. The reactants were allowed to warm slowly. A greenish yellow gas, presumably Cl_2, was formed, but the color disappeared as the vessel stood. After standing for some time, the products were pumped away at room temperature until the remaining nonvolatile colorless viscous liquid reached a constant weight of 0.3998 g. This was close to the weight (0.4072 g) theoretically expected for $WO(SO_3F)_4$.

Reaction of Peroxydisulfuryl Difluoride with Tungsten Hexachloride.—Tungsten hexachloride, 0.1648 g (0.415 mmol), was placed in a glass vessel. Peroxydisulfuryl difluoride, 1.524 g (7.80 mmol), was distilled into the vessel at −183°. The reactants were allowed to warm slowly as described earlier. A greenish yellow gas (probably chlorine) was observed, but the color slowly vanished, presumably due to conversion of chlorine to chlorine fluorosulfate. The colorless, nonvolatile viscous liquid was pumped to a constant weight of 0.243 g corresponding to $WO(SO_3F)_4$; theoretical weight 0.2474 g.

The volatile products from the above reaction were transferred into an nmr tube containing a sealed capillary filled with CCl_3F. The ^{19}F nmr spectrum at 56.4 MHz was determined using a Varian HA-60 high-resolution spectrometer. The peaks obtained at chemial shifts with respect to CCl_3F, in ppm, of −34.3, −39.2, and −47.2, correspond to the following substances: (a) chlorine fluorosulfate, reported shift −33.9,[6] (b) peroxydisulfuryl difluoride, reported shift −40.4,[7] and (c) pyrosulfuryl fluoride, reported shift −48.5.[7] Thus, the reaction of WCl_6 with $S_2O_6F_2$ in excess produced $WO(SO_3F)_4$, $S_2O_5F_2$, and $ClSO_3F$.

Analysis of Oxotetrakis(fluorosulfato)tungsten(VI).—A known weight of the compound, obtained by the reaction of tungsten hexachloride and peroxydisulfuryl difluoride, was hydrolyzed in 10% sodium hydroxide solution at ∼100° for about 40 hr. A test for Cl^- was negative in the hydrolysate. The solution was made acidic. The yellow tungstic acid which precipitated was removed by filtration (the filtrate was used for the determination of sulfur and fluorine) and was dissolved in 5% sodium hydroxide solution. The pH of this solution was then adjusted to around 7–8, and tungsten was determined by precipitation as barium tungstate. Sulfur was determined as barium sulfate, while fluorine was determined by titration with 0.1 *N* $Th(NO_3)_4$ solution using a fluoride ion selective electrode. *Anal.* Calcd for $WO(SO_3F)_4$: W, 30.85; S, 21.47; F, 12.75. Found: W, 30.33; S, 21.30; F, 12.23. The analysis of the other two samples of $WO(SO_3F)_4$ gave similar results.

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