negative. For the values of Santry and Segal,[26] negative R is obtained only for the S–S–H angle = 108°. Already for the S–S–H angle of 100°, R is positive for all ϕ between 0° and 180°, in disagreement with experiment. In summary, those parametrizations which lead to agreement with experiment for ϕ = 60° give results basically similar to those obtained from the Bergson model.

It is possible that an improvement of the calculations such as inclusion of d orbitals with their complicated nodal properties into our basis set would make the changes of the calculated rotatory strength with the dihedral angle less simple. However, it is unlikely that it could change the basic results: (i) the transition into the lowest excited state of disulfides is inherently optically active, but for dihedral angles close to 90°, the inherent activities of two such transitions, which both contribute to the observed first band in the uv or CD spectra, nearly cancel so that environmental effects dominate; (ii) for dihedral angles sufficiently larger than 90°, the first uv band would again become strongly inherently active and the left-handed helix would give positive rotatory strength.

Acknowledgment. The authors are indebted to Dr. Göran Claeson, A. B. Bofors, Nobel-Pharma, Mölndal, Sweden, and Dr. Albert Moscowitz, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota, for valuable discussions.

Conductometric Pulse Radiolysis of Sulfur Hexafluoride in Aqueous Solutions. Rate of Hydrolysis of Sulfur Tetrafluoride[1]

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Abstract: Changes in the conductivity of pulse-irradiated aqueous solutions saturated with SF_6 (*ca.* 2×10^{-4} *M*) have been observed as a function of time. In neutral solutions the conductivity increases in two steps. The fast first step is attributed to the reactions $e_{aq}^- + SF_6 \rightarrow \cdot SF_5 + F^-$ and $\cdot SF_5 + 2H_2O \rightarrow \cdot OH + SF_4 + H_3O^+ + F^-$. A lower limit for the rate constant of the reaction of $\cdot SF_5$ with H_2O of 6.3×10^3 M^{-1} sec^{-1} could be derived. The slow second step is due to the hydrolysis of SF_4. The observed pseudo-first-order rate constant for this reaction increases linearly with hydronium and hydroxide ion concentration and can be described by $k_\psi = k_0 + k_a[H_3O^+] + k_b[OH^-]$. The rate constant k_0 for the pH-independent hydrolysis is 9.5×10^3 sec^{-1}, and k_a and k_b for the acid- and base-catalyzed hydrolyses are 8.5×10^7 M^{-1} sec^{-1} and 7.0×10^9 M^{-1} sec^{-1}, respectively. Mechanisms for the hydrolysis of SF_4 are discussed.

Sulfur hexafluoride is known as an efficient electron scavenger in irradiated liquid and gaseous systems.[3–7] Recently it has been shown that the hydrated electron produced in the radiolysis of water

$$H_2O \rightsquigarrow e_{aq}^-, H_3O^+, \text{etc.} \qquad (1)$$

reacts with SF_6 according to

$$e_{aq}^- + SF_6 \xrightarrow{H_2O,\ \cdot OH} 6F^- + SO_4^{2-} + 7H_3O^+ \qquad (2)$$

and that the rate constant is equal to 1.65×10^{10} M^{-1} sec^{-1}.[6] SF_6 scavenges all hydrated electrons in γ-irradiated aqueous solutions under 6–10 atm of sulfur hexafluoride (*ca.* 10^{-3} *M*). A detailed mechanism for the overall process given in eq 2 has been proposed,[6] according to which the formation of SF_5 and the oxidation of water by SF_5 are the first two steps.

$$SF_6 + e_{aq}^- \longrightarrow \cdot SF_5 + F^- \qquad (3)$$

$$\cdot SF_5 + 2H_2O \longrightarrow \cdot OH + F^- + H_3O^+ + SF_4 \qquad (4)$$

The sulfur tetrafluoride formed in reaction 4 then hydrolyzes according to

$$SF_4 + 9H_2O \longrightarrow SO_3^{2-} + 4F^- + 6H_3O^+ \qquad (5)$$

and the sulfite subsequently is oxidized by species such as $\cdot OH$, H_2O_2, or $\cdot SF_5$.

$$SO_3^{2-} + (\cdot OH, H_2O_2, \cdot SF_5) \longrightarrow SO_4^{2-} \qquad (6)$$

Since the reaction of SF_6 with e_{aq}^- leads to charged products, conductivity measurements appeared to be a useful means for tracing the elementary processes described in reactions 3–6. A pulse radiolysis study in which changes in the conductivity of solutions containing SF_6 were recorded after a short electron pulse has, therefore, been carried out. The simultaneous observation of changes in optical absorption and conductivity has been utilized in several investigations and has been found to be a very suitable technique for studying elementary processes which involve the creation or destruction of charges.[8]

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[2] (a) Hahn–Meitner Institut für Kernforschung, Berlin, Germany; (b) Radiation Research Laboratories, Mellon Institute, Carnegie–Mellon University, Pittsburgh, Pa. 15213.

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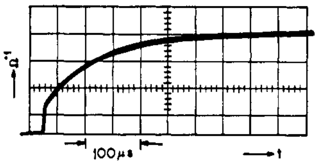

Figure 1. Conductivity change as a function of time in a pulse-irradiated 2×10^{-4} *M* aqueous SF_6 solution at pH 5.9; dose, 200 rads.

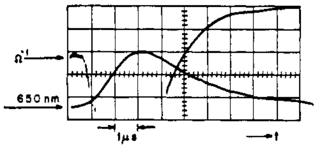

Figure 2. Changes in conductivity and absorbance at 650 nm as a function of time in a pulse-irradiated aqueous 2×10^{-5} *M* SF_6 solution at pH 6.6; dose, 400 rads; pulse length, *ca.* 1 μsec.

Experimental Section

The pulse radiolytic conductivity experiments were carried out using a 1.5-MeV Van de Graaff accelerator at the Hahn-Meitner-Institut in Berlin. The conductivity cell and associated electronic equipment has already been described.[9,10] The absorbed dose, generally *ca.* 200 rads/pulse (*ca.* 0.3 μsec/pulse, beam current: 10 mA), was monitored by a secondary emission foil. Simultaneous optical absorption and conductivity measurements of the nitrobenzene radical anion, formed by $C_6H_5NO_2 + e_{aq}^- \rightarrow C_6H_5NO_2\cdot^-$, or of the nitroform anion, formed by $C(NO_2)_4 + e_{aq}^- \rightarrow C(NO_2)_3^- + NO_2$ and $C(NO_2)_4 + \cdot H \rightarrow C(NO_2)_3^- + H^+ + NO_2$, allowed the calibration of the cell and served as a method for obtaining accurate dosimetry.[10]

The solutions were prepared from triply distilled, air-free water. SF_6 saturated solutions (*ca.* 2×10^{-4} *M*), obtained by bubbling with SF_6 for 1–2 hr, were pushed through a thermostated (18°) flow system into the irradiation cell using SF_6 gas. Solutions with lower concentrations of SF_6 were prepared by diluting a saturated solution in a gas-tight syringe (*ca.* 100 ml). Reagent grade perchloric acid and sodium hydroxide were used to adjust the pH of the solutions. The pH was monitored continuously throughout the experiments with an accuracy of ±0.05 pH unit. The background conductivity of H_3O^+ and OH^- ions limits the technique to the pH 3–10 region.

It is not possible to operate the irradiation cell at pressures greater than 1 atm; and in a solution saturated with SF_6 at 1 atm, not all of the electrons are scavenged by the solute due to the competition of H_3O^+, $\cdot OH$, H_2O, and e_{aq}^- for the hydrated electron. Appropriate corrections, therefore, have been made when necessary.

Quantitative analysis of the conductivity data are based on eq I,[10] which describes the observed voltage signal, ΔU_s, due to the conductivity change in the pulse-irradiated solution.

$$\Delta U_s = \frac{U_b R_a}{10^3 k_z} \sum_j \Delta c_j |z_j| \Lambda_j \tag{I}$$

U_b is the voltage between the electrodes, R_a (1 kΩ) is an operating resistance in series with the cell, k_z is the cell constant in cm^{-1}, z_j is the charge number, Δc_j is the molar concentration of the charged species, and Λ_j is the equivalent conductance of the charge carrier in $cm^2\ ohm^{-1}\ equiv^{-1}$. The change in conductivity, $\Sigma_j \Delta c_j |z_j| \Lambda_j$, can be expressed as $c\Delta\Lambda$, *i.e.*, the product of the concentration of the charged species produced as a result of the irradiation and the

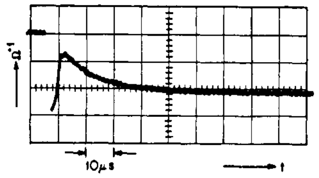

Figure 3. Conductivity change as a function of time in a pulse-irradiated 2×10^{-4} *M* aqueous SF_6 solution at pH 8.95. The signal in the first 2 μsec is distorted (see text).

total equivalent conductivity. $\Delta\Lambda$ then is given by

$$\Delta\Lambda = \frac{\Delta U_s k_z \times 10^3}{U_b R_a c} \tag{II}$$

The cell constant has been determined to $k_z = 0.65\ cm^{-1}$ and *c* can be derived from the 100-eV yields and the absorbed dose.

Results and Discussion

Interpretation of Conductivity–Time Curves. Figure 1 shows the change in conductivity as a function of time in a SF_6 saturated solution. It can be recognized that the conductivity increases in two steps. The first step occurs during the pulse, *i.e.*, is completed after *ca.* 1 μsec. This increase is followed by a first-order build-up of additional conductivity until a final value is reached after about 1 msec.

The *total change in equivalent conductivity*, $\Delta\Lambda$, as calculated from the observed ΔU_s and the known dose and $G(e_{aq}^-) = 2.76$,[6] *is* $2700 \pm 250\ cm^2\ ohm^{-1}$. *According to the stoichiometry given in eq 1 and 2* and the known specific conductances of the charged species involved ($\Lambda_{H_3O^+} = 314.5$, $\Lambda_{e_{aq}^-} = 190$, $\Lambda_{F^-} = 46.5$, and $\Lambda_{1/2SO_4^{2-}} = 68.3\ cm^2\ ohm^{-1}\ equiv^{-1}$),[8,11] a $\Delta\Lambda = 8\Lambda_{H_3O^+} + 6\Lambda_{F^-} + 2\Lambda_{1/2SO_4^{2-}} = 2900\ cm^2\ ohm^{-1}$ *is expected.* The agreement between the two values clearly suggests that the reaction mechanism given by eq 3–6 essentially is completed.

The first fast step of the curve given in Figure 1 amounts to *ca.* 25% of the overall conductivity change. This means that a total of $2H_3O^+$ and $2F^-$ ions are formed in the first increase in conductivity, *i.e.*, that both reactions 3 and 4 contribute to the initial formation of charged species. In order to study this step in more detail a dilute solution of SF_6 (2×10^{-5} *M*) was pulse irradiated, and the result is given in Figure 2. The lower curve shows the increase of the optical absorption of the hydrated electron at 650 nm during the pulse followed by a decrease, due to the reaction of e_{aq}^- with SF_6. The conductivity signal (upper curve) is strongly distorted during and immediately after (*ca.* 2 μsec) the pulse due to changes in the double layers on the electrodes and the outflow of charges from the electron beam.[10] The total increase of equivalent conductivity coinciding with the disappearance of the hydrated electron corresponds to *ca.* 430 $cm^2\ ohm^{-1}$. This is in agreement with the value calculated on the assumption that $2H_3O^+$ and $2F^-$ ions are produced in this step and taking into account that only 60–70% of the hydrated electrons are scavenged by the SF_6 at a concentration of 2×10^{-5} *M*.

From these results, therefore, it can be concluded that the oxidation of H_2O by SF_5 (eq 4) occurs very

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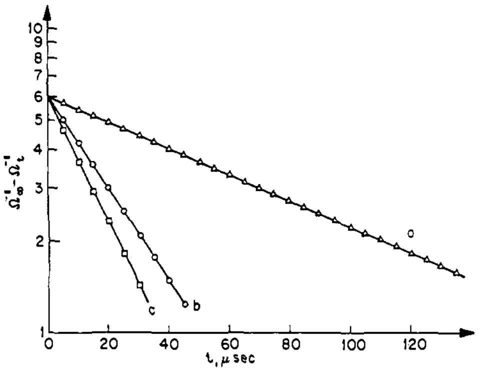

Figure 4. Plots of the normalized logarithm of the conductivity change, $|\Omega_\infty^{-1} - \Omega_t^{-1}|$, *vs.* time for the hydrolysis of SF_4: a, pH 6.0; b, pH 3.5; c, pH 8.7.

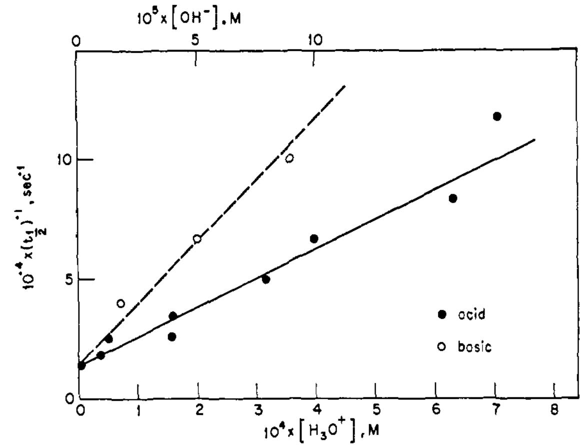

Figure 5. Plots of reciprocal half-lives for the hydrolysis of SF_4 *vs.* H_3O^+ and OH^- concentration.

fast, as has been previously suggested.[6] Since the SF_5 radical is obviously shorter lived than the electron in this experiment, *i.e.*, $t_{1/2} < 2$ μsec, an upper limit for the reaction of SF_5 with H_2O can be calculated

$$k_4 > \frac{\ln 2}{(2 \times 10^{-6})[H_2O]} = 6.3 \times 10^3\ M^{-1}\ sec^{-1}$$

Figure 3 shows the change in conductivity of a 2×10^{-4} *M* SF_6 solution at pH 8.95. The strong negative signal immediately during and after the pulse comes from the distorting effects mentioned above. Subsequently, the conductivity change is still negative and the signal further decreases to a constant value. This decrease in conductivity is observed in all basic solutions and results from the neutralization of the hydronium ions, produced in reactions 1-5, by OH^- ions. The net result, therefore, is the substitution of OH^- ions by anions such as F^- and SO_4^{2-}. Since the equivalent conductance of OH^- ($\Lambda_{OH^-} = 190$ cm^2 ohm^{-1} equiv^{-1})[11] is much larger than that of F^- and SO_4^{2-}, the total change in conductivity is negative.

Hydrolysis of SF_4. The slow change in conductivity (Figures 1 and 3) is attributed to the hydrolysis of sulfur tetrafluoride. Since $2F^-$ ions are eliminated from the SF_6 molecule in the first fast step of the reaction sequence, as discussed above, the only other possible intermediate that could be responsible for the slow conductivity change would be sulfur oxytetrafluoride, SOF_4. The formation of this species, however, would require an immediate reoxidation of the reduced sulfur. This does not seem to be the case since scavenging of the oxidizing OH radicals by 2-propanol has no affect on the overall formation of the F^- ions.

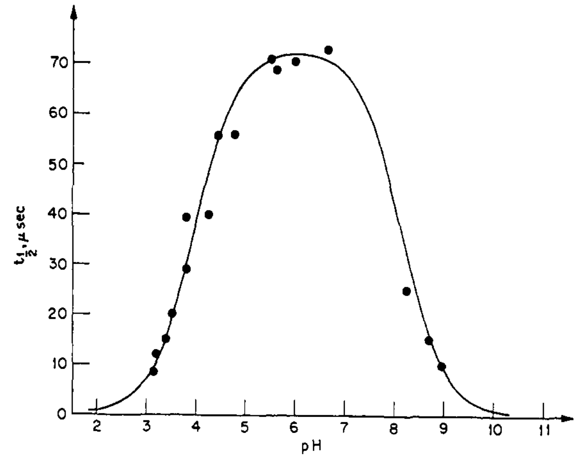

Figure 6. Plot of $t_{1/2}$ for the hydrolysis of SF_4 *vs.* pH: solid line, calculated from eq III and $t_{1/2} = \ln 2/k_\psi$; ●, experimental points.

A comparison of Figures 1 and 3 shows that the hydrolysis of SF_4 is much faster in basic than in neutral solutions. Similarly the rate of hydrolysis increases in acid solutions. In Figure 4, the change in conductivity resulting from this hydrolysis reaction is plotted on a logarithmic scale *vs.* time. Since small doses have been used, the concentration of H_3O^+ ions produced does not exceed 10^{-6} *M* and, therefore, the overall pH change during the course of the hydrolysis is negligible. Thus, the straight lines obtained for solutions of different pH indicate a first-order process. From the slopes of these lines the following rate constants were calculated: $k_\psi = 3.3 \times 10^4$ sec^{-1} at pH 3.5, 9.9×10^3 sec^{-1} at pH 6.0, and 4.6×10^4 sec^{-1} at pH 8.7. Figure 5 shows that a linear relationship exists between the concentration of H_3O^+ and OH^- ions and the reciprocal half-life of SF_4 (as measured by the time required for reaching half of the conductivity change of the slow step). From the slopes of these straight lines second-order rate constants for the acid- and base-catalyzed hydrolysis of $k_a = 8.5 \times 10^7$ and $k_b = 7.0 \times 10^9$ M^{-1} sec^{-1} were derived. The common intercept of the curves corresponds to a value of $k_0 = 9.5 \times 10^3$ sec^{-1}, which represents a pH-independent rate constant. The observed first-order rate constant for the hydrolysis of SF_4 at a given pH, then, can be expressed by

$$k_\psi = k_0 + k_a[H_3O^+] + k_b[OH^-] \qquad \text{(III)}$$

Figure 6 shows the hydrolysis profile of SF_4, *i.e.*, a plot of $t_{1/2}$ *vs.* pH. The first-order increase or decrease of the conductivity after the pulse also shows that the rate-determining step of the SF_4 hydrolysis must be the initial attack of H_3O^+, OH^-, or H_2O on SF_4. If one of the following elementary processes would be rate determining the conductivity change should exhibit a more complex time dependence.

Sulfur tetrafluoride exists as a trigonal bipyramid with a pair of electrons and two fluorine atoms in equatorial positions and can act as a Lewis acid or

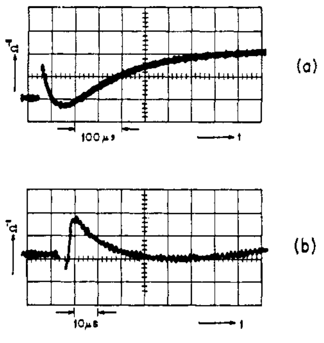

Figure 7. Conductivity change as a function of time in a pulse-irradiated 2 × 10^{-4} *M* aqueous SF_6 solution at pH 8; dose, 200 rads; (a) time scale, 50 μsec/cm; (b) time scale, 10 μsec/cm.

base.[12] Hydronium ions can therefore coordinate with the electron pair, thereby assisting sulfur–fluorine bond breaking (acid catalysis). Since the rate constant for the base-catalyzed reaction is much greater than that for the acid-catalyzed hydrolysis, the most likely reaction mechanism in basic solution is the nucleophilic attack of the hydroxide ion on the sulfur. Likewise, the relatively slow neutral hydrolysis could occur by nucleophilic attack of water on sulfur.

Combination of H_3O^+ and OH^- Ions. Figure 7 shows the change in conductivity of a solution at pH 8.0 which was irradiated with a dose that produces as many hydronium ions in the fast reactions 1 and 4 as there are OH^- ions present. Immediately after the pulse the conductivity increases due to the formation of $2H_3O^+$ and $2F^-$ per e_{aq}^- scavenged by SF_6. Then the neutralization

$$H_3O^+ + OH^- \longrightarrow 2H_2O \qquad (7)$$

leads to a decrease in conductivity. Subsequently the hydrolysis of SF_4 is responsible for the second increase. From the first half-life *ca.* $t_{1/2}$ = 7 μsec of the second-order decrease of the conductivity after the pulse and the known concentration of $[H_3O^+] = [OH^-] = 10^{-6}$ *M*, the rate constant for the neutralization reaction can be calculated as $k_7 = 1/(10^{-6} \times 7 \times 10^{-6}) = (1.4 \pm 0.3) \times 10^{11}\ M^{-1}\ sec^{-1}$, which is in good agreement with the results of other authors.[13]

Acknowledgment. It is a pleasure to acknowledge the benefit of helpful discussions with Professors A. Henglein and R. H. Schuler and Dr. E. J. Fendler.

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A Quantitative Investigation of the Ozonolysis Reaction. XII. Quantum Chemical Conformational Analysis of Primary Ozonides

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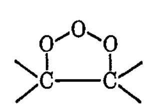
Abstract: Extended Hückel LCAO-MO calculations indicate that the half-chair conformation of the five membered 1,2,3-trioxolane ring is more stable than the envelope form. The equatorial conformation is preferred by all substituents in the primary ozonides of monosubstituted ethylenes. In the primary ozonides of *trans*-1,2-disubstituted ethylenes, the equatorial,equatorial conformation is preferred by small substituents (methyl, ethyl *n*-propyl), whereas the bulkier isopropyl and *t*-butyl groups prefer the axial,axial conformation. In the primary ozonides of *cis*-1,2-disubstituted ethylenes, the largest group prefers the equatorial conformation when both substituents are small, and the axial conformation when one of the substituents is at least as large as the *n*-propyl group. When one of the substituents is as large as the *t*-butyl group, the primary ozonide does not appear to possess a "stable" conformation.

The very unstable 1,2,3-trioxolanes (primary ozonides) I, which results from the electrophilic 1,3-dipolar cycloaddition[1] of ozone to a carbon–carbon double bond, have been the object of recent studies. Because of the great instability of the primary ozonides, any experimental study with these intermediates in the ozonolysis reaction must be performed at low temperatures (−78 to −130°).



I

Criegee and Schröder,[2] and Greenwood[3] have isolated α-diols by the treatment of ozonized solutions of olefins (−115°) in ether by an isopropyl Grignard reagent. The configurations of the α-diols obtained

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