

(4bzpy)₂]²⁻ is obtained. The spectral transition from [fac-ClRe(CO)₃(4bzpy)₂] to [fac-ClRe(CO)₃(4bzpy)₂]²⁻ is smooth. One-electron- and two-electron-reduced species exhibit nearly the same absorption maxima in the UV/vis region, but the intensity of the absorption band at 610 nm of the dianion is twice that of the monoanion. The UV/vis spectra of the reduced 4bzpy and Me-4bzpy⁺ have been measured also. The π-π* absorptions (λ_{max} at 258 nm for 4bzpy, λ_{max} at 272 nm for Me-4bzpy⁺) disappear upon reduction and two new bands appear (λ_{max} at 324 and 696 nm for 4bzpy⁻, λ_{max} at 330 and 508 nm for Me-4bzpy⁰). The reduced forms of the complexed ligand, the free ligand, and the methylated ligand have the same absorption pattern in the UV/vis region.

The number, position, structure, and intensity of the observed UV/vis spectral features indicate that the electrons added to [fac-ClRe(CO)₃(4bzpy)₂] are localized on the 4bzpy ligands. The first electron added produces one 4bzpy⁻ anion, and the second electron added produces the second 4bzpy⁻ anion. Therefore, the one-electron- and the two-electron-reduced species have the same UV/vis absorptions, but for the two-electron-reduced product, the intensity of the absorption band at 610 nm, attributable to the absorption of the Re-bound 4bzpy⁻ ligand, is twice that of the one-electron-reduced product. The UV/vis spectra again support the view that the added electrons are localized on the 4bzpy.

Reduction of Bound Ketone to Bound Alcohol. In the presence of CH₃COOH as a proton source, reduction of [fac-ClRe(CO)₃(4bzpy)₂] becomes chemically irreversible. [fac-ClRe(CO)₃(4bzpy)₂] can be electrochemically reduced to the bis(alcohol) complex in CH₃CN/0.1 M [*n*-Bu₄N]PF₆ with 0.1 M CH₃COOH by using a mercury pool as the working electrode of which the potential is controlled at -1.4 V vs SCE (eq 3). The result is consistent with the mechanism proposed for the photoreduction of [fac-ClRe(CO)₃(4bzpy)₂] where the first step in the photoreduction is one-electron reduction of the Re complex.¹⁰ It is well-known that ketones can be electrochemically reduced to alcohol,¹⁴ and [fac-ClRe(CO)₃(4bzpy)₂] is unexceptional in this regard.

Conclusions

The spectroelectrochemical studies of [fac-ClRe(CO)₃(4bzpy)₂], a complex having a lowest excited state corresponding to a Re to 4bzpy charge-transfer transition, allow comparison of IR and UV/vis spectra of the one-electron- and the two-electron-reduced products. The spectral and electrochemical data obtained are uniformly consistent with the conclusion that the reduced metal complex has the electron(s) localized on the 4bzpy ligand(s).

Acknowledgment. We thank the National Science Foundation for support of this research.

(14) Feoktistov, L. G.; Lund, H. In *Organic Electrochemistry*; Baizer, M. M., Ed.; Dekker: New York, 1973; Chapter VIII.

Contribution from the Department of Chemistry,
Portland State University, Portland, Oregon 97207-0751

(Pentafluoro-λ⁶-sulfanyl)(fluorosulfonyl)ketene

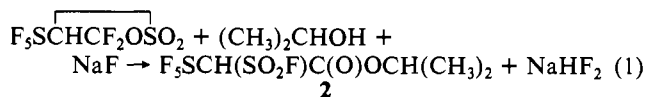
R. Winter and Gary L. Gard*

Received June 27, 1988

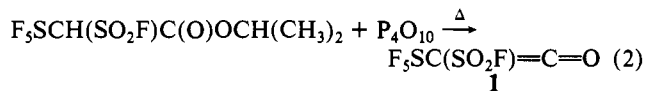
In an attempt to find pathways to potentially useful compounds containing the unique pentafluorothio (SF₅) and fluorosulfonyl (SO₂F) groups, the new ketene F₅SC(SO₂F)=C=O (**1**) was synthesized. Recently, we found that SF₅-containing sultones were effective precursors to a number of derivatives potentially useful as acid electrolytes, surface-active agents, and ion-exchange re-

sins.¹⁻³ It is anticipated that the new ketene and its derivatives will also serve in this role.

In order to obtain F₅SC(SO₂F)=C=O (**1**), it was necessary to prepare the new ester F₅SCH(SO₂F)C(O)OCH(CH₃)₂ (**2**) via reaction of the sultone F₅SCHCF₂OSO₂ with 2-propanol in the presence of sodium fluoride:

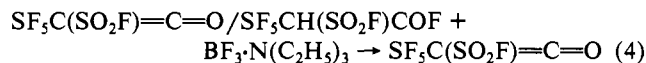
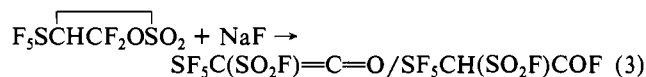


Treatment of the ester with P₄O₁₀ and heat resulted in the formation of the new compound (pentafluoro-λ⁶-sulfanyl)(fluorosulfonyl)ketene (**1**):

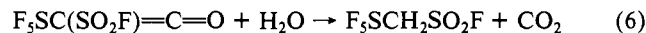
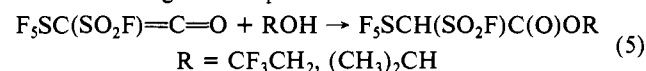


This procedure resulted in some contamination of **1** with SF₅C-H₂SO₂F, and although the yields varied from 49 to 89%, it was found that they decreased upon attempts to prepare larger amounts (e.g. from 8.7 g of ester, only about 1 g of the ketene could be collected). Due to these problems, an alternate procedure was

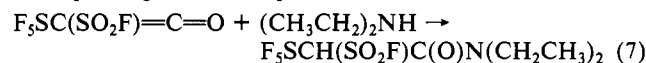
sought that involved dehydrofluorination of F₅SCHCF₂OSO₂ or its rearranged isomer, F₅SCH(SO₂F)COF. Interestingly, with the comparatively weak base NaF, the sultone underwent rearrangement and partial dehydrofluorination to produce a mixture (14:86) of the ketene **1** and F₅SCH(SO₂F)COF, respectively. Sodium fluoride failed to give pure **1** even upon warming to 135 °C (15 h); under this condition some COF₂ and a 50:50 mixture of **1** and F₅SCH(SO₂F)COF were produced. It was found, however, that treatment of the original mixture (14:86) with BF₃·N(C₂H₅)₃ resulted in essentially quantitative conversion to pure ketene **1**. Overall, the reaction sequence is summarized as



The ketene could not be directly prepared in pure form from the sultone and BF₃·N(C₂H₅)₃. Ketene **1** fumes slightly in air and has a faintly pleasant odor. It reacts readily with alcohols and water according to the equations



The proposed acid intermediate F₅SCH(SO₂F)C(O)OH is not stable and decarboxylates spontaneously.² With diethylamine the corresponding amide was produced:



(Pentafluoro-λ⁶-sulfanyl)(fluorosulfonyl)ketene is thermally stable; it can be recovered (98%) after heating (4 h) to 220 °C.

Compounds containing SF₅ or SO₂F groups show characteristic infrared bands; the pentafluorothio group shows very strong absorption bands in the region from 820 to above 900 cm⁻¹ (SF stretching modes) and absorption bands of medium strength in the region of 600 cm⁻¹ (SF deformation modes).⁴ Likewise, compounds with an SO₂ group exhibit a strong asymmetric stretching band in the region 1400-1470 cm⁻¹ and a strong symmetric stretching band in the region 1200-1300 cm⁻¹. The S-F

- (1) Canich, J. M.; Ludvig, M. M.; Gard, G. L.; Shreeve, J. M. *Inorg. Chem.* **1984**, *23*, 4403.
- (2) Terjeson, R. J.; Mohtasham, J.; Gard, G. L. *Inorg. Chem.* **1988**, *27*, 2916.
- (3) Olah, G. A.; Iyer, P. S.; Surya, P. *Synthesis* **1986**, 513.
- (4) Cross, L. H.; Cushing, G.; Roberts, H. L. *Spectrochim. Acta* **1961**, *17*, 344.

absorption band of the SO_2F group is usually located near 790 cm^{-1} .⁵ Ester **2** shows the corresponding bands (cm^{-1}) at 1443 (asym SO_2), 875 (str S-F), 801 (str SF), and 572 (def SF). No unambiguous assignment for the symmetric SO_2 stretching band can be made, as there are several bands in the region from 1200 to 1300 cm^{-1} that are also characteristic of saturated carboxylic esters. The C(O) stretching frequency at 1761 cm^{-1} is found in the same region as for other esters derived from the sultone, $\text{F}_3\text{SCHCF}_2\text{OSO}_2$.² For amide **3** the absorption band at 1661 cm^{-1} is attributed to the carbonyl stretching frequency; other characteristic frequencies and assignments are 1432 cm^{-1} (asym SO_2), 1222 cm^{-1} (sym SO_2), 860 cm^{-1} (str SF_5), 799 cm^{-1} (str SF of SO_2F), and 562 cm^{-1} (def SF).

Ketene **1** has a much simpler infrared spectrum. The characteristic ketene band ($\text{C}=\text{C}=\text{O}$) is found at 2193 cm^{-1} . This is in the region found for other fluorinated ketenes: $\text{F}_3\text{CC}(\text{SO}_2\text{F})\text{CO}$ (2200 cm^{-1}),⁶ $(\text{CF}_3)_2\text{CCO}$ (2203 cm^{-1}),⁷ F_3SCHCO (2177 cm^{-1}).⁸ Interestingly, the strongly electron-withdrawing SF_3 and SO_2F substituents do not produce any unusual shift in the ketene band. The other bands (cm^{-1}) are located at 1445 (asym SO_2), 1214 (sym SO_2), 875 (str SF), 801 (str SF), and 590 (def SF).

The ^{19}F NMR spectrum of ester **2** showed, for the SF_5 group, a collapsed AB_4 multiplet from which the coupling constants could not be determined; similarly, the sulfonyl fluoride resonance was a multiplet. In amide **3** a collapsed AB_4 pattern was observed; the SO_2F spectrum was a multiplet. The ^1H NMR spectrum is more interesting, as two different methyl group resonances were observed along with a complex methylene spectrum. Tentatively, we are assuming a structure invoking hindered rotation about the C-N bond. Ketene **1** with an AB_4X spectrum, had an inverted AB_4 pattern (SF_5) with the F_A resonance appearing upfield from the F_B doublet; the SO_2F resonance appeared as a pentet; the J_{AB} and J_{BX} coupling constant values are 155 and 6.8 Hz, respectively.

It is worthwhile to point out that the AB_4 inversion has also been observed with F_5SNCO ,⁹ F_5SCCH ,¹⁰ F_5SCHCO ,⁸ and F_5SOCN .¹¹ The shielding imparted to F_A seems to be related to the presence of a heteroallene or an alkyne system that is bonded to the SF_5 group. The SO_2F fluorine in the ketene is also strongly deshielded; it resonates at δ 76.3 ppm, well below the range where it is usually found (δ 50–60 ppm).^{6,2}

Experimental Section

Materials. The following were obtained commercially: SO_3 (MCB), NaF (Baker), $\text{CF}_3\text{CH}_2\text{OH}$ (PCR), $(\text{CH}_3)_2\text{CHOH}$ and $(\text{C}_2\text{H}_5)_2\text{NH}$ (MCB), KOH (MCB), and P_4O_{10} (Baker). $\text{F}_3\text{SCH}_2\text{CF}_2\text{Br}$,¹² $\text{BF}_3\cdot\text{N}(\text{C}_2\text{H}_5)_3$,¹³ and $\text{F}_3\text{SCHCF}_2\text{OSO}_2$ ² were prepared according to the literature; $\text{F}_3\text{SCH}=\text{CF}_2$ was obtained via a modified literature procedure.¹⁴ Sodium fluoride was dried at 180°C under vacuum for 5 h before use.

Gases were manipulated in a conventional Pyrex-glass vacuum line that was equipped with a mercury manometer and a Televac thermocouple gauge. Infrared spectra were obtained from the neat liquids or solids between KBr plates on a Nicolet 20 DX spectrometer. The ^{19}F and ^1H nuclear magnetic resonance spectra were recorded on a Varian Model EM-390 spectrometer operating at 90 MHz for proton and at 84.67 MHz for fluorine resonances or with a General Electric QE-300 FT NMR spectrometer. TMS and CFCl_3 were used as external standards. Mass spectra were obtained on a VG 7070 HS mass spectrometer at 70 eV. Gas chromatograms were run with a Varian Aerograph Model A-700 gas chromatograph, and elemental analyses were carried out by

Beller Mikroanalytisches Laboratorium, Göttingen, West Germany.

$\text{F}_3\text{SCH}=\text{CF}_2$. To an aqueous potassium hydroxide solution (81.5 g, 42.5% by weight) in a 100-mL Pyrex-glass round-bottomed flask, equipped with a magnetic stirring bar, was added $\text{F}_3\text{SCH}_2\text{CF}_2\text{Br}$ (33.70 g, 124.4 mmol) at room temperature. A 20-cm reflux condenser that was connected to a cold trap (-78°C) was also attached to the reaction vessel. The mixture was slowly heated with vigorous stirring to a temperature of 100°C , and warm water (40°C) was passed through the condenser; after the disappearance of the bottom layer in the reaction flask (30 min), heating was maintained for another 3 h. The product was collected in the cold trap (22.90 g, 120.5 mmol, 96.9% yield). A gas chromatogram (Carbowax, 20% on Chromosorb W, 100°C) showed only one product to be present; the IR spectrum agreed with the literature values.¹⁴

$\text{F}_3\text{SCH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}(\text{CH}_3)_2$. To a 100-mL Pyrex-glass reaction vessel, equipped with a Teflon stirring bar and a Kontes Teflon valve and containing dry sodium fluoride (30.08 g, 716.2 mmol), was added 2-propanol (10.13 g, 168.8 mmol) by vacuum condensation. The sultone $\text{F}_3\text{SCHCF}_2\text{OSO}_2$ was then added in three portions (12.37 g, 45.8 mmol; 8.70 g, 32.2 mmol; 15.91 g, 58.9 mmol) at -196°C , with the vessel being warmed to room temperature after each addition and the mixture stirred for a few minutes. For each addition slight warming was noticed when room temperature was reached. After addition was complete, the mixture was stirred at 52°C for 15 h and at 68°C for 0.5 h. The crude product was condensed (41.29 g), and distillation gave 100.5 mmol (31.12 g) of a colorless oily liquid with an unpleasant odor: yield 73.3%; bp $92\text{--}94^\circ\text{C}$ (26–28 Torr).

Infrared spectrum (cm^{-1}): 2995 (m), 2952 (sh), 1761 (s), 1443 (s), 1395 (vw), 1382 (w), 1352 (vw), 1296 (m), 1276 (m), 1221 (m), 1168 (w), 1102 (ms), 981 (vw), 875 (vs, sh 900), 837 (wm), 819 (wm), 801 (wm), 781 (w), 769 (w), 733 (vw), 688 (vw), 650 (vw), 612 (w), 572 (s), 491 (vw), 458 (vw).

^{19}F NMR spectrum (neat sample): multiplet, centered at δ 70.9 ppm, area 5.0 (SF_5); multiplet, δ 58.8 ppm, area 1.0 (SO_2F).

^1H NMR spectrum (neat sample): multiplet, δ 6.4 ppm, area 1.0 ($\text{F}_3\text{SC-H}$); septet, δ 5.4 ppm, area 1.1 ($\text{O-CH}(\text{CH}_3)_2$); doublet, δ 1.5 ppm, area 6.2 ($\text{O-CH}(\text{CH}_3)_2$), $J_{\text{H-H}} = 6.22\text{ Hz}$.

Mass spectrum (chemical ionization) (m/e , species, relative abundance): 311, MH^+ , 0.32; 269, $\text{M-H}_3\text{F}_2^+$, 4; 205, $\text{MH}-(\text{CH}_3)_2\text{CHCO}_2 - \text{F}^+$, 7.5; 143, $\text{S}_2\text{C}_2\text{OF}_2\text{H}^+$, 14.8; 127, SF_5^+ , CFO_2S_2^+ , 20.5; 125, $\text{C}_2\text{H}_2\text{FO}_3\text{S}^+$, 8.4; 99, $\text{C}_4\text{H}_3\text{SO}^+$, 9.2; 91, C_2FSO^+ , 4.2; 89, SF_3^+ , 100; 79, FSCO^+ , 4.1; 70, SF_2^+ , 10.8; 67, FSO^+ , 24.6; 65, CH_2FS^+ , 19; 59, $\text{C}_3\text{H}_7\text{O}^+$, 55.8; 58, $\text{C}_3\text{H}_6\text{O}^+$, 5.5; 55, $\text{C}_3\text{H}_5\text{O}^+$, 4.8.

Anal. Calcd for $\text{C}_5\text{H}_8\text{F}_6\text{O}_4\text{S}_2$: C, 19.36; H, 2.60; F, 36.8; S, 20.67. Found: C, 19.27; H, 2.55; F, 37.1; S, 20.82.

$\text{F}_3\text{SC}(\text{SO}_2\text{F})\text{C}=\text{O}$. Method I. In a representative experiment, $\text{F}_3\text{SCH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}(\text{CH}_3)_2$ (2.65 g, 8.55 mmol) was mixed with powdered P_4O_{10} (8.85 g, 31.1 mmol) in a 100-mL Pyrex-glass round-bottomed flask. The flask was connected to a short vacuum-transfer line equipped with a 10-mL receiving flask that was cooled to -196°C . The pressure was lowered to 500 Torr, and the mixture was heated to 100°C (10 min). The reaction flask was cooled to -196°C , evacuated, and reheated (100°C). In 30 min, 1.60 g (6.4 mmol) of crude ketene was collected. Prolonged heating led to transfer of unreacted ester (0.34 g, 1.1 mmol): yield 85.9% (with respect to recovered ester). In similar experiments, the yields varied from 49 to 89%. In this fashion, 4.92 g of crude ketene was obtained from 9.35 g (30.16 mmol) of ester. Distillation gave 4.09 g (16.36 mmol) of pure ketene in 54.2% overall yield; bp $55 \pm 1^\circ\text{C}$ (125–128 Torr).

Infrared spectrum (cm^{-1}): 2193 (vs), 1445 (vs), 1305 (m), 1214 (vs), 1025 (vs), 875 (vs), 845 (s, sh), 801 (s), 689 (m), 635 (m), 618 (m), 590 (m), 520 (w), 470 (w), 432 (vw).

^{19}F NMR spectrum (CDCl_3 , AB_4X spectrum): ϕ_A 73.1 ppm, area 1.0; ϕ_B 86.7 ppm, area 3.9; ϕ_X 76.3 ppm (SO_2F), pentet, area 1.0; $J_{\text{AB}} = 155\text{ Hz}$, $J_{\text{BX}} = 6.8\text{ Hz}$.

Mass spectrum (electron impact) (m/e , species, relative abundance): 250, M^+ , 16.4; 231, M-F^+ , 3.2; 129, $\text{M-SO}_2\text{F}_3^+$, 5.3; 127, SF_5^+ , CFO_2S_2^+ , 94.7; 91, C_2FOS^+ , 6.4; 89, SF_3^+ , 100; 72, SC_2O^+ , 1.9; 70, SF_2^+ , 11.6; 67, FSO^+ , 25.2; 63, CFS^+ , 7.1.

Anal. Calcd for $\text{C}_2\text{F}_6\text{O}_3\text{S}_2$: C, 9.60; F, 45.6; S, 25.63. Found: C, 9.86; F, 45.4; S, 25.82.

NaF-Catalyzed Rearrangement of $\text{F}_3\text{SCHCF}_2\text{OSO}_2$. In a dry-100-mL Pyrex-glass flask, equipped with a Kontes Teflon valve and a stirring bar, NaF (5.30 g, 126.2 mmol) was dried, and the sultone $\text{F}_3\text{SCHCF}_2\text{OSO}_2$ (14.99 g, 44.4 mmol) was then added. The mixture was stirred at $83\text{--}85^\circ\text{C}$ for 4 days. Vacuum transfer afforded 14.15 g of a product that consisted (^{19}F NMR spectrum) solely of a 14:86 mixture of the ketene $\text{F}_3\text{SC}(\text{SO}_2\text{F})\text{CO}$ and the acyl fluoride $\text{F}_3\text{SCH}(\text{SO}_2\text{F})\text{COF}$.

$\text{F}_3\text{SC}(\text{SO}_2\text{F})\text{C}=\text{O}$. Method II. To 5.00 g of the 14:86 mixture of ketene and acyl fluoride, as obtained from the NaF-catalyzed rear-

- (5) Ham, N. S.; Hambly, A. N.; Laby, R. H. *Aust. J. Chem.* **1960**, *13*, 443.
- (6) Krespan, C. G. *J. Fluorine Chem.* **1976**, *8*, 105.
- (7) England, D. C.; Krespan, C. G. *J. Am. Chem. Soc.* **1966**, *88*, 5582.
- (8) Krügerke, T.; Buschmann, J.; Kleemann, G.; Luger, P.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 799.
- (9) Duncan, L. C.; Rhyne, T. C.; Clifford, A. F.; Shaddix, R. E.; Thompson, J. W. *J. Inorg. Nucl. Chem. Suppl.* **1976**, *33*.
- (10) Canich, J. M.; Ludvig, M. M.; Paudler, W. W.; Gard, G. L.; Shreeve, J. M. *Inorg. Chem.* **1985**, *24*, 3668.
- (11) Schmuck, A.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 134.
- (12) Steward, J.; Kegley, L.; White, H. F.; Gard, G. L. *J. Org. Chem.* **1969**, *34*, 766.
- (13) Kraus, C. A.; Brown, E. H. *J. Am. Chem. Soc.* **1979**, *51*, 2690.
- (14) DeMarco, R. A.; Fox, W. B. *J. Fluorine Chem.* **1978**, *12*, 137.

range of the sulfone $F_3SCHCF_2OSO_2$, in a 25-mL Pyrex-glass round-bottomed flask, equipped with a stirring bar, was added the base $BF_3 \cdot N(C_2H_5)_3$ (3.17 g, 18.8 mmol). The flask was attached to a vacuum-transfer line equipped with a 10-mL receiving flask that was cooled to $-196^\circ C$. The pressure in the system was lowered to 500 Torr, and the mixture was heated to $100^\circ C$ over a 25-min period. At $\sim 85^\circ C$ a crystalline precipitate was observed in the homogeneous melt, which disappeared at $\sim 90^\circ C$, leaving an upper brown and a lower colorless liquid layer. Heating was continued at $100^\circ C$ (25 min). The product (4.45 g) was transferred under vacuum (30 min) to the 10-mL receiving flask cooled to $-196^\circ C$. The ^{19}F NMR and IR spectra showed that only the ketene was present; yield (based on the 14:86 mixture) 95%.

$F_3SC(SO_2F)C=O$ in a Sealed Tube. The ketene (0.49 g, 1.96 mmol) was heated in an evacuated dry 50-mL Carius tube to $220^\circ C$ for 4 h. The liquid inside was slightly discolored, but 0.48 g of unchanged ketene was recovered.

$F_3SC(SO_2F)C=O$ and 2-Propanol. To 118 mg of 2-propanol (1.94 mmol) in a 1-mL dry reaction vessel was added dropwise ketene **1** (497 mg, 1.92 mmol). Initially, the reaction was vigorous, but it subsided after addition of approximately half of the ketene. After addition was complete, the reaction vessel was kept at room temperature (0.5 h) and 568 mg of product was collected. The infrared and ^{19}F NMR spectra agreed with those found for ester **2**. Gas chromatography (Carbowax 20% on Chromosorb W, $110^\circ C$) showed the product to be essentially pure (>95%).

$F_3SC(SO_2F)C=O$ and 2,2,2-Trifluoroethanol. Into 0.50 g (2.0 mmol) of the ketene in a dry 30-mL Pyrex-glass reaction vessel, equipped with a Kontes Teflon valve, was condensed CF_3CH_2OH (0.24 g, 2.4 mmol) at $-196^\circ C$. The mixture was allowed to attain room temperature slowly and was heated to $83^\circ C$ for 1 h. The liquid product was transferred out and washed with water (2×0.5 mL); the lower layer was taken up with a pipet, transferred to a 5-mL flask, and dried (Na_2SO_4). The infrared spectrum of the product (0.59 g) was essentially identical with the published spectrum of $F_3SCH(SO_2F)C(O)OCH_2CF_3$.² The ^{19}F NMR spectrum revealed that the product was essentially trifluoroethyl ester with some $F_3SCH_2SO_2F$ as a minor impurity; yield 82% (NMR spectrum).

$F_3SC(SO_2F)C=O$ and H_2O . Into a 100-mL reaction vessel, equipped with a Kontes Teflon valve and containing water (40.5 mg, 2.25 mmol), was condensed ketene **1** (485.3 mg, 1.94 mmol). The mixture was warmed to room temperature and remained there for 2 h. It was then cooled to $-78^\circ C$, and the infrared spectrum of the volatile material showed CO_2 to be present; 85.4 mg (1.94 mmol) of CO_2 with trace impurities was formed in 100% yield. The residue was transferred at elevated temperature and dried (Na_2SO_4). A total of 369.0 mg product was collected. A gas chromatogram (Carbowax, 20%, 6 ft, on Chromosorb W, $100^\circ C$) showed only one product; its infrared and ^{19}F NMR spectra were identical with the published spectra of $F_3SCH_2SO_2F$;² yield 84.9%.

$F_3SC(SO_2F)C=O$ and $(C_2H_5)_2NH$. The ketene (0.49 g, 1.96 mmol) was condensed into a 50-mL Pyrex-glass reaction vessel, equipped with a Kontes Teflon valve and containing 2 mL of dry CH_2Cl_2 at $-196^\circ C$. The vessel was warmed above the melting point of the solution, shaken, and cooled again to $-196^\circ C$, and diethylamine (0.142 g, 1.94 mmol) was added. Upon being warmed to the melting temperature, the solution was shaken, frozen ($-196^\circ C$), and allowed to slowly attain room temperature. During warming to room temperature, the solution turned brownish. At room temperature it was decanted, concentrated, and recrystallized from CH_2Cl_2 , leaving 302 mg (0.93 mmol) of product $F_3SCH(SO_2F)C(O)N(CH_2CH_3)_2$; mp $108-110^\circ C$; yield 47.7%.

^{19}F NMR spectrum ($CDCl_3$): multiplet, δ 72.2 ppm, area 4.8 (SF_3); multiplet, ϕ 62.3 ppm, area 1.0 (SO_2F).

1H NMR spectrum: triplet, δ 1.19 ppm, $J_{H-H} = 7.1$ Hz, area 3.0 (CH_3); triplet δ 1.32, $J_{H-H} = 7.1$ Hz, area 3.0 (CH_3); multiplet, centered at 3.5 ppm, area 4.3 (CH_2); pentet, δ 6.00 ppm, $J_{H-F} = 4.0$ Hz, area 0.9 (CH).

Infrared spectrum: 2990 (w), 1661 (vs), 1460 (vw), 1432 (s), 1390 (w), 1363 (w), 1320 (w), 1278 (w), 1222 (m), 1212 (m), 1129 (w), 1096 (w), 1083 (vw), 953 (w), 899 (m), 860 (vs), 820 (m), 799 (m), 740 (w), 647 (w), 562 (m), 488 (w), 458 (w).

Mass spectrum (electron impact) (m/e , species, relative abundance): 323, M^+ , 1.6; 308, $(M-CH_3)^+$, 12.1; 280, $C_6H_4F_6NO_3S_2^+$, 2.0; 231, $C_2F_3O_3S_2^+$, 4.6; 196, $M-SF_5^+$, 14.9; 176, $M-HF-SF_5^+$, 5.8; 127, $(SF_5, CFO_2S_2)^+$, 7.4; 125, $C_2H_2FO_3S^+$, 2.9; 112, $(CH_3CH_2)_2NCOC^+$, 2.9; 105, $C_2HO_3S^+$, 2.7; 100, $C_5H_{10}NO^+$, 5.8; 89, SF_3^+ , 14.8; 73, C_2HOS^+ , 2.0; 72, $NC_4H_{10}^+$, C_5OS^+ , 42.4; 71, $NC_4H_9^+$, 3.4; 70, $NC_4H_8^+$, SF_2^+ , 4.4; 67, FSO^+ , 5.5; 58, $C_2H_4NO^+$, 100; 56, $NC_3H_6^+$, $C_2H_2NO^+$, 21.5; 54, C_2ON^+ , 2.0.

Anal. Calcd for $C_6H_{11}F_6NO_3S_2$: C, 22.29; H, 3.43; F, 35.3; N, 4.33; S, 19.83. Found: C, 22.37; H, 3.54; F, 35.2; N, 4.26; S, 19.91.

Acknowledgment. We express our appreciation to the Gas Research Institute (Grant 5084-260-1085) and the U.S. Department of Energy (Grant OE-FG21-88MC25142) for support of this work. Dr. Gary Knerr (University of Idaho) obtained the mass spectra.

Contribution from the Research Department, Paulsboro Research Laboratory, Mobil Research and Development Corporation, Paulsboro, New Jersey 08066, Research Department, Princeton Laboratory, Mobil Research and Development Corporation, Princeton, New Jersey 08540, and School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

Stability of Synthetic Zeolite ZSM-5 to Dealumination with Chromium(III) Salt Solutions

W. E. Garwood,* P. Chu, N. Y. Chen, and J. C. Bailar, Jr.

Received March 24, 1988

We have previously reported dealumination of dense zeolites such as erionite¹ and also the larger pore faujasites² by reaction of the zeolite with hot aqueous solutions of chromium(III) salts. The dealuminated dense zeolite residues are left with very little chromium, usually less than 1 wt %, while the dealuminated faujasite Y contains much more chromium, up to 7 wt %, with evidence that the chromium is "healing" to some extent the rupture in the silica alumina lattice created by hydrolysis and removal of the aluminum atoms.

We now find that the synthetic zeolite ZSM-5 undergoes less than 10% dealumination with $CrCl_3$ solutions under conditions giving greater than 40% dealumination of the dense zeolites and faujasite. In addition, the chromium content of the treated ZSM-5 is <0.1 wt %, demonstrating the intrinsic stability of this high silica zeolite in an acid environment.

Experimental Section

Hydrated chromium(III) chloride was obtained from Matheson Coleman and Bell.

Synthetic ZSM-5 was prepared by the method of Argauer and Landolt.³ Analysis by weight: 97.0% SiO_2 , 2.10% Al_2O_3 , 2.7% Na; calculated SiO_2/Al_2O_3 molar ratio 77/1. In the first experiment 8.7 g of the powdered zeolite was added to 300 mL of refluxing ($\sim 101^\circ C$) aqueous 2.0 N $CrCl_3$, pH 1.5, and the mixture was stirred for 2 h. The flask contents were then filtered through paper by suction, and the residue was treated twice more with 300 mL of $CrCl_3$ solution (total of 102 mL of solution/g of zeolite). In all cases, the filtrate remained clear. The final filter cake was water washed until chloride ion free and then dried overnight at $110^\circ C$. Analysis by weight: 98.0% SiO_2 , 1.98% Al_2O_3 , <0.01% Na, 0.02% Cr; calculated SiO_2/Al_2O_3 ratio 84/1; alumina removal 8 wt %.

In a second experiment using more severe treatment conditions, 6.0 g of the zeolite was added to 600 mL of refluxing 4.0 N $CrCl_3$, pH 1.4, and the mixture was stirred for 48 h (100 mL of solution/g of zeolite). The flask contents were filtered as in the first experiment; the filter cake was water washed until chloride ion free and then dried overnight at $110^\circ C$. Analysis by weight: 95.2% SiO_2 , 2.00% Al_2O_3 , <0.01% Na, 0.04% Cr; calculated SiO_2/Al_2O_3 ratio 8:1; alumina removal 5 wt %.

Discussion

In the earlier work dealuminating erionite with $CrCl_3$, it was found that treatment of the zeolite with HCl solutions of the same pH as the $CrCl_3$ solutions removed only about one-fourth as much alumina.¹ Further evidence was given of a complex of the chromium with the hydrolyzed alumina, accounting for its greater removal from the framework. Further, in the earlier work it was

* To whom correspondence should be addressed at the Paulsboro Research Laboratory.