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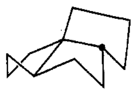

trans-**5**

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Addition of Sulfur Trioxide to Acid Halides and Esters

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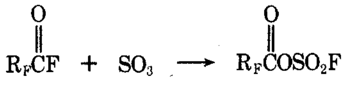
Sulfur trioxide inserts into the carbon–halogen bond of acid fluorides and acid chlorides under mild conditions. The acyl fluorosulfates so formed are more stable thermally than the acyl chlorosulfates, but both types of product can revert to starting materials at elevated temperatures. As a class, these mixed anhydrides are strongly electrophilic, and examples of cationic polymerization and ether cleavage are presented. One example of formation of a methyl acyl sulfate from sulfur trioxide and a methyl ester is also described.

Although polyfluoroacyl fluorides were prepared earlier from sulfur trioxide and alkyl polyfluoroalkyl ethers,[1,2] the reaction of sulfur trioxide with the product acid fluorides was not reported in the literature.[3] As is shown in this paper, such reactions provide a convenient route to polyfluoroacyl fluorosulfates in quantity. Previous syntheses of fluoroacyl fluorosulfates involved mainly reactions of peroxydisulfuryl difluoride with substrates such as fluorinated anhydrides,[4] trifluoroacetyl bromide,[5] and bis(trifluoromethyl)ketene.[6]

Acyl Fluorosulfates. Preparation. Sulfur trioxide adds readily to fluoroacyl fluorides at 25–100°, with the required time and temperature dependent on the specific acid fluoride. For example, trifluoroacetyl fluoride reacted under pressure over a period of weeks with sulfur trioxide at 25° to form trifluoroacetyl fluorosulfate (**1**), whereas both α-*H*-hexafluoroisobutyroyl fluoride and perfluoromethacryloyl fluoride give **2** and **3**, respectively, in mildly exothermic reactions. Yields were good in all cases, and the fluoroacyl fluorosulfates have been purifiable by distillation provided the temperature is kept well below 100°. The reaction is reversible, and at elevated temperatures significant amounts of acid fluoride and sulfur trioxide are present.[7] Thus fluorosulfate **3** distilled as such at 46–48° (20 mm), but when heated at 1 atm to 125–140°, **3** distilled as a mixture of its precursors at ca 49°.



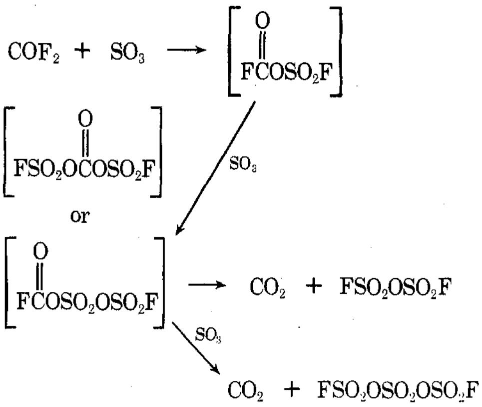
$$R_F\overset{O}{\overset{\|}{C}}F + SO_3 \longrightarrow R_F\overset{O}{\overset{\|}{C}}OSO_2F$$

$R_F = CF_3$ (**1**)
$R_F = CH(CF_3)_2$ (**2**)
$R_F = C(CF_3){=}CF_2$ (**3**)
$R_F = CHFCF_3$ (**4**)
$R_F = CF(CF_3)SO_2F$ (**5**)

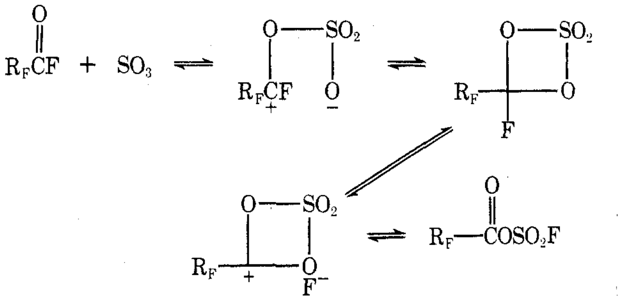
Side reactions are possible in some cases where α-H is present. Thermolysis of **2** at 120–155° (1 atm) gave 37% of bis(trifluoromethyl)ketene along with α-*H*-hexafluoroisobutyroyl fluoride. No such elimination of HF was observed when fluorosulfate **4** was pyrolyzed.

Carbonyl fluoride proved to be a special case. Reaction with sulfur trioxide occurred slowly in a glass vessel at 100° under pressure to give products apparently derived from fluorocarbonyl fluorosulfate. Major products were carbon dioxide, pyrosulfuryl fluoride, and bis(fluorosulfonyl) sulfate along with a trace of sulfuryl fluoride and small amounts of higher fluorosulfonyl compounds. The low yield of sulfuryl fluoride is an indication that fluorocarbonyl fluorosulfate is formed, but reacts readily with sulfur trioxide to form higher anhydrides which are degraded with loss of carbon dioxide to give fluorosulfonic anhydrides. The reaction should provide an attractive route to pyrosulfuryl fluoride, although one attempt to reproduce it on a molar scale at 125° in a metal bomb failed. Perhaps the equilibrium at

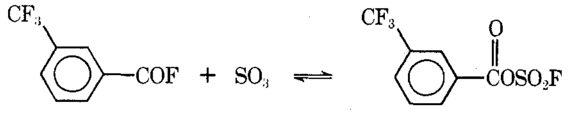
125° favors starting materials so greatly that an effective ceiling temperature near 100° was exceeded.



These reactions of sulfur trioxide with acid fluorides may proceed via preliminary coordination of sulfur trioxide to fluorine, followed by an ionization to acylium and fluorosulfate ions which recombine to product. However, the polarization of acid fluorides is such that another mechanism for these reactions should also be considered, one which involves an initial reversible cycloaddition to the carbonyl group. Assuming a conventional cycloaddition in accord with the Woodward–Hoffman rules, this addition would probably be stepwise and proceed by attack on the negatively charged carbonyl oxygen by sulfur trioxide to form a dipolar intermediate. Similar [2 + 2] cycloadducts of sulfur trioxide with fluoro olefins are well known.[8] 1–3 migration of fluoride ion from carbon to sulfur with concomitant ring-opening gives the more stable acyl fluorosulfate. With carbonyl fluoride, proposed intermediate fluorocarbonyl fluorosulfate can react further with sulfur trioxide, as observed, and elimination of carbon dioxide provides an irreversible pathway to sulfuric anhydrides.



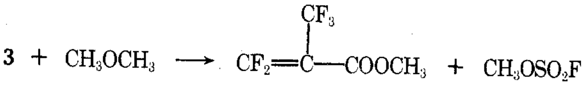
m-Trifluoromethylbenzoyl fluoride easily forms *m*-trifluoromethylbenzoyl fluorosulfate (**6**) at low temperatures. Other negatively substituted benzoyl fluorides and benzoyl fluoride itself will presumably give similar adducts. Distillation of **6** could be carried out at low temperature without appreciable sulfonation of the ring, but reversibility of the synthesis reaction hampered efforts to isolate the pure adduct.



6

Reactions. As indicated above, the acyl fluorosulfates dissociate near 100°, so that their isolation and reactions must be conducted at moderate temperatures. The products react violently with water, and those of sufficient volatility fume in air. Another indicator of reactivity is the attack of the acyl fluorosulfates on sodium chloride prisms, which necessitated the use of calcium fluoride plates for recording infrared spectra.

The acyl fluorosulfates exhibit pronounced electrophilic character. Compound **1** efficiently polymerized tetrahydrofuran to high molecular weight polymer, indicating high reactivity as a cationic initiator. Molar amounts of acyl fluorosulfate with an ether easily give the corresponding fluorinated ester. Thus, **2** reacted with diethyl ether at 0° to give a solid oxonium adduct which decomposed at 25°, leading to ethyl α-*H*-hexafluoroisobutyrate in 72% isolated yield. Similarly, **3** reacted with dimethyl ether to form methyl fluorosulfate and methyl perfluoromethacrylate (**7**). The mixture was difficult to separate by fractional distillation, but passage over sodium fluoride at 275° served to remove methyl fluorosulfate and allowed isolation of pure **7** in 79% yield. This synthesis is superior to known routes,[9] in that the ester is obtained from a simple sequence of reaction free of the saturated adduct with hydrogen fluoride.



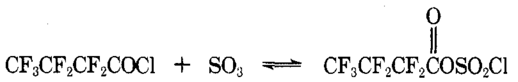
$$3 + \mathrm{CH_3OCH_3} \longrightarrow \mathrm{CF_2{=}\overset{CF_3}{\overset{|}{C}}{-}COOCH_3} + \mathrm{CH_3OSO_2F}$$

7

Acyl trifluoromethanesulfonates are reported[10] to acylate benzene at 20°. The possibility that fluoroacyl fluorosulfates would serve as acylating agents of equal potency was tested by mixing **2** and benzene at 25°. Since no reaction was observed, the reactivity of the fluoroacyl fluorosulfates must be less than that of the acyl trifluoromethylsulfonates. This result may be a direct consequence of the greater difficulty in forming fluoroacylium cations than acylium cations. At any rate, the amount of sulfur trioxide in equilibrium with the fluoroacyl fluorosulfate at 25° must be negligible, since the known exothermic reaction of sulfur trioxide with benzene did not occur. Therefore, the fluoroacyl fluorosulfates may prove useful in acylating activated rings.

Acyl Chlorosulfates. Few descriptions of acyl chlorosulfates are found in the literature. Acetyl chlorosulfate, as an example, is said to have been obtained from acetyl chloride and chlorosulfonic acid at 25° as a thermally unstable oil.[11] The 1:1 adduct from acetyl chloride and sulfur trioxide was also assigned the chlorosulfate structure on the basis of conductometric, cryoscopic, and infrared studies of its behavior in polar media, in which solutions acylium cation and chlorosulfate anion were detected.[12] In the same study, however, *chloroacetyl chloride* was concluded to have formed only a complex in which sulfur trioxide was coordinated with the carbonyl oxygen; the evidence was lack of conductance in solution and a decrease in the carbonyl infrared frequency rather than an increase as observed with acetyl chloride.

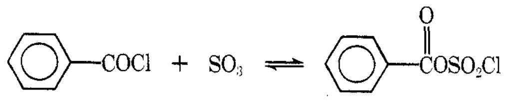
In our work, reactions of two acid chlorides were examined. Heptafluorobutyroyl chloride combined with sulfur trioxide at 100° under pressure to form *n*-heptafluorobutyroyl chlorosulfate (**8**). The latter appeared to revert to starting materials near 50° at 1 atm, a temperature much lower than that required to dissociate the related fluorosulfates.



$$\mathrm{CF_3CF_2CF_2COCl} + \mathrm{SO_3} \rightleftharpoons \mathrm{CF_3CF_2CF_2\overset{O}{\overset{\|}{C}}OSO_2Cl}$$

8

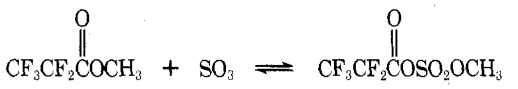
Benzoyl chloride combined exothermically with sulfur trioxide to form benzoyl chlorosulfate (**9**), which was distillable at very low pressure with slight decomposition. No mention of this reaction was uncovered in the literature, although it is well known that at higher temperatures (110–160°), benzoyl chloride and sulfur trioxide form *m*-carboxybenzenesulfonyl chloride.[13] The latter reaction and perhaps others, such as the rearrangement of acetyl chlorosulfate to sulfoacetyl chloride above 45°,[11] can now be understood to proceed by preliminary dissociation of a chlorosulfate to acid chloride and sulfur trioxide.



9

Part of the proof of structure for **9** rests on the shift of carbonyl infrared absorption to shorter wavelength than that of benzoyl chloride. This direction of shift is compatible with formation of the mixed anhydride in which a group more negative than chlorine is attached to the carbonyl, resulting in a more covalent double bond. Complex formation by association of sulfur trioxide with the carbonyl oxygen, on the other hand, would have resulted in a substantial shift of the carbonyl bond to longer wavelength.[14] The mixed anhydride structure is also supported by the facile reaction of **9** with dimethyl ether to give methyl benzoate, isolated in 60% yield. The possibility that complexed sulfur trioxide was present to form dimethyl sulfate with dimethyl ether, and dimethyl sulfate subsequently methylated benzoyl chloride to give methyl benzoate after aqueous work-up, was excluded by showing that dimethyl sulfate does not react at 25° with benzoyl chloride. Dissociation of **9** does occur readily, however, since reaction with benzene occurs exothermically to give only base-soluble products and a small amount of diphenyl sulfone. No benzophenone was detected.

Insertion into an Ester. In the only such case examined, methyl pentafluoropropionate slowly added sulfur trioxide at reflux to form methyl pentafluoropropionyl sulfate (**10**). This compound could be isolated by vacuum distillation at low temperature, but it also dissociates on heating. An attempt to interact **10** with benzene at reflux resulted in the formation of methyl pentafluoropropionate.



$$CF_3CF_2\overset{O}{\overset{\|}{C}}OCH_3 + SO_3 \rightleftharpoons CF_3CF_2\overset{O}{\overset{\|}{C}}OSO_2OCH_3$$

10

Experimental Section[15]

Trifluoroacetyl Fluorosulfate (1). Into each of two 100-ml heavy-walled polymer tubes were loaded 20 g (0.25 mol) of SO_3 and 32.5 g (0.28 mol) of trifluoroacetyl fluoride. The tubes were sealed and allowed to stand at 25° for 3 weeks, after which time single phases were present. Excess trifluoroacetyl fluoride was allowed to escape and the combined contents of both tubes were distilled to give 67.5 g (69%) of colorless product, bp 44–47° (ref 5, bp 46.5°), ^{19}F NMR +47.7 (s, 1, $-OSO_2F$) and −74.5 ppm (s, 3, CF_3).

Polymerization of Tetrahydrofuran. Into a flame-dried round-bottomed flask was injected 44.4 g (50 ml) of purified tetrahydrofuran. The contents were blanketed with dry N_2 and stirred at −25° while 0.10 ml of trifluoroacetyl fluorosulfate was injected. Stirring was continued while the mixture was allowed to warm to 25°. After 1 day the mixture was too viscous to be stirred magnetically. After 2 days, the polymerization was quenched in 250 ml of water containing 10 g of NaOH. This mixture was warmed and stirred for 1 hr, and the resulting semisolid polymer was washed with three 250-ml portions of hot water, then dried under vacuum to give 32.7 g (74%) of solid polytetrahydrofuran, η_{inh} 0.80 (0.1% solution in benzene at 25°).

***α-H*-Hexafluoroisobutyroyl Fluorosulfate (2).** Addition of 50 g (0.25 mol) of *α-H*-hexafluoroisobutyroyl fluoride to 24 g (0.30 mol) of sulfur trioxide resulted in a mildly exothermic reaction. After 2 days the mixture was distilled to afford 48.2 g (69%) of *α-H*-hexafluoroisobutyroyl fluorosulfate: bp 49° (50 mm); ir 3.37 (saturated CH, weak), 5.47 (C=O), 6.76 (SO_2F), and 7.2–8.5 μ (CF, SO_2); ^1H NMR 4.22 ppm [septet, J_{HF} = 7 Hz, $CH(CF_3)_2$]; ^{19}F NMR +46.6 (s, 1, OSO_2F), −64.6 ppm [d, 6, $CH(CF_3)_2$].

Anal. Calcd for $C_4HF_7O_4S$: C, 17.27; H, 0.36; F, 47.82. Found: C, 17.61; H, 0.69; F, 48.53.

Perfluoromethacryloyl Fluorosulfate (3). Equimolar amounts of perfluoromethacryloyl fluoride and SO_3 gave a mildly exothermic reaction to form an adduct. Attempted distillation at 125–140° and 1 atm resulted in cracking, presumably to starting materials, bp ~49°.

A 10-g sample of the distillate above, bp 49° (1 atm), was distilled under reduced pressure to give 7.5 g of perfluoromethacryloyl fluorosulfate: bp 46–48° (20 mm); ir 5.53 (C=O), 5.91 (C=C), 6.79 (SO_2F), and 7.2–8.5 μ (CF, SO_2); ^{19}F NMR +45.0 (s, 1, OSO_2F), −47.7 (m, 2, $=CF_2$), and −60.4 ppm (m, 3, CF_3).

Anal. Calcd for $C_4F_6O_4S$: C, 18.61; F, 44.17. Found: C, 18.78; F, 44.49.

Methyl Perfluoromethacrylate (7). Excess dimethyl ether was distilled into a flask topped by a −80° condenser and containing 41.7 g (0.16 mol) of perfluoromethacryloyl fluorosulfate maintained at 0°. The mixture was stirred at 0° for 1 hr and then allowed to warm to 25° while excess dimethyl ether was vented. The crude product was passed over a bed of dry NaF pellets in a hot tube at 275° (5 mm). After two passes, only traces of by-product methyl fluorosulfate remained and nearly pure methyl perfluoromethacrylate was collected in 79% (23.9 g) yield. Identity and purity were determined by comparison of the ir spectrum and GC retention time with those of an authentic sample.

***α-H*-Tetrafluoropropionyl Fluorosulfate (4).** A mixture of 37 g (0.25 mol) of *α-H*-tetrafluoropropionyl fluoride and 10 ml of sulfur trioxide was heated in a Carius tube overnight on a steam bath. Distillation gave 45.6 g (80%) of *α-H*-tetrafluoropropionyl fluorosulfate, bp 49° (65 mm).

Anal. Calcd for $C_3HF_5O_4S$: C, 15.80; H, 0.44; F, 41.67; S, 14.06. Found: C, 15.86; H, 0.60; F, 41.57; S, 14.07.

Pyrolysis of 4 in a platinum tube at 500° (1.6 mm) gave no indication of ketene formation.

***α*-Fluorosulfonyltetrafluoropropionyl Fluorosulfate (5).** The mixture of 46 g (0.20 mol) of *α*-fluorosulfonyl tetrafluoropropionyl fluoride and 16 g (0.20 mol) of sulfur trioxide was heated in a Carius tube overnight on a steam bath and the product distilled to afford 15.1 g (24%) of **5**: bp 71° (190 mm); ir 5.40 (C=O), 6.66, and 6.76 μ (SO_2F); ^{19}F NMR +52.1 (q, J_{FF} = 9.1 Hz, into d, J_{FF} = 4.0 Hz, 1, CSO_2F), +47.0 (s, 1, OSO_2F), −74.1 (d, J_{FF} = 9.1 Hz, into d, J_{FF} = 8.1 Hz, 3, CF_3), and −161.6 ppm (q, J_{FF} = 8.1 Hz, into d, J_{FF} = 4.0 Hz, 1, CF).

Polysulfuryl Fluorides from COF_2 and SO_3. A 100-ml heavy-walled glass tube was charged with 6.9 g (0.10 mol) of carbonyl fluoride and 16.0 g (0.20 mol) of sulfur trioxide, sealed, and heated at 100° for 5 days. Gaseous products identified by ir were carbon dioxide with traces of sulfuryl fluoride, sulfur dioxide, and silicon tetrafluoride. Distillation of liquid products gave 7.34 g (40%) of pyrosulfuryl fluoride, identified by comparison of the infrared spectrum with that of an authentic sample and by the presence of a single ^{19}F NMR peak at +48.6 ppm. A second product, trisulfuryl fluoride, $FSO_2OSO_2OSO_2F$, bp 64° (120 mm), 2.04 g (12%), was identified by ir and NMR (singlet ^{19}F NMR peak at +49.8 ppm).[16]

***m*-Trifluoromethylbenzoyl Fluorosulfate (6).** Addition of 7.5 g (0.094 mol) of SO_3 over a 10-min period to 19.2 g (0.10 mol) of *m*-trifluoromethylbenzoyl fluoride proceeded exothermically. Temperature was maintained at 30–40° by external cooling. After addition was completed, infrared analysis of the mixture showed strong bands at 5.49 (C=O) and 6.84 μ ($-OSO_2F$). Distillation at 42–47° (0.15–0.25 mm) afforded 14.2 g (~55%) of liquid. NMR analysis of a late fraction by ^{19}F NMR showed peaks at +45.3 (s, 1, $-OSO_2F$) and −64.1 ppm (s, 3, CF_3) with −COF peak present indicating ~9% starting acid fluoride as impurity; ir 3.23 (aromatic CH), 5.48 (C=O), 6.18 and 6.27 (aromatic C=C), and 6.84 μ (OSO_2F).

***n*-Heptafluorobutyroyl Chlorosulfate (8).** Reaction of heptafluorobutyroyl chloride with SO_3 at 25° did not proceed satisfactorily, as indicated by the continued presence of two phases after 3 days. The two reactants, when heated in a sealed glass tube at 100° for 2 hr, formed a homogeneous solution. After an additional 2 hr at 100°, the reaction mixture was cooled and transferred to a still. Distillation of about ⅕ of the mixture occurred readily at 33–34° with the pot at ~50°. Ir analysis of the distillate indicated it to contain a high proportion of heptafluorobutyroyl chloride (bp

39°); the corrosive, fuming nature of the distillate indicated SO_3 to be present in at least small amounts.

Ir analysis of the still pot contents showed it to contain not only heptafluorobutyroyl chloride (5.51 and 5.58 μ for C=O), but also heptafluorobutyroyl chlorosulfate (5.46 μ for C=O, 7.10 μ for OSO_2Cl).

Benzoyl Chlorosulfate (9). Benzoyl chloride (14.1 g, 0.10 mol) was stirred under dry N_2 while 8.0 g (0.10 mol) of SO_3 was added over 10 min with occasional cooling to keep the temperature at 30–40°. After the addition was completed, the mixture was allowed to stand for 1 hr, then distilled through a short Vigreux column to give 21.9 g (99%) of yellow oil, bp 37° (7.5 μ). ^1H NMR showed monosubstituted phenyl, nearly unchanged in chemical shift and in pattern from that of benzoyl chloride; ir 5.57 (C=O), 6.27 and 6.32 (aromatic C=C), and 7.07 μ (OSO_2Cl).

Methyl Pentafluoropropionyl Sulfate (10). To 27.0 g (0.15 mol) of methyl pentafluoropropionate stirred at 0° was added dropwise 12.0 g (0.15 mol) of SO_3. No exotherm was observed, so the reaction mixture was heated slowly to reflux (53°). Reflux was continued for 60 hr, at which time the pot temperature had leveled off at 73°. Distillation afforded 10.1 g (26%) of methyl pentafluoropropionyl sulfate: bp 38° (5 mm); ir 3.35 (saturated CH), 5.47 (C=O), 6.87 and 6.98 (SO_2), and broad 8 μ (CF); ^1H NMR δ 4.26 (OCH_3); ^{19}F NMR −83.3 (t, $J_{FF} = 1.6$ Hz, 3, CF_3) and −121.6 ppm (q, $J_{FF} = 1.6$ Hz, 2, CF_2).

Anal. Calcd for $C_4H_3F_5O_5S$: C, 18.61; H, 1.17; F, 36.80; S, 12.42. Found: C, 18.67; H, 1.33; F, 36.55; S, 13.04.

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Registry No.—**1,** 5762-53-8; **2,** 56114-18-2; **3,** 56114-19-3; **4,** 40416-27-1; **5,** 56114-20-6; **6,** 56114-21-7; **7,** 685-09-6; **8,** 56114-22-8; **9,** 56114-23-9; **10,** 56114-24-0; trifluoroacetyl fluoride, 354-34-7; SO_3, 7446-11-9; tetrahydrofuran, 109-99-9; polytetrahydrofuran, 24979-97-3; α-*H*-hexafluoroisobutyroyl fluoride, 382-22-9; perfluoromethacryloyl fluoride, 684-36-6; dimethyl ether, 115-10-6; α-*H*-tetrafluoropropionyl fluoride, 6065-84-5; α-fluorosulfonyltetrafluoropropionyl fluoride, 754-41-6; COF_2, 353-50-4; trisulfuryl fluoride, 13709-33-6; *m*-trifluoromethylbenzoyl fluoride, 328-99-4; heptafluorobutanoyl chloride, 375-16-6; benzoyl chloride, 98-88-4; methyl pentafluoropropionate, 378-75-6.

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Mechanism of Hydrolysis of an Unsymmetrical Ketene *O,O*-Acetal and of Ketene *O,S*-Acetals[1a]

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The hydrolyses of an unsymmetrical ketene *O,O*-acetal (2,2-dichloro-1-ethoxy-1-phenoxyethylene, **1**) and of two ketene *O,S*-acetals [2,2-dichloro-1-ethoxy-1-ethylthioethylene (**2**) and 1-ethylthio-1-phenoxyethylene (**3**)] have been studied in acidic solution at 30°. The observed catalysis by hydronium ion and acetic acid, the deuterium solvent isotope effect ($k_H/k_D = 3.0$ with **3**), and the nonlinear dependence of rate on buffer concentration at constant pH (with **3**) are in accord with a mechanism in which proton transfer to the olefinic bond is rate determining in HCl and $HClO_4$ solutions, and at low concentrations of acetate buffer. At high buffer concentration, the rate-limiting step is suggested to be the decomposition of a carbonium ion intermediate. The variation in the nature of the products of hydrolysis of **2** (mainly ester at $HClO_4 < 1\ M$, and mixtures of ester and thiol ester at higher acidity) is taken as evidence for a second intermediate on the reaction pathway. The products of hydrolysis of **1** and **3** are phenol and ethyl dichloroacetate or ethyl thiolacetate, respectively, and are essentially independent of acidity in the ranges examined. The pathways of breakdown of tetrahedral addition intermediates of varying structure are discussed.

A useful approach to the study of the elusive, highly reactive, tetrahedral addition intermediates which are formed in many acyl transfer reactions consists of the generation of these or closely related substances via reactions which do not lie on the reaction pathway for acyl transfer.[2] Extensive use has been made of the hydration of imidate[3] and thioimidate[4] esters to investigate the properties of the intermediates formed in the aminolysis of esters and thiol esters, and in the alcoholysis of amides. In recent publications, the results of a study[5a] of the hydrolysis of a ketene *O,S*-acetal were employed in the assignment of the rate-limiting steps in the acid-catalyzed formation[5b] and hydrolysis[5a] of thiol esters. The present paper describes experiments with additional ketene *O,S*-acetals and with an unsymmetrical ketene *O,O*-acetal, and was designed to provide further information on the factors which control the pathways of breakdown of the intermediates formed in the hydrolysis and alcoholysis of esters and thiol esters. In the course of this research, kinetic data have been obtained which suggest the occurrence of a change in rate-determin-