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Preparation of an Acyl Fluoride from an O-Fluorosulfate; Some New O-Fluorosulfates

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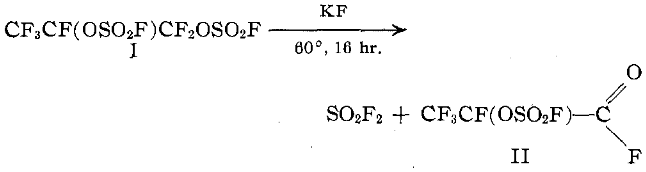
We wish to report the synthesis of tetrafluoro-2-O-fluorosulfatopropionyl fluoride (II) by a novel defluorosulfurylation reaction involving hexafluoro-1,2-bis(O-fluorosulfato)propane (I) and potassium fluoride. Compound II is the first member of a new series of compounds. The reaction proceeded quantitatively when the reactants were held at 60° for 16 hr. in a Pyrex bulb according to the equation



$$\underset{\mathrm{I}}{\mathrm{CF_3CF(OSO_2F)CF_2OSO_2F}} \xrightarrow[60^\circ,\ 16\ \mathrm{hr.}]{\mathrm{KF}} \mathrm{SO_2F_2} + \underset{\mathrm{II}}{\mathrm{CF_3CF(OSO_2F)}}\!-\!\mathrm{C}\!\begin{smallmatrix}\nearrow \mathrm{O}\\ \searrow \mathrm{F}\end{smallmatrix}$$

Compound II was prepurified by passing the reaction products through cold traps on a conventional vacuum line. It was retained in a −126° trap and all the SO_2F_2 was found in a −196° trap. The contents of the −126° trap showed only one peak when passed through a 10 ft. silicone on Fluoropack gas chromatographic column.

The characterization of II was by elementary analysis (*Anal.* Calcd. for II: F, 46.3. Found: F, 48.8), molecular weight by vapor density measurement (calcd. 246.1; found: 245.6), infrared spectrum (bands at 5.29 μ, C=O of $-\mathrm{C}\begin{smallmatrix}{/\!\!/}\mathrm{O}\\ \diagdown \mathrm{F}\end{smallmatrix}$ stretching mode[1]; 6.70 μ, S=O; 7.6–8.2 μ [complex], S=O and C—F; 8.60, 9.1, and 9.82 μ, C—F; 11.4 μ, unassigned; 11.80 μ, S—F; 13.3 μ [broad], S—O and C—C; and 14.9 μ, unassigned), ^{19}F n.m.r. (resonances at −48.1 ϕ, S—F; −24.4 ϕ, C—F of the $-\mathrm{C}\begin{smallmatrix}{/\!\!/}\mathrm{O}\\ \diagdown \mathrm{F}\end{smallmatrix}$ linkage characteristically found at low field; 82.9 ϕ, CF_3; and 129.8 ϕ,[2] C—F, and having area ratios very nearly 1:1:3:1, respectively), and mass spectrum (most intense absorptions at mass numbers 31, CF^+; 47, COF^+; 69, CF_3^+; 83, SO_2F^+ [relative intensity = 100]; 97, $C_2F_3O^+$; 131, $C_3F_5^+$; and 180, $C_2F_3(OSO_2F)^+$). Compound II is a colorless liquid which decomposes to a brown oil slowly on standing in the liquid phase at room temperature. This decomposition may explain the poor results from the fluoride analysis.

An attempt was made to convert II to the keto-acid fluoride, $\mathrm{CF_3}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\!-\!\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\!-\!\mathrm{F}$, by employing a stronger Lewis base such as rubidium fluoride. Although elimination of SO_2F_2 occurred, only degradation products (CO_2, CO, O_2, and various carbon–fluorine compounds) were isolated. No evidence for the formation of the desired product was found.

In order to determine the generality of the reaction several other perfluoroalkyl bis(O-fluorosulfates) were treated with alkali metal fluorides. Tetrafluorobis(O-fluorosulfato)ethane (III) was found not to react with KF at room temperature. However, the reaction did proceed slowly when CsF was used. Total decomposition to SO_2F_2, CO_2, CO, O_2, and perfluoroalkanes occurred with nearly quantitative recovery of the SO_2F_2. Similarly, hexafluoro-1,2-bis(O-fluorosulfato)cyclobutane (IV) and octafluoro-2,3-bis(O-fluorosulfato)butane (V) were completely degraded to fluorocarbons, CO_2, CO, and O_2 when treated with KF or RbF. The recovery of SO_2F_2 was, again, nearly quantitative.

The perfluoroalkyl bis(O-fluorosulfates) used in the above study were prepared by the method of Shreeve and Cady[3] employing an excess of the perfluoro olefin. Compounds I, III, IV, and V were purified by vacuum line fractionation and were retained in −78, −78, −35, and −78° traps, respectively. All impurities passed through these traps. The bis(O-fluorosulfates) (I, IV, and V) were, hitherto, unreported and are all colorless liquids.

Compound I was characterized by elementary analysis (*Anal.* Calcd. for I: C, 10.34; F, 43.7. Found: C, 10.55; F, 42.9), its infrared spectrum (bands at 6.70 μ, S=O; 7.7–8 μ [complex and broad], S=O and C—F; 8.48, 9.12, and 10.00 μ, C—F; 11.8 μ [complex], S—F and unassigned; 12.98 μ, S—O; and 13.4 μ, C—C), ^{19}F n.m.r. (complex resonances at −48.4 ϕ, S—F; 80.2 ϕ, CF_3; 83.3 ϕ, CF_2; and 141.0 ϕ, C—F, and having area ratios 1.92:2.82:1.82:1, respectively), and its mass spectrum (mass numbers of high intensity at 47, COF^+; 67, SOF^+; 69, CF_3^+; 83, SO_2F^+ [relative intensity = 100]; 97, $C_2F_3O^+$; 147, $C_3F_5O^+$; and 260, $C_2F_3(OSO_2F)_2^+$).

Compound IV was apparently unstable at ambient temperature and became cloudy. Difficulty was experienced obtaining a satisfactory elemental analysis. *Anal.* Calcd. for IV: F, 42.2; S, 17.8. Found: F, 39.7; S, 17.2. Compound V was more stable. *Anal.* Calcd. for V: F, 47.7; Found: F, 47.9. The infrared spectrum of IV exhibited the following bands: 6.70, 7.65, 8.02 (complex), 8.59, 10.30, 11.73 (complex), 12.3, and 12.65 μ; that for V: 6.70, 7.6–8.2 (broad and complex), 8.55, 8.80, 9.15, 9.53, 9.72, 10.50, 11.20, 11.82 (complex), 12.20, 12.70, and 13.58 μ. The ^{19}F n.m.r. of IV indicated resonances at −48.1 ϕ (complex and unresolved), S—F; 128.2 and 129.0 ϕ, C—F of the CF_2 groups; 135.4 and 137.9 ϕ, C—F. The area ratio

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[1] J. H. Simons, "Fluorine Chemistry," Vol. II, Academic Press, 1954, p. 485.

[2] All samples in this investigation were measured neat at room temperature using a 40-Mc. probe.

[3] J. M. Shreeve and G. H. Cady, *J. Am. Chem. Soc.*, **83**, 4521 (1961).

of the total S—F to C—F was found to be 1.0:2.8. The ^{19}F n.m.r. spectrum of V consisted of three peaks in the S—F, CF_3, and C—F regions having an area ratio of almost exactly 1:3:1, respectively.

The formation of the acyl fluoride discussed above probably involves the basic attack of the fluoride ion from potassium fluoride on the electropositive sulfur atom forming SO_2F_2 and the intermediate potassium alkoxy compound with subsequent formation of the acyl fluoride.

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Kinetics of Exchange of Chromium(II) Ion and Azidopentaaquochromium(III) Ion[1]

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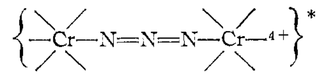
Relatively rapid exchange of chromium atoms between chromium(II) ion and azidochromium(III) ion at 0° has been reported by Ball and King.[4] A more

$$CrN_3^{2+} + \overset{\otimes}{Cr}{}^{2+} = Cr^{2+} + \overset{\otimes}{Cr}N_3^{2+}$$

detailed kinetic study of this reaction as a function of temperature (0 to 36.4°) is the subject of the present note. The principal pathway for exchange in this temperature range involves the azide-bridged transition state



Experimental

Preparation of Reagents.—Acidic chromium(II) perchlorate solutions were prepared by reduction of chromium(III) perchlorate in perchloric acid with amalgamated zinc. The resulting solution containing one-half mole of zinc ion per mole of chromium(II) ion was separated from the metallic zinc and stored under a positive pressure of nitrogen in a bottle closed with a self-sealing rubber gasket. Aliquots of the solution were removed with a syringe and hypodermic needle.

The chromium(II) ion was tagged with chromium-51 by addition of a relatively small amount of radioactive hexaaquochromium(III) ion; after several days, atoms of chromium-51 are randomly distributed between the two oxidation states of chromium.[5] The relatively small amount of tagged hexaaquochromium(III) ion does not interfere with the exchange experiments.

Azidochromium(III) ion was prepared and isolated by the procedure used earlier,[4] namely, oxidation of chromium(II) ion with iron(III) in an acidic solution containing azide followed by an ion-exchange separation of this species. In several preparations, the azide to chromium ratio ranged from 1.00 to 1.02. For analysis, solutions of azidochromium(III) ion were made alkaline, causing decomposition of the complex to give azide ion and chromite ion. The azide ion was oxidized in sulfuric acid solution by cerium(IV), the excess of which was titrated with standard iron(II) solution. Spectrophotometric analyses for chromium were performed after conversion to chromate ion by alkaline hydrogen peroxide.

Exchange Experiments.—Exchange experiments were performed by addition of tagged chromium(II) ion to deoxygenated perchloric acid solutions containing azidochromium(III) ion. At three to eight different times during each experiment, portions of reaction mixture were forced by nitrogen pressure into dilute acidic solutions containing iron(III) ion which quenched the exchange reaction by rapidly oxidizing chromium(II) ion to aquochromium(III) ion. After oxidation of the resulting iron(II) ion with hydrogen peroxide, azidochromium(III) ion (the only chromium species of charge +2) was separated from species of charge +3, chromium(III) ion and iron(III) ion, by elution from a column of Dowex-50 ion-exchange resin with 0.75 *M* perchloric acid. The specific activity of eluted azidochromium (III) ion was determined by combination of the chromium analysis as already described with a determination of radioactivity using a γ-ray spectrometer (scintillation detector).

During most kinetic experiments, one or more analyses for chromium(II) ion were made by delivering aliquots of reaction mixture into a solution containing iron(III) ion. Spectrophotometric analysis of the resulting solution for iron(II) using 1,10-phenanthroline allows calculation of the concentration of chromium(II) ion. The decrease of chromium(II) ion concentration during most experiments was slight.

The fraction exchange, *f*, was obtained by comparison of the specific activity of azidochromium(III) ion in the aliquots taken with the infinity-time specific activity calculated from the composition of the solution and the measured specific activity of the stock chromium(II) ion. Plots of log $(1 - f)$ *vs.* time were nicely linear for all experiments, indicating the absence of appreciable net chemical change. The straight line was not constrained to go through the origin. Most lines did, however, and the others intersected the $\log(1 - f) = 0$ axis within a few seconds of $t = 0$. Empirical second-order rate coefficients were calculated from slopes of these linear plots

$$k_2 = \frac{2.3\ \Delta \log(1 - f)}{([Cr^{2+}] + [CrN_3^{2+}])\Delta t}$$

Experimental Results

At each temperature in the range 0–36°, the empirical second-order rate coefficient was essentially independent of the concentrations of chromium(II) ion and azidochromium(III) ion. Therefore, in this temperature range the exchange is governed by the second-order rate law[6]

$$\text{exchange rate} = k_2[Cr^{2+}][CrN_3^{2+}]$$

Table I summarizes values of k_2. The mild dependence of this quantity upon acidity observed at 0° can be attributed to variation of electrolyte concentration.

At 0° the reaction of chromium(II) ion and *cis*-diazidochromium(III) ion *via* a double-bridged transition state[7] is ~45 times faster than the present reaction involving a single-bridged transition state. In contrast to this, the reaction[3] of chromium(II) ion

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[2] National Science Foundation predoctoral fellow 1959–1961.

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[4] D. L. Ball and E. L. King, *J. Am. Chem. Soc.* **80**, 1091 (1958).

[5] A. Anderson and N. A. Bonner, *ibid.*, **76**, 3830 (1954).

[6] The second-order rate coefficients for exchange observed in unreported experiments run in this work at temperatures in the range 38–50° were higher than expected from an extrapolation of the lower temperature results and appeared to depend upon the concentration of complex.

[7] R. Snellgrove and E. L. King, *J. Am. Chem. Soc.*, **84**, 4609 (1962).