Stable Carbocations. CLXIII.[1] Complexing, Ionization, and Fragmentative Alkylcarbenium Ion Formation from Alkyl Haloformates, Thiolhaloformates, and Halosulfites with Antimony Pentafluoride

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Abstract: Alkyl (aryl) haloformates, thiolhaloformates, and halosulfites form complexes with antimony pentafluoride in SO_2 or SO_2ClF solution. The complexes of alkyl thiolhaloformates gave alkylthiolcarbonyl cations through subsequent ionization, although complexes of alkyl haloformates and halosulfites lost immediately CO_2 and SO_2, respectively, to give corresponding alkyl fluoroantimonates. Thus, the intermediate alkoxycarbonyl and alkoxysulfinyl cations could not be observed as long-lived compounds. In methylation of CO_2, COS, and SO_2 with methyl fluoroantimonate the methoxycarbonyl, methylthiolcarbonyl, and dimethoxyfluorosulfonium ions could be observed, respectively.

Friedel–Crafts reactions of alkyl (aryl) chloroformates,[3] alkyl (aryl) thiolchloroformates,[4] and alkyl chlorosulfites[5] with benzene and substituted benzenes have been studied. Depending on the chloroformates used, either alkylated or alkyl carboxylated aromatics were obtained as a consequence of the difference in the fragmentative ability of the systems. Alkyl chloroformates in the presence of Lewis acids act exclusively as alkylating agents, whereas the alkyl thiolchloroformates either act as carboxylating agents (in case the alkyl groups are methyl, ethyl, *n*-propyl, *n*-butyl, etc.) or as alkylating agents (in case the alkyl groups are isopropyl or *tert*-butyl). The aryl derivatives of both the chloroformates and thiolchloroformates, however, are exclusive carboxylating agents. The reaction of alkyl chlorosulfites with benzenes in the presence of Lewis acids gave only the corresponding alkylated products.

Besides their Friedel–Crafts reactions, the fragmentative behavior of haloesters was also studied in the presence of various Lewis acids, mainly aluminum chloride, on the basis of products formed in the reactions. As the main products of the fragmentation the corresponding alkyl chlorides and olefins, as well as CO_2, COS, SO_2, and HCl, were observed.[6,7] The Ag^+ assisted fragmentation of alkyl chloroformates was also studied.[8,9]

Since it seemed to be of general interest to obtain a more detailed insight of the fragmentation of haloformates, thiolhaloformates, and halosulfites with Lewis acids, we undertook an investigation of their interaction with antimony pentafluoride under stable ion conditions. This allows observation of the entire reaction path, starting with the initial complex formation with the Lewis acid halide, leading eventually to the fragmentation product ions, by use of pmr, fmr (^{19}F), and cmr (^{13}C) spectroscopy.

Results and Discussion

Complexing and Ionization of Alkyl Chloro- or Fluoroformates. Addition of methyl chloroformate to a solution of SbF_5 in SO_2 or SO_2ClF at $-78°$ gives the CH_3OCOCl–SbF_5 complex (**1**) with the Lewis acid attached to the carbonyl oxygen.[10,11] At $-78°$, besides the major pmr peak at δ 4.90 in SO_2ClF (δ 4.47 in SO_2), there is also observed a minor peak which exhibits its resonance more deshielded at δ 4.99 (δ 4.65 in SO_2). Relative to the starting material the protons are deshielded by 0.90 and 0.99 ppm (0.72 and 0.90 ppm in SO_2), respectively. Raising the temperature to $-20°$ results in a gradual change with the minor peak gradually disappearing, whereas the intensity of the major peak increases accordingly. If the temperature is lowered again to $-70°$, the two separate absorptions reappear. To explain this temperature dependence, it is suggested that besides the carbonyl oxygen coordinated complex and low temperature there is also present another complex (either oxygen or halogen coordinated) which is, however, less stable and rearranges (reversibly) at higher temperatures into the former (Scheme I).

At $-10°$ complex **1** with loss of carbon dioxide slowly cleaves, giving through formation of methyl fluoroantimonate[12] (singlet absorption of δ 5.55 in SO_2ClF, $\delta_{^{13}C}$ 116[13] in SO_2 solution, respectively)

(1) Part CLXII: G. A. Olah, G. Liang, P. v. R. Schleyer, E. M. Engler, M. J. S. Dewar, and R. C. Bingham, *J. Amer. Chem. Soc.*, **95**, 6829 (1973).

(2) Postdoctoral Research Associates.

(3) (a) Ng. Ph. Buu-Hoi and J. Janicaud, *Bull. Soc. Chim. Fr.*, **12**, 640 (1945); (b) C. Friedel and J. M. Crafts, *C. R. Acad. Sci.*, **84**, 1450 (1884); (c) C. Friedel and J. M. Crafts, *Ann. Chim. (Paris)*, **6**, 449 (1884); **1**, 527 (1884); (d) V. V. Korshank and G. S. Kolesnikov, *J. Gen. Chem. USSR*, **14**, 435 (1944); (e) F. Kunckell and G. Ulex, *J. Prakt. Chem.*, (2) **86**, 518 (1912); **87**, 227 (1913); (f) E. H. Rennie, *J. Chem. Soc.*, **41**, 33 (1882); (g) S. Yura, *J. Chem. Soc. Jap., Ind. Chem. Sect.*, **51**, 157 (1948); (h) for a review, see M. Matzner, R. P. Kurkjy, and R. J. Kotter, *Chem. Rev.*, **64**, 645, 670 (1964).

(4) (a) G. H. Berezin and G. H. Harris, U. S. Patent 3,219,679 (1961); (b) *Proc. Int. Congr. Pure Appl. Chem.*, **19**, 264 (1963); (c) G. A. Olah and P. Schilling, *Justus Liebigs Ann. Chem.*, **761**, 77 (1972).

(5) G. A. Olah and J. Nishimura, *J. Amer. Chem. Soc.*, in press.

(6) (a) H. W. Underwood, Jr., and O. L. Bail, *J. Amer. Chem. Soc.*, **53**, 2200 (1931).

(7) S. Nakanishi, T. C. Myers, and E. V. Jensen, *ibid.*, **77**, 5033 (1955).

(8) R. Boschan, *J. Amer. Chem. Soc.*, **81**, 3341 (1959).

(9) D. A. Simpson, S. G. Smith, and P. Beak, *ibid.*, **92**, 1071 (1970).

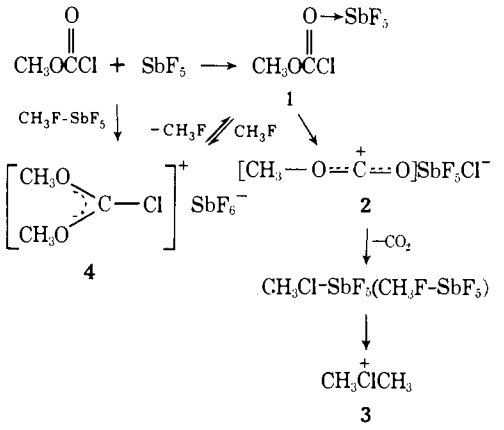
(10) A. Bertoluzza, C. Castellari, and M. A. B. Morelli, *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Natur., Rend.*, **41**, 505 (1966).

(11) A. Bertoluzza, *Corsi Semin. Chim.*, 89 (1967).

(12) Methyl chloride–antimony pentafluoride complex exchanges chlorine with excess antimony pentafluorine to give methyl fluoroantimonate.

(13) G. A. Olah, J. R. DeMember, R. H. Schlosberg, and Y. Halpern, *J. Amer. Chem. Soc.*, **94**, 156 (1972).

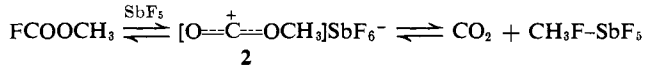
Scheme I



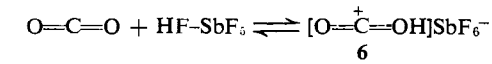
and methyl chloride the dimethylchloronium ion **3** (δ 4.55 in SO_2ClF, δ 4.44 in SO_2). The nmr spectra of the SO_2 solution clearly shows that the stable cleavage product formed at $-10°$ is not methoxycarbonyl cation **2**, which is unstable under the reaction conditions and readily undergoes further cleavage. During the cleavage in SO_2 at $-20°$ a small broadened peak appears at δ 4.75, which at $-40°$ splits into two separate singlets of 1:1 ratio at δ 4.64 and 4.83. This compound is assigned to methylated methyl chloroformate **4**, which can be prepared by the methylation of methyl chloroformate with methyl fluoroantimonate.

Methyl fluoroformate in SO_2 in the presence of SbF_5 shows only a singlet at δ 4.50 (between -78 and $-20°$), deshielded by 0.85 ppm from that of the precursor, characteristic of the donor–acceptor complex CH_3OCOF–SbF_5 (**5**). The fmr spectrum shows a relatively broad fluorine signal in this temperature range, which is found at ϕ 4.43, deshielded by 13.9 ppm from that of the precursor (ϕ 18.34). At 0° the fluorine signal disappears due to the irreversible fragmentation of the complex into methyl fluoroantimonate.

The methoxycarbonyl cation **2** is of substantial interest, not only as a possible intermediate in the acid-catalyzed fragmentative methylations with methyl haloformates but also as the product of the possible electrophilic methylation of carbon dioxide.



Indeed, when methyl fluoroantimonate (CH_3F–SbF_5 complex) reacts with CO_2 at $-20°$, under ~35 atm of CO_2, the resulting solution forms two layers and cooled back to $-70°$ indicates formation of **2** displaying in SO_2ClF solution a singlet at δ 5.60.[14] The reversibility of the cleavage of the methoxycarbonyl cation **2** is thus experimentally proven, as direct methylation of CO_2 can be achieved, similarly to obtained evidence of protonation of CO_2 to CO_2H^+ (**6**) in superacids.[15] The role of **2** and **6** in methoxycarbonylation (or fragmentative

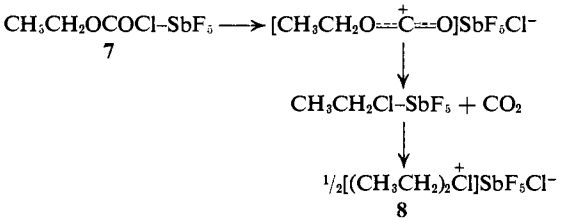


methylation) and carboxylation reactions, respectively, will be discussed separately.

(14) G. A. Olah and K. Dunne, unpublished work.
(15) G. A. Olah and J. Shen, *J. Amer. Chem. Soc.*, **95**, 3582 (1973).

Ethyl chloroformate reacts with SbF_5 in SO_2ClF at $-78°$ giving the CH_3CH_2OCOCl–SbF_5 complex **7**, with SbF_5 attached to the carbonyl oxygen atom. At $-60°$ the pmr spectrum consists of two overlapping triplets (δ 2.08 and 2.04, J_{HH} = 7.0 Hz) and two overlapping quartets (δ 5.55 and 7.60, J_{HH} = 7.0 Hz) due to the two conformers (carbonyl group located cis and trans to the ethyl group). At $-10°$ one sharp triplet at δ 2.20 (J_{HH} = 7.0 Hz) and one sharp quartet at 5.70 (J_{HH} = 7.0 Hz) can be observed indicating a fast rotation around the C–O bond. When the solution is cooled back to $-60°$ the two isomers can be observed again separately. Keeping the solution at 10° results in the ionization of **7** giving the diethylchloronium ion **8** as the stable fragmentation product (δ 2.30, triplet, J_{HH} = 8.0 Hz; δ 5.90, quartet, J_{HH} = 8.0 Hz) (Scheme II). The ethoxycarbonyl cation could not be observed.

Scheme II



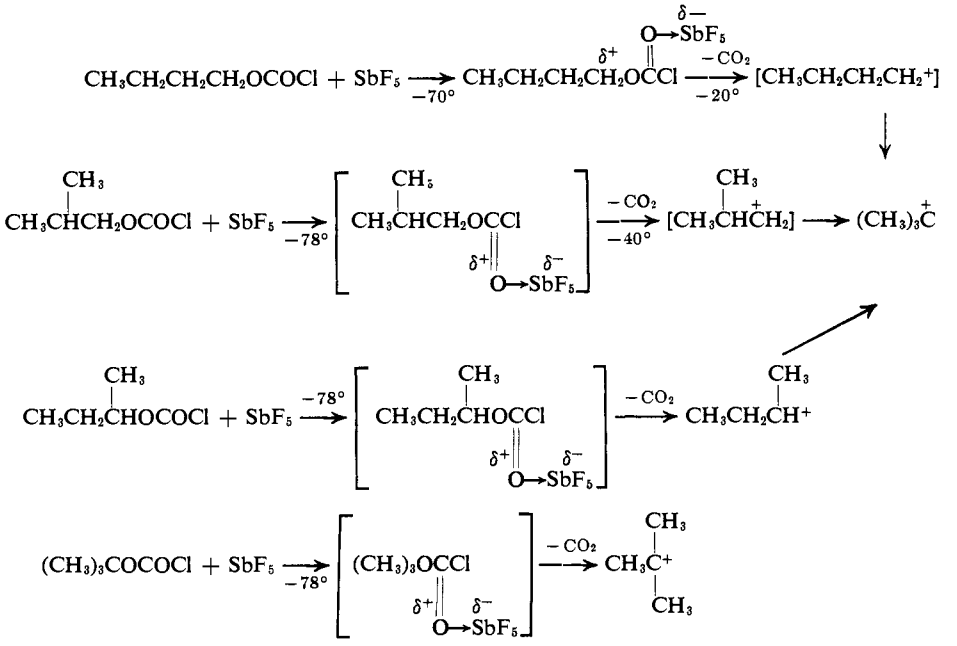
Using SO_2 as the solvent the fragmentation of **7** already takes place at $-20°$ giving **8** as the stable end product (δ 1.80, triplet, J_{HH} = 7.0 Hz; δ 5.05, quartet, J_{HH} = 7.0 Hz), through obvious ethylation of intermediately formed ethyl chloride.

Ethyl fluoroformate forms upon reaction with SbF_5 in SO_2 at $-70°$ the CH_3CH_2OCOF–SbF_5 complex **9** (δ 1.30, triplet, J_{HH} = 7 Hz; δ 4.95, quartet, J_{HH} = 7 Hz). No ionization of this complex occurs in the temperature range -80 to $-20°$ since in the pmr spectrum the quartet at δ 6.22 and the triplet at δ 1.94 characteristic for ethyl fluoroantimonate (**10**) (CH_3CH_2F–SbF_5 complex) cannot be detected. The fmr spectrum of **9** shows a quintet at ϕ 3.72 (J_{FF} = 8 Hz) deshielded by 13.74 ppm from the precursor which shows a singlet at ϕ 17.46 (SO_2, $-60°$). When raising the temperature to $-20°$ the quintet disappears and only a broad absorption with the same chemical shift can be observed; cooling the solution back to $-70°$ results in the reappearance of the quintet. This behavior of the complex indicates intramolecular equilibration. By further increasing the temperature the singlet absorption merges with that of solvent SbF_5 indicating intermolecular fluorine exchange.[16a]

***n*-Propyl chloroformate** forms with SbF_5 in SO_2ClF at $-70°$ the C_3H_7OCOCl–SbF_5 complex **11** exhibiting a triplet at δ 1.55 (J_{HH} = 7 Hz) and two broad multiplets at δ 2.44 and 5.57. Relative to the precursor the absorptions of **11** are deshielded by 0.42, 0.54, and 1.17 ppm, respectively. On warming the solution to $-20°$ a low intensity doublet at δ 4.60 (J_{HH} = 5 Hz) appears indicative of the intermediate formation of the isopropyl cation exchanging with isopropyl chloride in the system[16b] (see subsequent discussion). The same ion is observed when isopropyl chloroformate is reacted with SbF_5. When the temperature of the solu-

(16) (a) G. A. Olah, Y. K. Mo, and Y. Halpern, *J. Org. Chem.*, **37**, 1169 (1972); (b) G. A. Olah and Y. K. Mo, *J. Amer. Chem. Soc.*, in press.

Scheme III



tion is kept at −20° as final reaction product a mixture of *tert*-hexyl cations[17] is formed.

Isopropyl chloroformate forms the relatively unstable *i*-C_3H_7OCOCl–SbF_5 complex **12** at −78° in SO_2ClF. The pmr spectrum of **12** shows a triplet at δ 2.08 (as a result of two overlapping doublets at δ 2.05 and 2.10) and a broad signal at δ 6.40 for the methine proton. Relative to the starting material the signals are deshielded by 0.63 and 1.80 ppm, respectively. By raising the temperature the complex then starts to cleave and at −50° the pmr spectrum shows a doublet for the methyl protons at δ 4.60 and the relatively broad signal for the methine proton at δ 9.75. This spectrum is characteristic of the exchanging isopropyl cation (**13**)–diisopropylchloronium ion (**14**) system.[16b] For the isopropyl cation (**13**), the corresponding proton shifts are at δ 4.50 and 13.0, whereas for the diisopropylchloronium ion (**14**) they are at δ 1.92 and 4.68. Keeping the solution at −30° for 30 min results in the irreversible formation of a mixture of *tert*-hexyl cations.[17]

***n*-Butyl chloroformate** forms with SbF_5 at −70° in SO_2ClF the donor–acceptor complex C_4H_9OCOCl–SbF_5 (**15**) which is stable to about −40°. The pmr spectrum of **15** consists of a relatively broad triplet at δ 1.40 and three broad signals at δ 1.95, 2.26, and 5.55, deshielded by 0.35, 0.35, 0.60, and 1.15 ppm, respectively, from the precursor. The broad signals are indicative of exchange in the systems. On warming the solution to −20° the *tert*-butyl cation is formed besides a small amount of polymeric material.

Isobutyl chloroformate also forms a donor–acceptor complex with SbF_5, *i.e.*, *i*-C_4H_9OCOCl–SbF_5 (**16**) at −70° in SO_2ClF. The pmr spectrum consists of a doublet at δ 1.50 and two broad multiplets at δ 2.66 and 5.30. These signals are deshielded by 0.50, 0.64, and 1.20 ppm, respectively, from the starting material. At −40° the complex is completely cleaved and rearranged to the *tert*-butyl cation.

***sec*-Butyl and *tert*-butyl chloroformate** are too reactive to allow observation even at −78° of complexes with SbF_5. The immediately observed cleavage product in both cases is the *tert*-butyl cation (Scheme III).

Phenyl and substituted phenyl chloroformates form stable donor–acceptor complexes (**17**) with SbF_5 at −78°. No cleavage is observed when the solutions are warmed up to −20°. At higher temperatures bimolecular reactions give diphenylcarbonates. In the case of electron-donating substituents on the aromatic ring (CH_3, CH_3O, and CH_3S), polycondensation or reaction of SbF_5 with the aromatic rings prevents the observation of stable donor–acceptor complexes. For a summary of the pmr data of the complexes see Table I.

Complexing and Ionization of Alkyl Thiolchloro- and Thiolfluoroformates. Methyl thiolchloroformate reacts with SbF_5 in SO_2 or SO_2ClF at −78° to give the corresponding donor–acceptor complex CH_3SCOCl–SbF_5 (**18**), which is stable up to −30°. In both solvents the pmr spectrum of **18** shows a temperature-independent singlet at δ 2.80 in SO_2 and δ 3.43 in SO_2ClF, which is deshielded by 0.58 (SO_2) and 0.88 (SO_2ClF) ppm from the precursor. At −30° ionization to the (methylthiol)-carbonyl cation CH_3SCO^+ (**19**) occurs. The pmr spectrum of **19** consists of a singlet at δ 3.57 in SO_2 (3.97 in SO_2ClF). The cmr spectrum clearly shows the ion **19** by two resonances at $\delta_{^{13}C}$ 172 for the methyl and $\delta_{^{13}C}$ 34.6 for the carbonyl carbon in SO_2 at −50°.

In SO_2ClF even in the presence of a large excess of SbF_5 the donor–acceptor complex **18** undergoes only partial ionization. In contrast to corresponding methoxycarbonyl cation **2**, ion **19** shows high stability and does not fragment below 25°. Even under more severe conditions, for example when complex **18** was heated in AsF_3 to 60°, no fragmentation could be observed. However, when CH_3SCOCl is treated with $SbCl_5$ in methylene chloride, fragmentation takes place at 0° giving CH_3Cl and COS. In the temperature range −100 to 0° the donor–acceptor complex CH_3SCOCl–$SbCl_5$ (**20**) is observed (δ 3.23, singlet). When the solution is kept at 0° the fragmentation reaction (which is a relatively slow process at this temperature) can be observed with formation of the CH_3Cl–$SbCl_5$ complex

(17) G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **89**, 4739 (1967).

Table I. ^{1}H-Nmr Spectroscopic Parameters of Alkyl (Aryl) Chloro- (Fluoro-) Formates, Their Donor–Acceptor Complexes with SbF_5, and Their Fragmentation Products

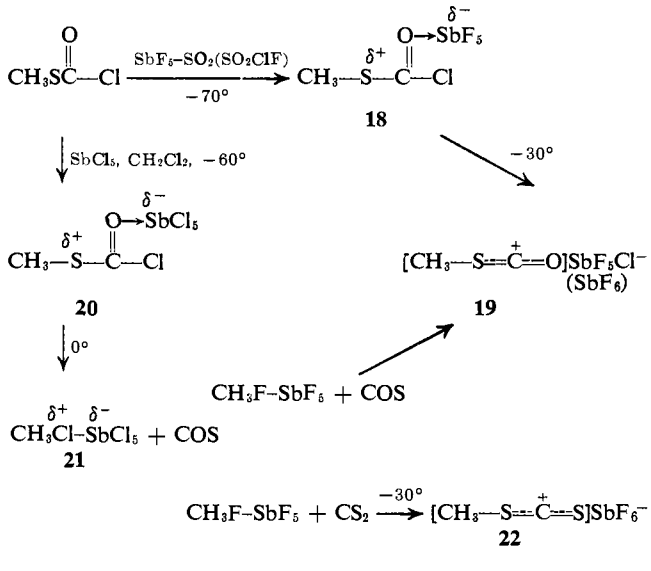
Substrate	Solvent	Precursor	Donor–acceptor complex	Fragmentation products
CH_3OCOCl	SO_2	3.75 (s)	4.47 (s), 4.65 (s) −70° [a]	Methyl fluoroantimonate[b] 5.34 (s) and dimethylchloronium ion 4.44 (s)
	SO_2ClF	4.00 (s)	4.90 (s), 4.99 (s) −70° [a]	Methyl fluoroantimonate 5.55 (s) and dimethylchloronium ion 4.55 (s)
CH_3OCOF	SO_2	3.65 (s)[c]	4.50 (s)[d]	
C_2H_5OCOCl	SO_2	1.08 (t), 4.10 (q)	1.50 (t), 4.95 (q)	Diethylchloronium ion 1.80 (t), 5.05 (q)
	SO_2ClF	1.45 (t), 4.46 (q)	2.04 (t), 2.08 (t), 5.55 (m), 5.70 (q) −70°	Diethylchloronium ion 2.30 (t), 5.90 (q)
C_2H_5OCOF	SO_2	1.05 (t), 3.92 (q)[e]	1.30 (t), 4.95 (q)[f]	
n-C_3H_7OCOCl	SO_2	0.70 (t), 1.36 (m), 4.05 (q)	1.10 (t), 2.00 (m), 5.00 (m)	*tert*-Hexyl cations
	SO_2ClF	1.13 (t), 1.90 (m), 4.40 (t)	1.55 (t), 2.44 (m), 5.57 (m)	Isopropyl cation → isomeric *tert*-hexyl cations
i-C_3H_7OCOCl	SO_2		Not observed	*tert*-Hexyl cations
	SO_2ClF	1.45 (d), 4.60 (spt)	2.05 (d), 2.10 (d), 6.40 (m)	Isopropyl cation → isomeric *tert*-hexyl cations
n-C_4H_9OCOCl	SO_2	0.80 (t), 1.10–1.90 (m), 4.20 (t)	0.90 (t), 1.60 (m), 1.90 (m), 5.00 (t)	*tert*-Butyl cation
	SO_2ClF	1.05 (t), 1.30–2.00 (m), 4.40 (t)	1.40 (t), 1.95 (m), 2.26 (m), 5.55 (t)	*tert*-Butyl cation
i-C_4H_9OCOCl	SO_2ClF	1.00 (d), 2.02 (m), 4.10 (d)	1.50 (d), 2.66 (m), 5.30 (m)	*tert*-Butyl cation
sec-C_4H_9OCOCl	SO_2ClF	1.13 (t), 1.48 (d), 1.78 (q), 5.01 (m)	Not observed	*tert*-Butyl cation
t-C_4H_9OCOCl	SO_2ClF	1.58 (s)	Not observed	
C_6H_5OCOCl	SO_2	7.16 (m)	7.45 (m)	
4-FC_6H_4OCOCl	SO_2	7.00 (m)	7.20 (m)	
4-ClC_6H_4OCOCl	SO_2	6.98 (m), 7.23 (m)	7.28 (m), 7.60 (m)	
4-BrC_6H_4OCOCl	SO_2	7.07 (m), 7.48 (m)	7.25 (m), 7.68 (m)	
4-$NO_2C_6H_4OCOCl$	SO_2	7.30 (m), 8.09 (m)	7.95 (m), 8.92 (m)	
4-$CH_3C_6H_4OCOCl$	SO_2	2.10 (s), 6.86 (m), 7.10 (m)	2.30 (s), 7.33 (s)	

[a] During fragmentation, methylated methyl chloroformate was observed (see text). [b] $\delta_{^{13}C}$ 116. [c] ϕ 18.34. [d] ϕ 4.43. [e] ϕ 17.46. [f] ϕ 3.72 (quintet, J_{FF} = 8).

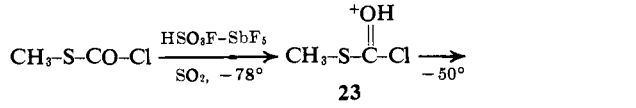
21 as stable end product (δ 3.65, singlet). The intermediate (methylthiol)carbonyl cation **19** cannot be observed in the $SbCl_5$ containing system.

Ion **19** cannot only be formed by ionization of methyl thiolchloroformate but also by methylation of COS with methyl fluoroantimonate. When COS is condensed into a solution of methyl fluoroantimonate, in SO_2 at −60°, besides the singlet absorption of methyl fluoroantimonate at δ 5.45, a new singlet at δ 3.62 appears in the pmr spectrum of the solution. The chemical shift for the methyl protons indicates that methylation of COS takes place exclusively on sulfur, which has the higher nucleophilicity. CS_2 was also methylated by the same method giving the (methylthiol)thiocarbonyl cation CH_3SCS^+ (**22**) whose pmr spectrum shows a singlet at δ 3.40, close to the absorpton of S-methylated COS, **19** (Scheme IV).

Scheme IV



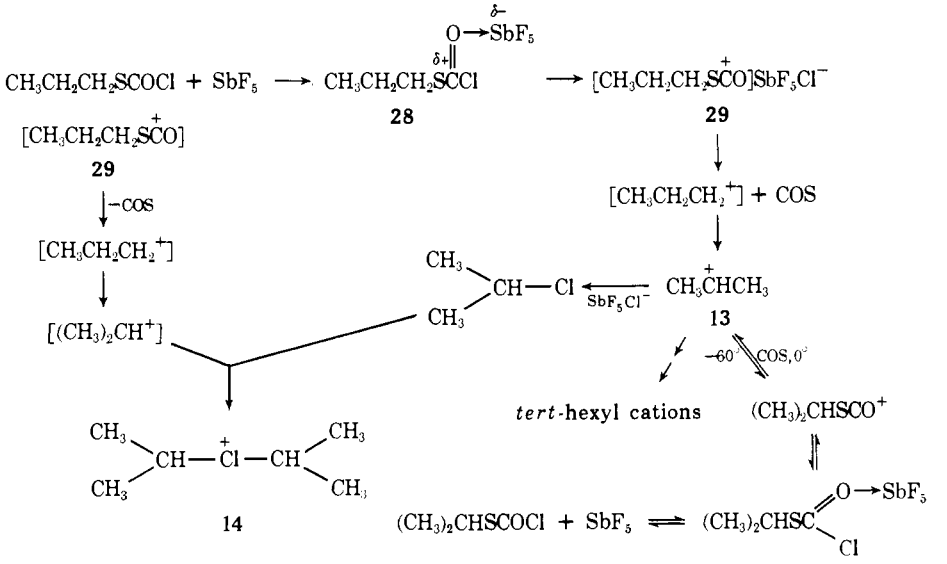
When CH_3SCOCl is dissolved in FSO_3H–SbF_5 (1:1)–SO_2 the corresponding O-protonated species **23** can be observed at −78°. The pmr spectrum shows the methyl protons as a singlet at δ 3.15 and the proton on oxygen as a singlet at δ 14.15. On warming the solution to −50° the low-field OH signal disappears and the signal of the methyl group is shifted to δ 3.66, characteristic of the methyl shift of the methylthiolcarbonyl cation **19**.



Methyl thiolfluoroformate when treated with SbF_5 in SO_2 at −78° gives the O-coordinated complex CH_3SCOF–SbF_5 (**24**). Warming the solution to −30° results in ionization to the (methylthiol)carbonyl cation **19**. The pmr shift of **24** is δ 2.85 (SO_2). The fmr spectrum consists of a quintet at ϕ −40.57 which is shielded by 2.76 ppm from that of methyl thiolfluoroformate (ϕ −43.33). The quintet (J_{FF} = 7.8 Hz) indicates that complexed SbF_5 is coupled to the fluorine of CH_3SCOF. At −30° the fluorine signal disappears as a result of ionization of the donor–acceptor complex and formation of the (methylthiol)carbonyl cation **19**.

Ethyl thiolchloroformate when treated with SbF_5 in SO_2 or SO_2ClF at −70° gives the O-coordinated donor–acceptor complex CH_3CH_2SCOCl–SbF_5 (**25**). The pmr spectrum of **25** in both solvents consists of a triplet (δ 200 in SO_2ClF and δ 1.42 in SO_2) and a quartet (δ

Scheme V



3.97 in SO_2ClF and δ 3.40 in SO_2) with a coupling constant J_{HH} = 7.8 Hz. Relative to its precursor the proton shifts of complex **25** are deshielded by 0.43 and 0.94 ppm in SO_2ClF and by 0.24 and 0.55 ppm in SO_2. Ionization of **25** gave the (ethylthiol)carbonyl cation $C_2H_5SCO^+$ (**26**) at −50° in SO_2 and at −30° in SO_2ClF solution. In the latter solvent, no complete ionization does occur even in the presence of a large excess of SbF_5 and keeping the solution for several hours at −10°. The proton signals for ion **25** are found at δ 2.37 (triplet, J_{HH} = 7 Hz) and δ 4.78 (quartet) using SO_2ClF as the solvent [δ 1.83 (triplet, J_{HH} = 7 Hz) and δ 4.40 (quartet) when SO_2 is used]. The proton shifts in ion **26** are deshielded by 0.37 and 0.81 ppm (SO_2ClF) and 0.41 and 1.00 ppm (SO_2) relative to the donor–acceptor complex **25**. The same ion **26** could be obtained by adding ethyl thiolchloroformate to a solution of SbF_5 in AsF_3 at −10° (triplet at δ 2.55, J_{HH} = 7; quartet at δ 4.98). Further fragmentation of **26** did not occur in SO_2ClF and AsF_3 solution. In SO_2 solution at −20°, however, partial fragmentation with formation of COS and diethylchloronium ion **8** (*via* ethylation of formed ethyl chloride) can be observed.

Ethyl thiolfluoroformate with SbF_5 at −70° in SO_2 gives the C_2H_5SCOF–SbF_5 complex **27**. The pmr spectrum of **27** is quite similar to those of the chloroformate complex **25**. The fmr spectrum of **27** shows a quintet at ϕ −42.66 shielded by 2.65 ppm from the precursor (ϕ −45.35).

***n*-Propyl thiolchloroformate** reacts differently with SbF_5 in SO_2ClF at −78°. Besides the donor–acceptor complex C_3H_7SCOCl–SbF_5 (**28**), the major reaction product observed even at this temperature is the diisopropylchloronium ion **14**. The pmr spectrum of **28** consists of a triplet at δ 1.42 (J_{HH} = 7 Hz), a multiplet at δ 2.11, and a multiplet at δ 3.70. Ion **14** shows a doublet at 1.92 (J_{HH} = 8 Hz) and a septet at δ 4.68. The proton chemical shifts of the donor–acceptor complex **28** are deshielded by 0.29, 0.26, and 0.70 ppm, respectively, from the precursor. The spectra are temperature independent between −80 and −30°, thus indicating no exchange processes to take place. Keeping the solution at −20° results in the formation of a mixture of *tert*-hexyl ions[17] (Scheme V). The same behavior is observed when the reaction is carried out in SO_2 solution. However, when *n*-propyl thiolchloroformate is added to a large excess of SbF_5 in SO_2ClF at −78° only a small amount of the donor–acceptor complex **28** can be detected in the pmr spectrum of the solution. The major feature of the spectrum at −60° consists of a doublet at δ 3.55 (J_{HH} = 7 Hz) and a multiplet at δ 9.32. The spectrum is temperature dependent and at 0° the doublet is shifted to δ 4.22 and the multiplet is found at δ 11.85. Since this process is reversible and no formation of *tert*-hexyl cations occurs even at 0°, we have to assume a temperature-dependent equilibration most probably between the isopropyl cation **13** and diisopropylchloronium ion **14** formed in the system. The same behavior is observed when isopropyl thiolchloroformate is reacted with SbF_5, to be discussed subsequently. The (*n*-propylthiol)carbonyl cation, **29**, which must be intermediately formed in the process, is not observed directly under the reaction conditions.

Isopropyl thiolchloroformate reacts with SbF_5 in SO_2 or SO_2ClF at −78° to give the corresponding *i*-C_3H_7-SCOCl–SbF_5 complex **30**. The pmr spectrum consists of two overlapping doublets for the methyl protons at δ 1.80 and 1.95 (J_{HH} = 6.8) and a multiplet for the methine proton at δ 4.46 in SO_2ClF as solvent. In SO_2 the corresponding proton shifts are found at δ 1.63, 1.79, and 4.20, respectively. Relative to the starting material the shifts of **30** are deshielded by 0.38, 0.53, and 0.66 ppm in SO_2ClF and 0.43, 0.59, and 0.62 in SO_2. At −40° (in SO_2ClF) complex **30** ionizes to the isopropyl cation **13**, which shows the temperature-dependent equilibrium with diisopropylchloronium ion **14** which is formed in the solution, as discussed previously. At −80° the doublet for the methyl protons is found at δ 2.70 and the broad unresolved multiplet for the methine proton at δ 7.40. Warming the solution to −20° results in deshielding of the absorptions. The doublet which appears as a broad singlet at this temperature is found at δ 3.98 and the broad multiplet for the methine proton is at δ 11.40. Keeping the solution at −10° for a longer period results in the slow formation of the isomeric *tert*-hexyl cations formed from the isopropyl cation, which is not stable under the reaction conditions.

***n*-Butyl thiolchloroformate** reacts with SbF_5 in SO_2 or

Table II. ^{1}H-Nmr Spectroscopic Parameters of Alkyl (Aryl) Thiolchloro- (fluoro-) formates, Their Donor–Acceptor Complexes with SbF_5, Alkylthiolcarbonyl Cations, and Their Fragmentation Products

Substrate	Solvent	Precursor	Donor–acceptor complex	Alkylthiolcarbonyl cation	Fragmentation products
CH_3SCOCl	SO_2	2.22 (s)	2.80 (s)	3.75 (s) ($\delta^{13}C$ 34.6 and 172)	
	SO_2ClF	2.55 (s)	3.43 (s)	3.97 (s)	
CH_3SCOF	SO_2	2.25 (s)[a]	2.85 (s)[b]	3.60 (s)	
C_2H_5SCOCl	SO_2	1.18 (t), 2.85 (q)	1.42 (t), 3.40 (q)	1.83 (t), 4.40 (q)	Diethylchloronium ion 1.83 (t), 5.06 (q)
	SO_2ClF	1.47 (t), 3.03 (q)	2.00 (q), 3.97 (q)	2.37 (t), 4.78 (q)	
C_2H_5SCOF	SO_2	1.18 (t), 2.83 (q)[c]	1.50 (t), 3.40 (q)[d]	1.90 (t), 4.40 (q)	
n-C_3H_7SCOCl	SO_2	0.76 (t), 1.50 (m), 2.77 (t)	1.18 (t), 1.92 (m), 3.50 (m)	Not observed	Isomeric *tert*-hexyl cations
	SO_2ClF	1.13 (t), 1.85 (m), 3.00 (t)	1.42 (t), 2.11 (m), 3.70 (t)	Not observed	Diisopropylchloronium ion 1.92 (d), 4.68 (spt)
i-C_3H_7SCOCl	SO_2	1.20 (d), 3.58 (spt)	1.63 (d), 1.79 (d), 4.20 (m)	Not observed	Isomeric *tert*-hexyl cations
	SO_2ClF	1.42 (d), 3.80 (spt)	1.80 (d), 1.95 (d), 4.46 (m)	Not observed	Equilibrium between diisopropylchloronium ion (2.70 (d), 7.20 (m) −80°) and isopropyl cation (3.98 (s), 11.40 (m) −20°)
n-C_4H_9SCOCl	SO_2	0.65 (t), 1.00–1.70 (m), 2.79 (t)	0.95 (t), 1.50–2.30 (m), 3.50 (m)	Not observed	*tert*-Butyl cation
	SO_2ClF	1.05 (t), 1.40–2.10 (m), 3.05 (t)	1.22 (t), 1.70–2.40 (m), 3.90 (m)	Not observed	*tert*-Butyl cation
t-C_4H_9SCOCl	SO_2ClF	1.60 (s)	Not observed	Not observed	*tert*-Butyl cation
C_6H_5SCOCl	SO_2	7.37 (s)	7.71 (s)	7.70–7.20 (m)	
	SO_2ClF	7.60 (s)	8.17 (m)	8.38 (m)	
4-FC_6H_4SCOCl	SO_2	7.08 (m), 7.40 (m)	7.80 (m)	7.55 (m), 8.14 (m)	
4-ClC_6H_4SCOCl	SO_2	7.33 (s)	7.76 (s)	7.76 (m), 8.06 (m)	
4-BrC_6H_4SCOCl	SO_2	7.26 (m), 7.50 (m)	7.65 (m), 7.84 (m)	8.00 (m)	
4-$CH_3C_6H_4SCOCl$	SO_2	2.17 (s), 7.10 (m), 7.22 (m)	2.50 (s), 7.60 (s, broad)	7.68 (m), 8.00 (m)	
4-$NO_2C_6H_4SCOCl$	SO_2	7.33 (m), 8.05 (m)	8.28 (m), 8.90 (m)		

[a] ϕ −43.33. [b] ϕ −40.57 (quintet, J_{FF} = 7.8). [c] ϕ −45.35. [d] ϕ −42.66.

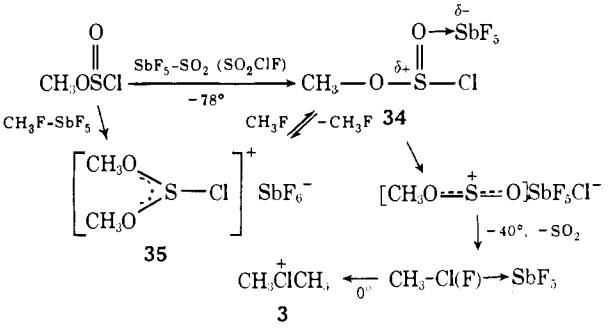
SO_2ClF at −78° to give the donor–acceptor complex $C_4H_9SOCOCl$–SbF_5 (**31**). The pmr spectrum of **31** consists of a triplet at δ 1.22, two overlapping multiplets at δ 1.70–2.40, and a multiplet at δ 3.90. (In SO_2 the corresponding proton absorptions are found at δ 0.95, 1.50–2.30, and 3.50, respectively.) Warming the solution of **31** to −20° resulted in formation of the *tert*-butyl cation as the only observable product formed through ionization of **31** followed by fragmentation and rearrangement.

***tert*-Butyl thiolchloroformate** with SbF_6 even at −78° gives the *tert*-butyl cation. No intermediate complex could be observed.

Phenyl- and substituted phenyl thiolchloroformates give stable donor–acceptor complexes, **32-X**, when treated with SbF_5 in SO_2 or SO_2ClF at −70°. Except in the cases when electron-donating substituents are present on the aromatic ring (CH_3O and CH_3), these complexes are stable up to −40°. The pmr data are summarized in Table II. At −30° ionization of the donor–acceptor complexes to the corresponding cations **33-X** occurs. The latter ions are stable and no further cleavage occurs in the temperature range studied (up to 10°).

Complexing and Ionization of Alkyl Chloro- and Fluorosulfites.[18] **Methyl chlorosulfite,** when reacted with SbF_5 in SO_2 or SO_2ClF at −78°, forms the corresponding donor–acceptor complex CH_3OSOCl–SbF_5 (**34**). The pmr spectrum of **34** shows in both solvents a singlet (δ 4.77 in SO_2ClF and δ 4.55 in SO_2) which is deshielded from that of the precursor by 0.50 ppm (SO_2ClF) and 0.57 ppm (SO_2). On warming the solutions to −40° fragmentation to methyl fluoroantimonate takes place, consistent with the singlet at δ 5.65 (SO_2ClF) (δ 5.40 in SO_2). Prolonged warming of the solution to −20° (SO_2) or 0° (SO_2ClF) results in the formation of the dimethylchloronium ion **3**. Even if the precursor and SbF_5 were mixed in SO_2 (SO_2ClF) at −80 to −90° carefully, another singlet besides **34** (25–35% based on **34**) appeared at δ 4.67 (SO_2) (δ 4.87 in SO_2ClF) in the pmr spectrum. This slightly low-field peak from **34** coincides with that of O-methylated methyl chlorosulfite **35** from the reaction of methyl chlorosulfite and methyl fluoroantimonate, which also fragments to give methyl fluoroantimonate and complex **34** (Scheme VI).

Scheme VI



Methyl fluorosulfite shows the same behavior as methyl chlorosulfite. However, if it was mixed carefully with SbF_5 in SO_2 at −78°, the complex CH_3OSOF–SbF_5 (**35**) (δ 4.66, ϕ −28.1) could be prepared in the pure state. Warming up to −20°, the complex loses

(18) G. A. Olah, A. T. Ku, and J. A. Olah, *J. Org. Chem.*, **35**, 3929 (1970).

Table III. ^{1}H-Nmr Spectroscopic Parameters of Alkyl Chlorosulfites, Their Donor–Acceptor Complexes with SbF_5, and Their Fragmentation Products

Substrate	Solvent	Precursor	Donor–acceptor complex	Fragmentation products
CH_3OSOCl	SO_2	3.98 (s)	4.55 (s)[a]	Methyl fluoroantimonate 5.40 (s)
	SO_2ClF	4.27 (s)	4.77 (s)[a]	Methyl fluoroantimonate 5.65 (s), dimethylchloronium ion 4.60 (s)
CH_3OSOF	SO_2	3.79 (s) (ϕ −52.9)	4.66 (s)[a] (ϕ −28.1)	Methyl fluoroantimonate 5.47 (s) ($\delta_{^{13}C}$ 116)
	SO_2ClF	4.05 (s) (ϕ −53.1)	4.60 (s)[a] (ϕ −27.4)	Methyl fluoroantimonate
CH_3CH_2OSOCl	SO_2	1.22 (t), 4.40 (q)	1.58 (t), 5.10 (q)[a]	Ethyl fluoroantimonate, diethylchloronium ion 1.80 (t), 5.05 (q)
	SO_2ClF	1.57 (t), 4.70 (m)	1.87 (t), 5.33 (q)[a]	Diethylchloronium ion 2.14 (t), 5.32 (q)
CH_3CH_2OSOF	SO_2	1.29 (t), 4.60 (q) (ϕ −56.6)	1.57 (t), 5.10 (q)[a] (ϕ −31.6)	Ethyl fluoroantimonate
	SO_2ClF	1.53 (t), 4.64 (q) (ϕ −57.0)	1.78 (t), 5.10 (q)[a] (ϕ −33.2)	Ethyl fluoroantimonate
n-C_3H_7OSOCl	SO_2	0.78 (t), 1.62 (m), 4.28 (t)	Not observed	Isopropyl cation giving *tert*-hexyl cations
i-C_3H_7OSOCl	SO_2	1.23 (d), 5.36 (spt)	Not observed	Isopropyl cation giving *tert*-hexyl cations
n-C_4H_9OSOCl	SO_2	0.71 (t), 1.00–1.90 (m), 4.29 (t)	Not observed	*tert*-Butyl cation
i-C_4H_9OSOCl	SO_2	0.80 (d), 1.90 (m), 4.13 (d)	Not observed	*tert*-Butyl cation
sec-C_4H_9OSOCl	SO_2	0.80 (t), 1.30 (d), 1.33 (m), 5.12 (m)	Not observed	*tert*-Butyl cation

[a] During fragmentation, methylated methyl halosulfite or ethylated ethyl halosulfite was formed.

SO_2 to give methyl fluoroantimonate (δ 5.47). The cmr spectrum shows only one peak at $\delta_{^{13}C}$ 116, which is identical with the shift of methyl fluoroantimonate.[13] At 0° the methyl fluoroantimonate reacts with solvent SO_2, followed by methylation with excess methylating agent to give O-methylated methyl fluorosulfite **37** (doublet at δ 4.89, J_{HF} = 2.0; septet at ϕ −16.7) as the end product. The structure could be assigned based on identity with the product of the reaction of methyl fluorosulfite and methyl fluoroantimonate. This also proves the reversibility of the fragmentation reaction of complex **36**.

$$CH_3F\text{–}SbF_5 + SO_2 \rightleftharpoons CH_3O(O\rightarrow SbF_5)F \quad \underset{-CH_3F\text{–}SbF_5,\ +SbF_5}{\overset{+CH_3F\text{–}SbF_5,\ -SbF_5}{\rightleftharpoons}}$$

36

$$[CH_3O(OCH_3)SF]\ SbF_6^-$$

37

Ethyl chlorosulfite also forms with SbF_5 at −78° in SO_2 or SO_2ClF as solvent a donor–acceptor complex (C_2H_5OSOCl–SbF_5 (**38**)) and ethylated ethyl chlorosulfite. The pmr spectrum at −80° consists of two overlapping triplets at δ 1.58 and 1.60 (J_{HH} = 7.8 Hz) in SO_2 and δ 1.87 and 1.90 (J_{HH} = 7.5 Hz) in SO_2ClF and two overlapping quartets at δ 5.10 and 5.20 (J_{HH} = 7.8 Hz) in SO_2 and δ 5.33 and 5.40 (J_{HH} = 7.5 Hz) in SO_2ClF. Slightly low-field signals can be made also by the ethylation of ethyl chlorosulfite with ethyl fluoroantimonate (**10**). On warming the solution gradually to −20°, ionization of the complex can be observed. The intermediate ethoxysulfinyl cation **39** is not observed. The only stable species present in the solution is the diethylchloronium ion **8**, showing a triplet at δ 1.80 (J_{HH} = 7.1 Hz) in SO_2 (δ 2.14, J_{HH} = 7.1 Hz in SO_2ClF) and a quartet at δ 5.05 in SO_2 (δ 5.32 in SO_2ClF) in its pmr spectrum. In the case, however, where a large excess of SbF_5 is used the ethyl fluoroantimonate (**10**) is formed in addition to **8**. As described previously, the pmr spectra of **10** show temperature dependence due to the fast intramolecular proton exchange reaction. In the present case, **10** can be identified in the pmr spectrum of the solution of **38**, after it was kept at −20° and then cooled back to −60°. At this temperature a new quartet at δ 6.27 and a triplet at δ 1.95 (J_{HH} = 7.1 Hz) appear. Warming the solution back to −20° these absorptions disappear, whereas the spectrum of the diethylchloronium ion remains unchanged. These data indicate that at the higher temperature C_2H_5F–SbF_5 exchanges with solvent SbF_5 but no exchange with the diethylchloronium ion takes place.

Ethyl fluorosulfite forms the complex $C_2H_5OSOF\rightarrow SbF_5$ (**40**) with SbF_5 at −78° in SO_2. Besides this complex, small amounts of ethylated ethyl fluorosulfite (**41**) appear at slightly lower field from **40**. The pmr spectrum shows a quartet at δ 5.10 (J_{HH} = 7.0 Hz), a quartet at δ 5.45 (J_{HH} = 7.0 and J_{HF} = 2.0), and two overlapping triplets at δ 1.58 and 1.77. Both decrease at −20° and make the C_2H_5F–SbF_5 complex, which finally condenses at 0° to give *tert*-butyl cation and isomeric *tert*-hexyl cations. The ethylated ethyl fluorosulfite also was formed in the SO_2 solution of the C_2H_5F–SbF_5 complex but could not be obtained in high yield because of the fast rate of the condensation of the C_2H_5F–SbF_5 complex. In SO_2ClF, ethyl fluorosulfite reacts with SbF_5 to give complex **40** and ethylated ethyl fluorosulfite (**41**) in about equal amounts at −78°. The fmr spectrum shows two resonances at ϕ −31.6 for **40** in SO_2 (ϕ −33.2 in SO_2ClF) and at ϕ −23.3 for **41** (ϕ −23.3 in SO_2ClF).

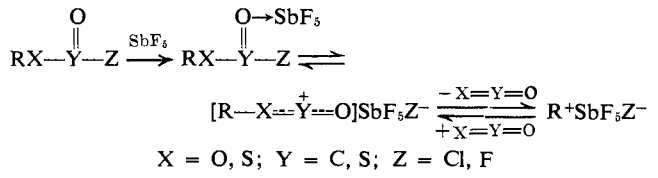
***n*-Propyl and isopropyl chlorosulfite** are too reactive to allow observation of donor–acceptor complexes with SbF_5 at −78° in SO_2 as solvent. Addition of SbF_5 to either *n*-propyl- or isopropyl chlorosulfite at −78° resulted in solutions whose pmr spectra show a doublet at δ 2.00 (J_{HH} = 6 Hz) and a broad multiplet at δ 6.80. The spectra showed little change until the temperature was increased to −40°, resulting in coalescence of the doublet into a somewhat broadened singlet at δ 2.08 and to the deshielding of the signal for the methine proton to δ 7.10. Keeping the solution at this temperature results in the formation of a mixture of *tert*-hexyl cations. The observed nmr spectra are characteristic of the diisopropylchloronium ion **14** as the first observable intermediate, which undergoes exchange in the system.

***n*-Butyl, isobutyl, and *sec*-butyl chlorosulfite** when treated with SbF_5 in SO_2 at −78° gave the *tert*-butyl

cation as the only observable reaction product, indicating fragmentative ionization followed by rapid rearrangement to the most stable tertiary ion.

Conclusion

As a result of our investigation it is found that the ability of the initially formed donor–acceptor complexes of alkyl haloformates, alkyl thiolhaloformates, and alkyl halosulfites with antimony pentafluoride undergo ionization giving alkoxycarbonyl, alkylthiolcarbonyl, and alkoxysulfinyl cations, which subsequently fragment to give alkylcarbenium ions.



Generally the ionization is facilitated in the sequence primary < secondary < tertiary alkyl groups. This trend was already observed in the ionization of other precursors such as alcohols,[19] ethers,[20] and mercaptans.[19b]

The reversibility of the fragmentation processes was established in case of the methylated ions. CO_2 under pressure reacts with methyl fluoroantimonate to give the unstable methoxycarbonyl cation. Carbonyl sulfide (COS) gives the methylthiolcarbonyl cation by methylation with methyl fluoroantimonate. Sulfur dioxide can also be methylated by methyl fluoroantimonate, the methoxysulfinyl cation formed reacting further with the methylating agent giving dimethoxyfluorosulfonium ion **37**.

Except methyl-, ethyl-, and arylthiolcarbonyl cations, $[RX{=}Y{=}O]^+$ type ions generally were not observed due to their instability. The methoxycarbonyl cation was previously studied in the gas phase and it was reported to be more labile than the acetyl cation.[21] The methoxysulfinyl cation is also considered to be an unstable species. On the other hand, the methylthiolcarbonyl cation was observed as a stable species. The stability of this cation is attributed to the high nucleophilicity of sulfur. Furthermore, we have to take into account that in the case of the (methylthiol)-carbonyl cation, the possibility of a C_{2p}–S_{3d} overlap could contribute to its stability. This type of orbital overlap was also suggested by Baker and Harris to explain the differences of the carbonyl frequencies in the ir spectra of methyl thiolchloroformate and methyl chloroformate.[22]

Experimental Section

Materials. Alkyl chloroformates and thiolchloroformates used were commercially available (Stauffer Chemical Co.). Aryl chloroformates and thiolchloroformates were prepared by reacting phosgene with phenols[23] or thiophenols[24] in the presence of pyridine in methylene chloride at 0°. Generally, 0.15 mol of $COCl_2$ was condensed in 50 ml of CH_2Cl_2 at −78° and 0.1 mol of the corresponding thiophenol or phenol was added. To the clear solution 0.1 mol of pyridine was then added dropwise and the reaction mixture subsequently was allowed to warm up to 0°. After 1 hr the reaction mixture was poured into ice water and the organic layer separated and washed several times with water. The dried CH_2Cl_2 solution was then worked up and products were purified by vacuum distillation.

Alkyl fluoroformates and alkyl thiolfluoroformates were prepared by exchange reaction from the corresponding chlorides with HF.[25]

Alkyl chlorosulfites were prepared according to Voss and Blanke[26] by adding $SOCl_2$ dropwise to the corresponding alcohols (cooled with ice water) while a constant stream of nitrogen is passed through the reaction mixture to expel the HCl formed during the reaction. The reaction mixtures were then distilled through a Vigreux or spinning band column. Alkyl fluorosulfites were prepared using the halogen exchange reaction of alkyl chlorosulfites with KSO_2F.[27]

All haloformates, thiolhaloformates, and halosulfites were reported compounds and their physical properties agreed with literature data.

Nuclear magnetic resonance spectra were obtained on Varian Associates Models A56/60A and HA-100 FT (25.16 MHz) nmr spectrometers equipped with a variable-temperature probe. TMS, CCl_3F, and $^{13}CH_3I$ were used as external references for pmr, fmr, and cmr spectra, respectively.

Preparation of the Ions. A solution (~10%) of the precursor chloroformates, thiolchloroformates, or chlorosulfites in SO_2 or SO_2ClF was added to an excess of SbF_5 in SO_2 or SO_2ClF and mixed at −78° with vigorous stirring. Reactions using AsF_3 as a solvent were carried out similarly by mixing a solution (~10%) of the precursor in AsF_3 with excess SbF_5 in AsF_3 at 0°.

Acknowledgment. We wish to thank Dr. Philip W. Westerman for taking several cmr spectra. Support of our work by National Institutes of Health and the National Science Foundation is gratefully acknowledged.

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