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

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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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Results and Discussion

Vibrational Spectra of Oxotetrakis(fluorosulfato)-tungsten(VI).—To obtain the Raman spectrum of the compound, a sample was prepared in a tube (12-mm o.d.) and sealed. A Spex 1401 double spectrometer equipped with a Model 52 argon–krypton ion laser was used. The prominent vibrational peaks are tabulated in Table I. Satisfactory infrared spectra were not obtained, because of the reaction of $WO(SO_3F)_4$ with the cell windows or the mulling agents.

TABLE I

VIBRATIONAL SPECTRA OF OXOTETRAKIS(FLUOROSULFATO)TUNGSTEN(VI)

Bands, cm^{-1}	Assignment (tentative)	Bands, cm^{-1}	Assignment (tentative)
1464	SO_2 asym str	644	SO_3 sym str
1416			
		552	SO_2 bend (bridging SO_3F)
1240	SO_2 sym str		
1163	SO_2 asym str (bridging SO_3F)	455	S—F wag
1044		421	S—F def
964	W=O str		
944		280	W—O str
		273	
873	S—F str	214	
853			
826		184	W—O bend modes
801		154	
707	SO_3 asym bend (bridging SO_3F)	141	
700			

The viscous nature of the compound and the large number of Raman bands, all of which were polarized, indicated the polymeric nature of the compound. Polymerization can be thought to occur *via* bridging fluorosulfate groups, as shown in Figure 1.

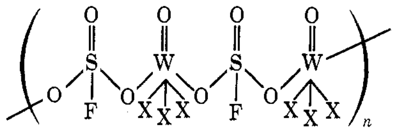

Figure 1.—Structure of oxotetrakis(fluorosulfato)tungsten(VI) ($X = OSO_2F$).

The SO_3F^- ion has C_{3v} symmetry. Covalent unidentate and bidentate fluorosulfate groups are both expected to have C_s symmetry.[8] For the fluorosulfate ion,[9] the symmetric SO_2 stretching mode is found at 1080 cm^{-1}, and the doubly degenerate antisymmetric stretching mode, at 1290 cm^{-1}. The vibrational frequencies given in Table I rule out the possibility of the SO_3F^- ion. The SF stretching frequencies around 800–873 cm^{-1} may be due to the fluorosulfate groups in different environments. The W=O stretching frequency has been reported at ~960 cm^{-1} in some of the complexes of tungsten oxyhalides with phosphine oxide.[10] We therefore, assign the vibrational band around 944 and 964 cm^{-1} to be due to W=O stretching motion.

^{19}F Nmr Spectrum of Oxotetrakis(fluorosulfato)-tungsten(VI).—The polymeric structure *via* bridging fluorosulfate groups is further supported by the ^{19}F nmr spectrum of the compound. A sample of $WO(SO_3F)_4$ was prepared in an nmr tube having a capillary containing CCl_3F. The compound was dissolved in $S_2O_6F_2$. Its spectra at room temperature and at −45° were much alike. In a polymeric chain (Figure 1), the bridging fluorosulfate groups may either be cis or trans to each other, as has been argued for the compound $SbF_4(SO_3F)$.[11] A peak observed at a chemical shift −42.4 ppm with respect to CCl_3F may be attributed to the terminal fluorosulfate groups, while the peaks at chemical shifts −41.9, −41.6, and −41.1 ppm with respect to CCl_3F may be attributed to the bridging fluorosulfate groups, which can be in different environments, *i.e.*, cis–cis, trans–trans, or cis–trans with respect to the neighboring fluorosulfate groups. It is also possible that cyclic polymers may exist.

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Tetra-*n*-butylammonium Salts of $B_5H_8^-$ and $B_6H_9^-$ and Decomposition Products of the Anions

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The deprotonation of pentaborane(9)[1-3] and hexaborane(10)[3,4] has been established and the physical properties and thermal stabilities of the alkali metal salts have been reported.[3] In our studies of the $B_5H_8^-$ and $B_6H_9^-$ anions, we have found that the tetra-*n*-butylammonium salts are thermally more stable than their alkali metal counterparts. Furthermore they are readily soluble in nonbasic solvents such as methylene chloride, while the alkali metal salts are insoluble. In view of the possible advantages afforded by tetra-*n*-butylammonium salts, we report herein metathesis reactions for the preparation of $(n\text{-}C_4H_9)_4NB_5H_8$ and $(n\text{-}C_4H_9)_4NB_6H_9$ and the thermal decomposition products of these anions. We also wish to report that the previously claimed $(CH_3)_4N\text{-}i\text{-}B_5H_8$[2,3] was in fact a mixture of decomposition products of $(CH_3)_4NB_5H_8$.

Results and Discussion

Metathesis Reactions.—Tetra-*n*-butylammonium salts of $B_5H_8^-$ and $B_6H_9^-$ were prepared by means of

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