Stable Carbocations. CLXI.[1] Protonation and Lewis Acid Halide Complex Formation of Carbamyl Halides and Alkyl (Aryl) Isocyanates and Isothiocyanates. A Study of Carbamyl, Thiocarbamyl, and Allophanyl Cations

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Abstract: Carbamyl chlorides and fluorides form complexes with Lewis acid halides (aluminum trichloride, antimony pentachloride, and pentafluoride) through carbonyl oxygen coordination. Protonation of *N,N*-dimethylcarbamyl, *N*-methylcarbamyl, and carbamyl fluoride with FSO_3H and FSO_3H–SbF_5 results in the resonance-stabilized, carbonyl-protonated *N,N*-dimethylamino-, *N*-methylamino-, amino-, hydroxy-, and fluorocarbenium ions. Protonation of alkyl (aryl) isocyanates and isothiocyanates gives the corresponding allophanyl cations and thiocarbamyl cations, respectively.

Aluminum chloride addition compounds of carbamyl chlorides were first prepared by Hopff and used as carbamylating agents.[3] The nature of the complexes has, however, never been fully established.[4] We have, therefore, extended our previous investigations of acyl halide complexes[5] to the study of carbamyl halide–Lewis acid halide complexes, and also studied the behavior of carbamyl halides in superacids, such as FSO_3H–SbF_5. We further extended our studies to the protonation of alkyl (aryl) isocyanates and isothiocyanates which give carbamyl and thiocarbamyl cations.

Results and Discussion

Lewis Acid Halide Complex Formation and Protonation of Carbamyl Halides. The aluminum chloride and antimony pentachloride complexes of carbamyl, *N,N*-dimethylcarbamyl, and *N,N*-diethylcarbamyl chloride were studied by nmr (in SO_2 solution) and ir spectroscopy (as mulls in Fluorolube). Tables I and II summarize the data obtained.

Table I. Infrared Carbonyl Frequency of Carbamyl Chlorides (Fluorides) and Their Lewis Acid Halide Complexes

Compound	cm^{-1}	Compound	cm^{-1}
$(CH_3)_2NCOCl$	1750	$(CH_3CH_2)_2NCOCl$–$SbCl_5$	1610
$(CH_3)_2NCOCl$–$AlCl_3$	1660	H_2NCOCl	(dec)
$(CH_3)_2NCOCl$–$SbCl_5$	1625	H_2NCOCl–$AlCl_3$	1690
$(CH_3CH_2)_2NCOCl$	1740	$(CH_3)_2NCOF$	1801
$(CH_3CH_2)_2NCOCl$–$AlCl_3$	1640	$(CH_3)_2NCOF$–SbF_5	1645

The nmr spectra of dimethyl- and diethylcarbamyl chloride show the nonequivalence of the *N*-methyl and ethyl groups, respectively, due to the hindered rotation around the C–N bond. Even at 60° (in AsF_3 solution) the $(CH_3)_2NCOCl$–$SbCl_5$ complex also clearly shows the nonequivalent methyl groups (δ 3.72 and 3.88), although the methyl lines of dimethylcarbamyl chloride itself start to coalesce at 40°. The $(CH_3CH_2)_2NCOCl$–$SbCl_5$ complex shows similar behavior to the methyl complex.

Table II. Nmr Shifts and Coupling Constants of Carbamyl Chlorides and Their Lewis Acid Halide Complexes in Sulfur Dioxide Solution at 0° (δ in ppm)

Compound	δ CH_3	δ CH_2
$(CH_3)_2NCOCl$	3.02, 3.14	
$(CH_3)_2NCOCl$–$AlCl_3$	3.43, 3.49	
$(CH_3)_2NCOCl$–$SbCl_5$	3.43, 3.48	
$(CH_3CH_2)_2NCOCl$	1.17 (3), 1.22 (3)	3.39 (4), 3.51 (4)
$(CH_3CH_2)_2NCOCl$–$AlCl_3$	1.35 (3), 1.38 (3)	3.74 (4), 3.79 (4)

The $AlCl_3$ and $SbCl_5$ complexes have analogous spectra, but the corresponding proton resonances are slightly deshielded. The spectra clearly indicate that the complexes are not ionic carbamyl salts, because ionization should cause much larger deshielding, and further the ions should become symmetrical and therefore the two *N*-alkyl groups should become equivalent.

The ir study of the complexes strongly supports coordination at the oxygen atom. Such coordination would tend to increase the single bond character of the carbonyl group and thus shift its stretching to lower frequencies. If coordination on chlorine or on nitrogen took place, the carbonyl frequency shift would be in the opposite direction. These results are in accordance with studies on the Lewis acid adducts of acyl halides,[5] as well as amides such as *N,N*-dimethylformamide.[6-8]

We also prepared and studied complex formation of *N,N*-dimethylcarbamyl, *N*-methylcarbamyl, and carbamyl fluoride with antimony pentafluoride, as well as protonation of these carbamyl fluorides in superacids under a wide variety of conditions. Results are summarized in Table III.

Neat *N,N*-dimethylcarbamyl fluoride shows one singlet line at δ 3.08 for the *N*-methyl groups and a

(1) Part CLX: G. A. Olah and P. W. Westerman, *J. Amer. Chem. Soc.*, **95**, 7530 (1973).
(2) Postdoctoral research associates.
(3) H. Hopff, *Angew. Chem.*, **60**, 245 (1948).
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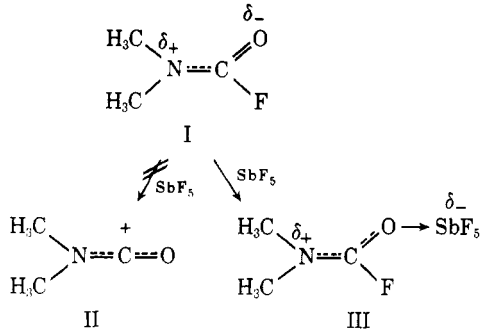
Table III. Proton and Fluorine Nmr Data of Protonated Carbamyl Fluorides and Their Antimony Pentafluoride Complexes in $FSO_3H(-SbF_5-)SO_2ClF$ or SO_2 Solutions

Carbamyl fluoride	Solvent	Temp, °C	Chemical shift (ppm)[a] CH₃	NH	OH	F
$(CH_3)_2NCOF$	Neat	−20	3.08 (1)			25.4 (br)
	SO_2	−60	3.02 (2, J = 0.7), 2.98 (2, J = 0.9)			24.9 (br)
	SO_2ClF	−40	3.07 (1)			25.8 (br)
	SbF_5	+70	4.00 (1) 4.03 (1)			26.1 (br)
	SbF_5–SO_2ClF	−40	3.68 (1) 3.66 (1)			37.7 (br)
	FSO_3H–SbF_5–SO_2ClF	−40	3.74 (2, J = 1.2), 3.72 (2, J = 1.2)		10.72 (1)	37.7
		−100	3.70 (2, J = 1.5), 3.68 (2, J = 1.5)		10.88 (1)	37.7
	HF–SbF_5–SO_2ClF	−40	3.65 (2, J = 1.7), 3.62 (2, J = 1.7)		10.38 (1)	37.8
	FSO_3H	−40	3.63 (2, J = 1.8), 3.61 (2, J = 1.8)		10.61	38.2 (7, J = 1.8)
	FSO_3H–SbF_5	+40	3.98 (2, J = 2.0), 3.96 (2, J = 2.0)			37.0 (7, J = 2.0)
CH_3NHCOF	Neat	Rt	2.97 (2, J = 5.0)	6.69 (br)		18.2 (2, J = 7.5)
	SO_2	−40	2.63 (2, J = 5.0)	5.99 (br)		17.4 (2, J = 7.2)
	SbF_5	+70	4.03 (4, J = 5.0, J = ~1.0)	8.34 (br)		21.3 (m)
	SbF_5–SO_2ClF	−80	3.65 (br)	8.23 (br)		24.8 (br)
	HF–SbF_5–SO_2ClF	−30	3.65 (4, J = 5.0, J = ~1.0)	8.37 (br)	11.57 (2, J = 2.8)	33.3 (m)
	FSO_3H–SbF_5–SO_2	−80	3.52 (2, J = 5.0)	8.35 (br)	11.57 (2, J = 2.5)	32.4 (m)
	FSO_3H–SO_2	−80	3.33 (2, J = 5.0)	8.27 (br)		33.5 (m)
H_2NCOF	SO_2	−40		5.57 (br)		12.7 (doublet of m)
	SbF_5	+20		8.43 (br)		15.4 (doublet of 2, $J_{HN-CF(cis)}$ + $J_{HN-CF((trans)}$ ≅ 27.5)
	SbF_5–SO_2ClF	−60		8.12 (br)		
	FSO_3H–SbF_5–SO_2	−80		8.48 (br)	11.07 (2, J = 2.0)	27.8 (doublet of 2, $J_{HN-CF(trans)}$ + $J_{HN-CF(cis)}$ ≅ 21.5)
	FSO_3H–SO_2	−80		8.43 (m)		28.7 (doublet of 2, $J_{HN-CF(cis)}$ + $J_{HN-CF(trans)}$ ≅ 29.5)

[a] Multiplicity and coupling constants (in Hz) are given in parentheses.

singlet in the fluorine resonance spectrum at ϕ +25.4. Using sulfuryl chloride fluoride as solvent, the spectrum remains nearly unchanged (N–CH_3 at δ 3.07, C–F at ϕ +25.8) between 10 and −20°. Therefore, in both cases even at −20° the methyl groups seem equivalent and no fluorine coupling is observable. In SO_2 solution at −60°, however, the two *N*-methyl groups are becoming nonequivalent (δ 3.02 and 2.98) due to freezing out the hindered rotation caused by the contribution of partial double bond shown in form I. Also



the ^{19}F long range coupling (0.7–0.9 Hz) becomes observable, causing each line to become a doublet.

Attempted ionization of I in SbF_5–SO_2 or SbF_5–SO_2ClF solution to obtain the *N,N*-dimethylcarbamyl cation II was unsuccessful. The pmr spectra indicate only complex formation of the carbonyl oxygen atom, with two methyl absorptions at δ 3.68 and at 3.66. The ionized carbamyl cation in contrast should give only a single deshielded methyl absorption. The

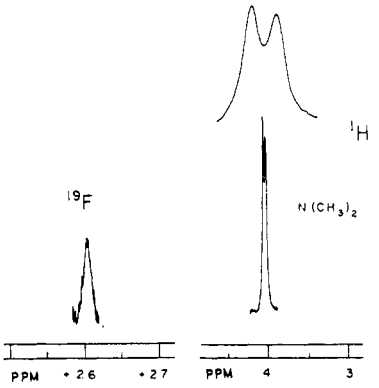


Figure 1. ^{19}F and ^1H spectra of *N,N*-dimethylcarbamyl fluoride in neat SbF_5 at +70°.

^{19}F spectrum shows a slightly broadened line at ϕ +37.7. This means that the fluorine atom is still bonded to the carbon atom and is further shielded by complex formation with SbF_5. The spectra are basically unchanged even when run at much higher temperatures (Figure 1), and no coalescence of the two methyl peaks was observed. We obtained spectra of *N,N*-dimethylcarbamyl fluoride in neat antimony pentafluoride up to 150°, the boiling point of SbF_5. The two methyl absorbances are shifted further downfield, but are still resolved (δ 4.03–4.00). The two methyl absorbances are considered to be those of the two nonequivalent *N*-methyl groups in complex III, the enhanced partial double bond character between carbon and nitrogen being due to the coordination of antimony pentafluoride to the carbonyl oxygen. The ^{19}F spectrum shows at

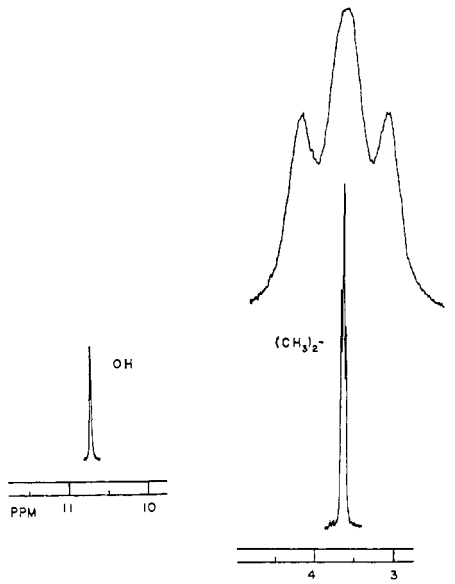


Figure 2. Pmr spectrum of $(CH_3)_2NC(O)F$ in FSO_3H–SbF_5–SO_2ClF at −40°.

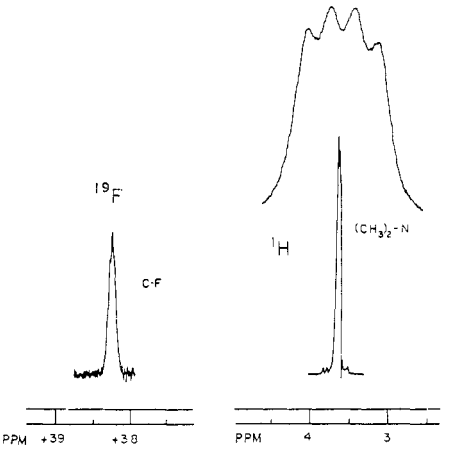


Figure 3. ^1H and ^{19}F nmr spectra of $(CH_3)_2NC(O)F$ in FSO_3H at −40°.

ϕ +26.1 a multiplet (the resolution was not sufficient to accurately measure the coupling constant). Heteronuclear spin–spin decoupling collapses the signals into singlets. Quenching of the solution with wet SO_2 gave back in an 80% yield the starting *N,N*-dimethylcarbamyl fluoride.

Next we turned our interest to the study of protonation of *N,N*-dimethylcarbamyl fluoride in superacid media such as 1:1 *M/M* FSO_3H–SbF_5 (magic acid) diluted with SO_2ClF. At −40° we observed for the methyl groups a 1:2:1 triplet like pattern at δ 3.74, with a small coupling constant of 1.2 Hz. A sharp low field singlet at δ 10.72 indicates O-protonation. We had already discussed in our studies on the protonation of alkyl carbamates the coupling of the proton coordinated on carbonyl oxygen with the proton bonded to nitrogen, as well as the negligible rotational barrier around the C–O bond compared with that around the N–C bond.[9] The sharp OH singlet means that the coupling of the proton coordinated to the carbonyl oxygen with the fluorine atom is negligible. The

(9) G. A. Olah and M. Calin, *J. Amer. Chem. Soc.*, **90**, 401 (1968).

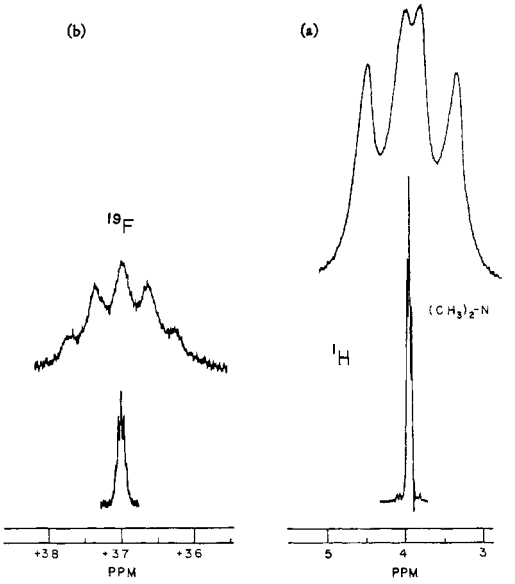
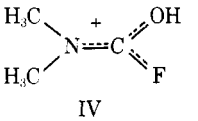


Figure 4. ^1H (a) and ^{19}F (b) spectra of *N,N*-dimethylcarbamyl fluoride in neat 1:1 HSO_3F–SbF_5 (magic acid) at 40°.

spectrum is shown in Figure 2. The ^{19}F spectrum shows a septuplet at ϕ +37.7. We interpret the septuplet as two overlapping quartets caused by the long range F-coupling of the two nonequivalent *N*-methyl groups. To prove this assignment, we varied the acid conditions hoping that the two doublets should be observable. In HF–SbF_5 solution diluted with SO_2ClF at −40° we observed an unchanged spectrum (Table III). However, in neat FSO_3H at −40°, it was possible to clearly resolve the four lines (the shift difference is about 0.9 Hz) (Figure 3). At +100°, the two methyl groups still appear at different chemical shifts due to their nonequivalency. The ^{19}F spectrum shows a broad multiplet at ϕ +38.2; the coupling constant J_{CH_3N-COF} is about 1.8 Hz. In fluorosulfuric acid as solvent, no hydroxyl proton is observable, due to exchange with the acid.

The spectrum of I in undiluted 1:1 *M/M* FSO_3H–SbF_5 at +40° was also observed (Figure 4). The methyl groups appear again nonequivalent at δ 3.98 each split into a doublet by fluorine coupling of 2.0 Hz as shown in Figure 4a. The fluorine spectrum shows a septuplet (five resolved lines, two shoulders) at ϕ +37.0, with the coupling constant J_{CH_3N-COF} = 2.0 Hz (Figure 4b). By quenching the solution with wet SO_2 (water in SO_2), it was possible to recover the starting material, *N,N*-dimethylcarbamyl fluoride. If the FSO_3H–SbF_5 solution is diluted with SO_2ClF at −40° a low field sharp OH singlet at δ 10.72 is observed. The OH absorption does not show any fine splitting even at −100°. This means that in protonated *N,N*-dimethylcarbamyl fluoride, vicinal fluorine and proton have no detectable coupling, although vicinal F–H coupling (1.7 Hz) has been known in protonated fluoromethyl alcohol.[10]



IV

(10) G. A. Olah and G. D. Mateescu, *J. Amer. Chem. Soc.*, **93**, 781 (1971).

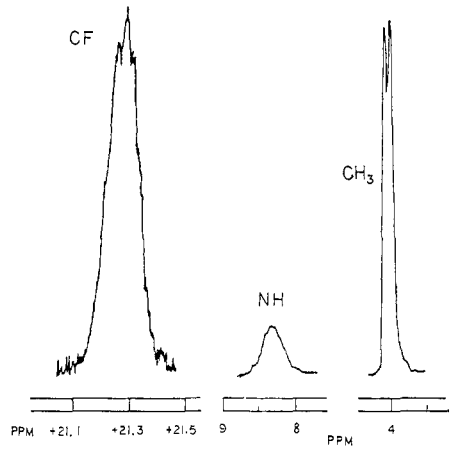
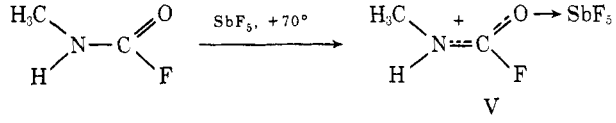


Figure 5. ^1H and ^{19}F nmr spectra of *N*-methylcarbamyl fluoride in neat SbF_5 at +70°.

Neat *N*-methylcarbamyl fluoride at room temperature shows one doublet at δ 2.97 for the methyl group (J = 5.0 Hz), a broad peak at δ 6.69 for the imino group, and a doublet in the ^{19}F spectrum at ϕ +18.2 (J_{HN-CF} = 7.5 Hz). The pmr spectrum of the fluoride in SO_2 at −40° remains nearly unchanged.

N-Methylcarbamyl fluoride forms in SbF_5 solution a complex (Figure 5). The spectrum shows a quartet at δ 4.03 (J_{NH-CH_3} = 5.0 Hz, J_{FC-NCH_3} = 1.2 Hz) for the *N*-methyl group, a broadened peak at δ 8.34 for the imino group, and a multiplet in the ^{19}F spectrum at ϕ +21.3, which clearly indicates the formation of the complex. The multiplicity of the fluorine resonance indicates the existence of the hindered rotation about the N–C(F) bond, comparing the temperature dependence of the ^{19}F spectrum of the protonated *N*-methylcarbamyl fluoride.



V

The clear solution of *N*-methylcarbamyl fluoride in FSO_3H–SO_2 gives the spectrum, which shows a doublet at δ 3.33 for the *N*-methyl group (J_{HN-CH_3} = 5.0 Hz), a broad peak at δ 8.27 for the imino group, and a multiplet at ϕ +33.5 for the ^{19}F resonance. The peaks of imino proton and fluorine show temperature dependence; *i.e.*, a broad singlet for the imino proton, at −20°, which becomes a broad multiplet at −80°, and a rather sharp singlet at −20°, which again becomes a broad multiplet at −80° for the fluorine (Figure 6). This temperature dependence is due to the hindered rotation around the N–C(F) bond. In FSO_3H–SO_2 solution, the OH peak could not be observed, because of rapid exchange with the solvent. In FSO_3H–SbF_5–SO_2 solution at −80°, however, the hydroxyl proton is observed at δ 11.57 as an unsymmetrical doublet (J_{HOC-NH} = 2.5 Hz), due to the overlapping singlet and doublet absorption[9] (Figure 7). This hydroxy proton resonance means that hindered rotation about the C–N bond results in the observation of cis and trans isomers and in VIa these protons bear a W-type relation to each other and show long range coupling, but VIb shows no detectable four-bond

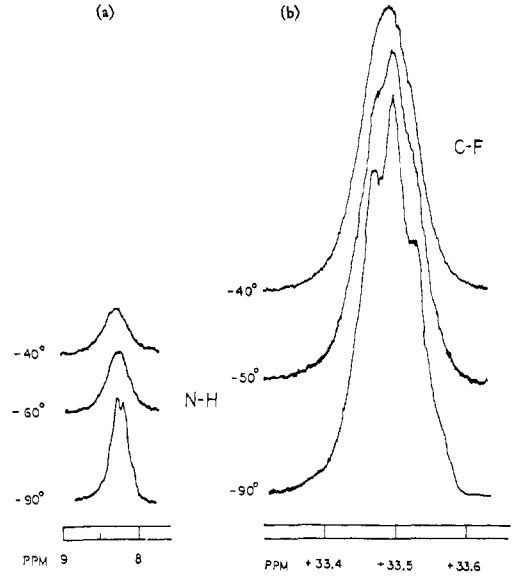


Figure 6. Temperature dependent ^1H (a) and ^{19}F (b) spectra of *N*-methylcarbamyl fluoride in FSO_3H–SO_2 solution; (a) shows only N–H proton.

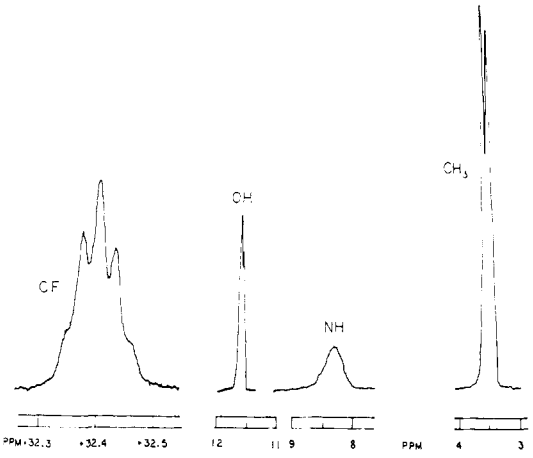
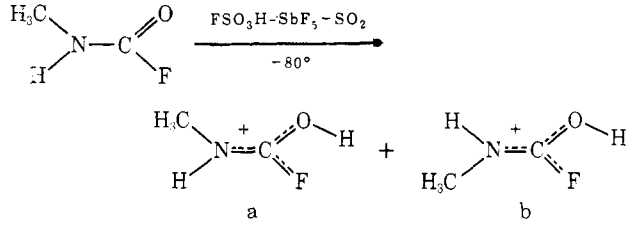


Figure 7. ^1H and ^{19}F spectra of *N*-methylcarbamyl fluoride in FSO_3H–SbF_5 (1:1)–SO_2 solution at −80°.



VI

coupling.[9] These results indicate O-protonation of *N*-methylcarbamyl fluoride at the carbonyl oxygen atom without ionization to the *N*-methylcarbamyl cation, or exchange of the fluorine atom in a polarized complex.

The parent carbamyl fluoride was also studied. The sulfur dioxide solution of carbamyl fluoride at −40° shows a broad multiplet at δ 5.57 for the amino protons and in the fluorine spectrum a doublet of multiplet at ϕ +12.7 for the acyl fluoride. Due to the quadrupole interaction of nitrogen, the amino protons give a broad, complicated peak, but the pattern of the fluorine resonance indicates an ABX spin system, due to hindered rotation around the N–C(F) bond.

Table IV. Pmr Parameters of Protonated *N,N*-Dimethylformamide and *N*-Methyl-*N*-phenylformamide

Protonated formamide	Conditions	Chemical shift (δ) OH	H	H^1	H^2
CH_3^1 OH, CH_3^2 H	Neat FSO_3H, −80°[a]	9.98 (2, J = 4.7)	8.38 (2, J = 4.7)	3.43 (1)	3.53 (1)
	Neat FSO_3H, +40°		8.56 (1)	3.54 (2, J = 1.1)	3.65 (2, J = 0.9)
	FSO_3H–SbF_5 (1:1) in SO_2, −60°	9.43 (2, J = 5.0)	8.33[b] (2, J = 5.0)	3.49 (2, J = 1.0)	3.58 (1)
	FSO_3H–SbF_5 (1:1) in SO_2ClF, −20°	9.82 (2, J = 4.9)	8.62[b] (2, J = 4.9)	3.73 (2, J = 1.0)	3.82 (2, J = 0.7)
CH_3^1 OH, Ph^2 H	FSO_3F–SbF_5 (1:1) in SO_2, −53°	10.49 (2, J = 5.1)	8.78[b] (2, J = 5.1)	3.88 (2, J = 1.0)	7.16 (m)

[a] Reference 9. [b] The methine proton is highly broadened due to long range coupling with the N–CH_3 group.

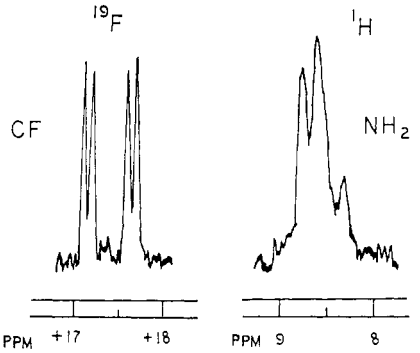
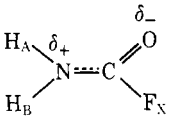
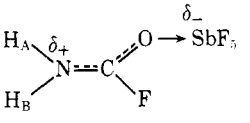


Figure 8. ^1H and ^{19}F spectra of carbamyl fluoride in neat SbF_5 at 20°.



Carbamyl fluoride in SbF_5 solution at 20° (a very clear solution can be obtained) shows similar properties to the related complexes of *N*-methyl- and *N,N*-dimethylcarbamyl fluoride (Figure 8). A broad peak at δ 8.43 and a pair of doublets at ϕ +15.4 appear for the amino proton and the fluorine atom, respectively. The ^{19}F spectrum also indicates hindered rotation around the N–C(F) bond of the complex.



VII

Protonation of carbamyl fluoride in FSO_3H–SO_2 solution takes place without ionization to the carbamyl cation. The spectrum of the amino proton and fluorine atom depends on the temperature, as shown in Figure 9. This dependency again shows hindered rotation around the N–C(F) bond in the protonated carbamyl fluoride, although the barrier is low. In FSO_3H–SbF_5–SO_2 solution of carbamyl fluoride, the hydroxyl proton appears at δ 11.07 as a doublet ($J_{HOC-NH} \cong 2.0$ Hz).

In conclusion of the study of the behavior of carbamyl fluorides with antimony pentafluoride and their protonation by fluorosulfuric acid or FSO_3H–SbF_5, it

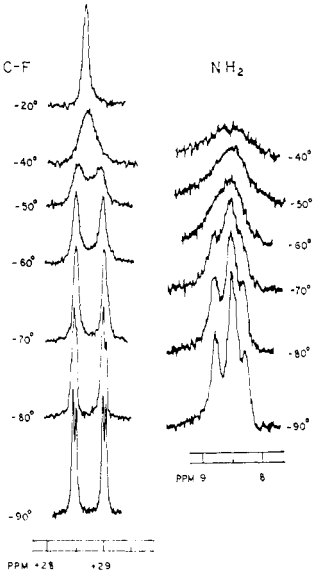
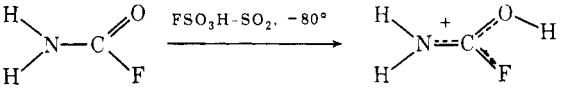


Figure 9. Temperature dependence of ^1H and ^{19}F spectra of carbamyl fluoride.



VIII

appears that both take place with interaction at the carbonyl oxygen atom but without ionization to the corresponding carbamyl cations.

The rotational barriers around the N–C(F) bond in protonated carbamyl fluoride and *N*-methylcarbamyl fluoride can be estimated to be very low (<5 kcal/mol) based on the coalescence of proton peaks. However, O-protonated *N,N*-dimethylcarbamyl fluoride shows in fluorosulfuric acid, even at 100°, nonequivalence of the two methyl groups. This may be due to the significant contribution by structure IV, which has almost a full double bond between nitrogen and carbon, and is stabilized by hyperconjugation with the two methyl groups.

We consequently extended our studies to protonation of *N,N*-dimethylformamide and *N*-methyl-*N*-phenylformamide to examine these as model compounds. The results are summarized in Table IV.

Dimethylformamide gives in fluorosulfuric acid,[11]

(11) R. J. Gillespie and T. Birchall, *Can. J. Chem.*, **41**, 148 (1963).

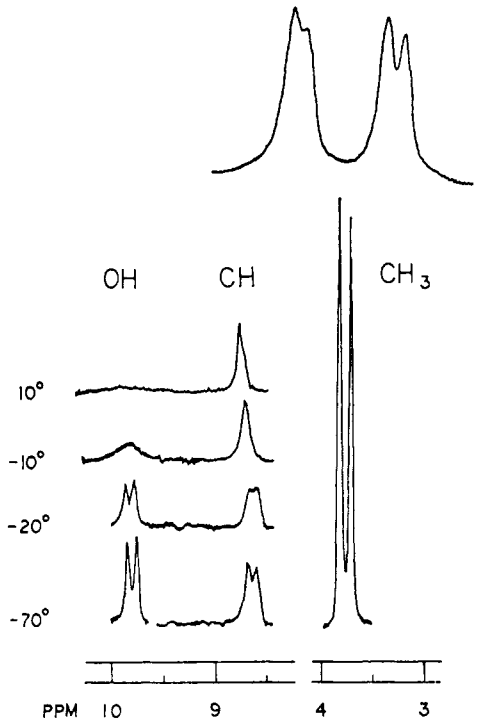


Figure 10. Temperature dependent pmr spectra of *N,N*-dimethylformamide in fluorosulfuric acid.

FSO_3H–SbF_5–SO_2, and FSO_3H–SbF_5–SO_2ClF almost the same spectra (Figure 10). Two methyl groups appear nonequivalent in fluorosulfuric acid, and do not coalesce even at 100°. This shows the formation of tighter bond between nitrogen and carbon, similar as shown in structure IV. The hydroxyl proton is observed as a doublet with a coupling constant of 4.7 Hz at low temperature, but at higher temperature becomes a broadened singlet due to rapid proton exchange with the solvent.[11] The resonance of the methine proton shows the splitting due to the coupling with the hydroxyl proton at low temperature, although both resonances are broad multiplets due to the long range coupling with methyl groups.

Formation of Allophanyl Cations *Via* Protonation of Alkyl (Aryl) Isocyanates. We had hoped, after we were unsuccessful in preparing carbamyl cations from carbamyl halides, to obtain them by protonation of isocyanic acid and alkyl (aryl) isocyanates.

Isocyanic acid and isocyanates can be easily protonated in FSO_3H–SO_2 at −78°, although in FSO_3H–SbF_5–SO_2 (or SO_2ClF) and HF–SbF_5–SO_2 (or $-SO_2$-ClF) they gave very complicated spectra. Isocyanic acid in FSO_3H at −80° shows two broad singlets at δ 8.23 and 8.05, which collapse upon raising the temperature and become a broad singlet at δ 8.14. This means that there are two protons which are different at low temperature, but at higher temperature become equal. This species is not the carbamyl cation IX, because IX should have two equivalent protons. After quenching the acid solution with excess cold ethanol, ethyl allophanate was obtained in yield exceeding 60%. Therefore, the ionic species observed in the solution is not the carbamyl cation, but the allophanyl cation X, which shows restricted rotation around the N–C bond. The amino proton is not observed due to rapid exchange of proton at enol form (XIb).[12]

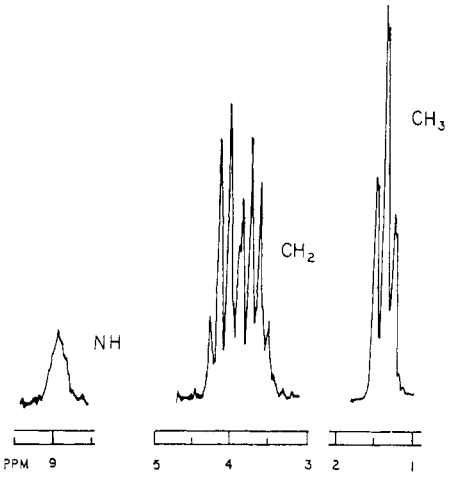
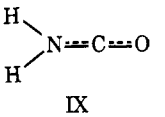
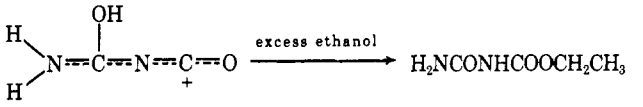


Figure 11. Pmr spectrum of α,γ-diethylallophanyl cation in FSO_3H–SO_2 at −60°.

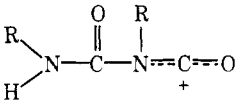


IX



X

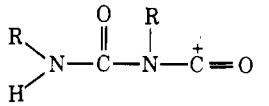
Methyl isocyanate forms in FSO_3H–SO_2 solution at −60° the α,γ-dimethylallophanyl cation, with the HN proton appearing at δ 8.55 as a multiplet, the α-methyl group at δ 3.48 as a doublet (J = 5.0 Hz) and the γ-methyl group at δ 3.82 as a singlet. The integrated ratio of these peaks is 1:3:3. When the acid solution was quenched with excess cold methanol, it gave methyl α,γ-dimethylallophanate in 60% yield. Ethyl isocyanate in FSO_3H–SO_2 (Figure 11) shows at −60° a broad peak at δ 9.00 for the imino proton, a multiplet at δ 3.75 ($J_{CH_3-CH_2}$ = 7.5 Hz, J_{HN-CH_3} = 5.5 Hz) and a triplet at δ 1.37 ($J_{CH_3-CH_2}$ = 7.5 Hz) for the γ-methyl group, and a quartet at δ 4.01 ($J_{CH_3-CH_2}$ = 7.5 Hz) and a triplet at δ 1.38 ($J_{CH_3-CH_2}$ = 7.5 Hz) for the α-methyl group. The integrated ratio of the imino, methylene, and methyl groups is 1:4:6. *tert*-Butyl isocyanate in FSO_3H–SO_2 also gave the α,γ-di-*tert*-butylallophanyl cation, the amino group of which appears at δ 8.12 and the *t*-Bu group of which shows a slightly broad singlet at δ 1.53. Peak area integration is in accord with the allophanyl cation structure. *p*-Tolyl isocyanate in FSO_3H–SO_2 at −80° shows two singlets for *p*-methyl group at δ 2.32 and 2.42, due to their different magnetic



XIa, R = CH_3
b, R = CH_3CH_2
c, R = $(CH_3)_3C$
d, R = C_6H_5
e, R = *p*-$CH_3C_6H_4$
f, R = *p*-$CH_3C_6H_4SO_2$

(12) Cyanuric acid shows no observable pmr absorption at −80° in FSO_3H–SO_2 solution.

Table V. Pmr Data of α,γ-Substituted Allophanyl Cations in Fluorosulfuric Acid–Sulfur Dioxide Solution



Starting material	Allophanyl cation (R)	Solvent	Temp, °C	Chemical Shift (δ) NH	H^1	H^2
HNCO		Neat	Rt	5.17 (br)		
		SO_2	−40	4.60 (3, br, (J_{HN} = 68.0)[a]		
	H	FSO_3H–SO_2	−80	8.23 (br) 8.05 (br)		
			−20	8.14 (br)		
CH_3NCO		SO_2	−60		2.93 (1)	
	CH_3	FSO_3H–SO_2	−60	8.55 (br)	3.48 (2, J = 5.0)[b] 3.82 (1)[c]	
$CH_3{}^1CH_2{}^2NCO$		SO_2	−60		1.03 (3, J = 7.5)	3.24 (4, J = 7.5)
	$CH_3{}^1CH_2{}^2$	FSO_3H–SO_2	−60	9.00 (br)	1.37 (3, J = 7.5)[b] 1.38 (3, J = 7.5)[c]	3.75 (m, J = 7.5, J = 5.5)[b] 4.01 (4, J = 7.5)
$(CH_3)_3CNCO$		SO_2	−40			1.17 (1)
	$(CH_3)_3C$	FSO_3H–SO_2	−40	8.12 (br)	1.53 (1, br)[d]	
C_6H_5NCO		SO_2	−40		7.10 (m)	
	C_6H_5	FSO_3H–SO_2	−40	8.30 (br)	7.72 (m)[d]	
p-$CH_3{}^1C_6H_4{}^2NCO$		SO_2	−80		2.08 (1)	7.04 (m)
	p-$CH_3C_6H_4$	FSO_3H–SO_2	−80	8.00–7.35[e]	2.32 (1)[b] 2.42 (1)[c]	7.56 (m)[d]
p-$CH_3{}^1C_6H_4{}^2SO_2NCO$		SO_2	−20		2.23 (1)	7.46 (4, J = 7.0)
	p-$CH_3C_6H_4SO_2$	FSO_3H–SO_2	−80	8.45–7.90[e]	2.50 (1)[d]	7.80 (4, J = 8.0)[d]

[a] J. Nelson, R. Spratt, and S. M. Nelson [*J. Chem. Soc.*, 583 (1970)] and K. M. Mackay and S. R. Stobart [*Spectrochim. Acta, Part A*, **27**, 923 (1971)] reported J_{N-H} = 64 ± 1 and 69 ± 5 Hz, respectively. [b] For γ substituent. [c] For α substituent. [d] For α and γ substituents. [e] Imino proton absorption overlapped aromatic absorption.

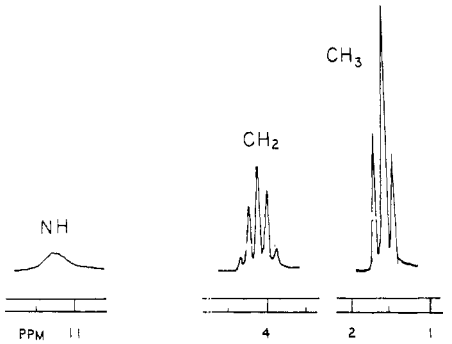
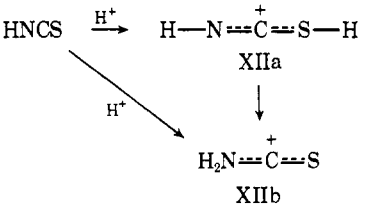


Figure 12. Pmr spectrum of ethylthiocarbamyl cation in FSO_3H–SO_2 at −40°.

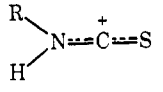
environments in the allophanyl cation. The multiplet for the imino and phenyl groups is between δ 7.35 and 8.00. Phenyl and *p*-tosyl isocyanate give in superacid at low temperature the corresponding α,γ-substituted allophanyl cations. Data are summarized in Table V.

Formation of Thiocarbamyl Cations *Via* Protonation of Alkyl (Aryl) Isothiocyanates. Protonation of isocyanates did not give carbamyl cations, but allophanyl cations as stable end products. However, it was considered that if a more positive element would be introduced into the system, the related cation can be stabilized sufficiently to be observed without dimerization. We thus extended our studies to protonation of isothiocyanates. Isothiocyanic acid (HNCS)[13] shows in the pmr spectrum a sharp singlet at δ 6.53, due to the lower quadrupole coupling constant of nitrogen atom than in the case of isocyanic acid.[14] The FSO_3H–SO_2 solution of isothiocyanic acid shows a slightly broadened singlet at δ 11.03. For the structure of protonated isothiocyanic acid, two alternates are possible. XIIa



is the sulfur protonated form, whereas XIIb is the nitrogen protonated form, which can also be obtained by the rearrangement of XIIa. Since the S-protonated form (XIIa) should show two separate proton peaks for the imino and thiol groups, the *N*-protonated structure (XIIb) seems to be the observed form of protonated isothiocyanic acid.

Methyl isothiocyanate in similar superacid solution at −60° shows a broad peak at δ 10.95 for the imino group, and a doublet at δ 3.86 (J_{NH-CH_3} = 5.0 Hz) for the methyl group. The integrated ratio of these peaks is 1:3. These data indicate the formation of the *N*-methylthiocarbamyl cation (XIIIa).

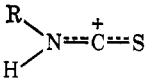


XIIIa, R = CH_3
b, R = CH_3CH_2
c, R = $(CH_3)_3C$
d, R = C_6H_5

Ethyl isothiocyanate in FSO_3H–SO_2 at −40° (Figure 12) forms the *N*-ethylthiocarbamyl cation. The imino

(13) J. R. Durig and D. W. Wertz, *J. Chem. Phys.*, **46**, 3069 (1967).
(14) J. N. Schoolery, R. G. Shulman, and D. M. Yost, *ibid.*, **19**, 250 (1951).

Table VI. Pmr Data for Thiocarbamyl Cations in Fluorosulfuric Acid–Sulfur Dioxide Solution

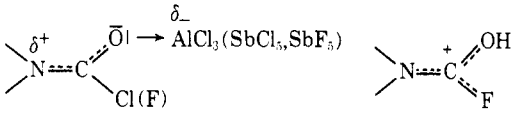


Starting material	Thiocarbamyl cation (R)	Solvent	Temp, °C	Chemical shift (−δ ppm) NH	H^1	H^2
HNCS		SO_2	−80	6.53 (1)		
	H	FSO_3H–SO_2	−80	11.03 (br)		
CH_3NCS		SO_2	−80		3.46 (1)	
	CH_3	FSO_3H–SO_2	−80	10.95 (br)	3.86 (2, J = 5.0)	
$CH_3{}^1CH_2{}^2NCS$		SO_2	−40		1.30 (3, J = 7.0)	3.65 (4, J = 7.0)
	$CH_3{}^1CH_2{}^2$	FSO_3H–SO_2	−40	11.20 (br)	1.55 (3, J = 7.0)	4.08 (5, J = 7.0)
$(CH_3)_3CNCS$		SO_2	−80		1.35 (1)	
	$(CH_3)_3C$	FSO_3H–SO_2	−80	10.90 (br)	1.82 (1)	
C_6H_5NCS		SO_2	−80		7.28 (1)	
	C_6H_5	FSO_3H–SO_2	−80	12.53 (br)	7.42 (1)	

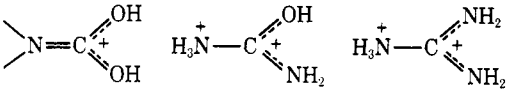
group appears at δ 11.20 as a broad singlet, the methylene group at δ 4.08 as a quintet (J_{NH-CH_2} = 7.0 Hz, $J_{CH_3-CH_2}$ = 7.0 Hz), and the methyl group at δ 1.55 as a triplet ($J_{CH_3-CH_2}$ = 7.0 Hz). *tert*-Butyl isothiocyanate in the superacid solution shows at −80° a broad peak at δ 10.90 for the imino group and a singlet at δ 1.82 for the *tert*-butyl group. The integrated areas satisfy structure XIIIc. The protonation of phenyl isothiocyanate also results in the formation of the phenylthiocarbamyl cation. Results are summarized in Table VI.

Conclusions

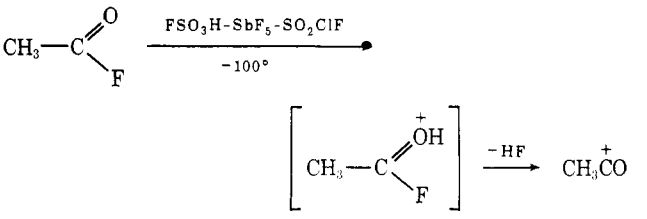
Complex formation of carbamyl chlorides and fluorides with Lewis acid halides (aluminum trichloride, antimony pentachloride, and antimony pentafluoride) takes place at the carbonyl oxygen atom. Similarly, protonation of carbamyl halides also takes place at



the carbonyl oxygen atom. These observations are closely related to protonated carbamic acid and diprotonated urea and guanidine, which were reported in our preceding work.[15]

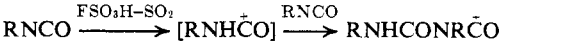


Protonated carbamyl fluorides show remarkable stability and no apparent tendency for HF elimination and formation of carbamyl cations. (A significant difference from the corresponding acyl fluorides, *vide infra*.) The high degree of stability of a hydroxyl group and fluorine atom at the same carbon is remarkable (the only previous known case to our knowledge is that of protonated fluoromethyl alcohol[10]). There also seems to be a close correlation with protonated formamides in which, whereas protonation takes place on the carbonyl oxygen atom, the charge is substantially localized on nitrogen in the highly resonance stabilized systems. In comparsion, all attempts to observe protonated acetyl fluoride (or related acyl fluorides) were unsuccessful in FSO_3H–SbF_5 or FSO_3H–SbF_5–SO_2ClF solution even at −100°. Ionization to the acetyl cation (or related acyl cations) takes place by the time nmr spectra could be observed.[5]



In comparing protonated acetyl fluoride (and other acyl fluorides) with protonated carbamyl fluorides, the stabilization of the latter is due to the great ability of the amino group to delocalize charge.

As carbamyl halides form O-coordinated (protonated) complexes with Lewis acid halides and strong Brønsted acids, the preparation of carbamyl cations by an alternate route, *e.g.*, protonation of alkyl (aryl) isocyanates in superacids was attempted. Isocyanic acid and isocyanates did not give the stable carbamyl cations, but instead lead further to the corresponding allophanyl cations as stable end products.



On the other hand, isothiocyanic acid and isothiocyanates gave the corresponding thiocarbamyl cations in FSO_3H–SO_2 solution. This is considered to be due to the stabilization of the thiocarbamyl cations by sulfur, a more positive element than oxygen.

The study of the intermediate carbamyl, thiocarbamyl, and allophanyl cations, or their precursor complexes, gives significant information relating to the nature of the mechanism of the acid-catalyzed carbonylation reactions.

Experimental Section

Materials. Isocyanic acid[16] and isothiocyanic acid[17] were prepared by reported methods. *N*,*N*-Dimethylcarbamyl fluoride (bp 39–41° (16 mm)) was synthesized from the corresponding chloride and mercuric fluoride by means of the fluorine–chlorine exchange reaction.[18] *N*-Methylcarbamyl fluoride (bp 48° (6 mm)) and carbamyl fluoride (mp 47° (lit.[18] 46–47°)) were prepared by

(15) G. A. Olah, A. M. White, and D. H. O'Brien, *Chem. Rev.*, **70**, 561 (1970), and references cited therein.

(16) N. Groving and A. Holm, *Acta Chem. Scand.*, **19**, 1768 (1965).
(17) V. Rück and H. Steinmetz, *Z. Anorg. Chem.*, **77**, 51 (1912).
(18) Unpublished work.

addition of hydrogen fluoride or pyridine–poly(hydrogen fluoride)[18] to methyl isocyanate and isocyanic acid, respectively.[19] Other reagents were all commercially available.

Nmr and Ir Spectra. Varian Associates Model A-56/60 A spectrometer, equipped with a variable-temperature probe, was used. Chemical shifts are reported in ppm (δ) from external (capillary) tetramethylsilane or ppm (ϕ) from capillary fluorotrichloromethane. A Perkin-Elmer Model 421 grating spectrophotometer was used for ir spectroscopy.

Preparation of Solutions of Complexes and Ions. The procedure used in the preparation of solutions of protonated or metal halide complexes studied in this paper was identical with those described previously.[20]

Quenching of Ion Complexes. The fluorosulfuric acid–sulfur dioxide solution of the corresponding ion (or complex) at −78° was gradually poured into methanol (or wet SO_2), which was also cooled to −78°. The methanol (or SO_2) solution then was poured into ice–water to give a clear homogeneous solution, which was extracted by ether. The ether extract was dried over magnesium sulfate and evaporated. Finally the residue was distilled under reduced pressure. Products were identified by glc, nmr, and ir and compared with authentic samples. For example, methyl α,γ-dimethylallophanate was obtained by distillation at 104–107° (15 mm) (lit.[21] 104–105° (14 mm)). The nmr spectrum shows a doublet at δ 3.32 (J = 5.0 Hz) for γ-methyl, a singlet at 3.66 for α-methyl, a singlet at 4.24 for methoxyl group, and a broad peak at 8.92 for the imino group.

The procedure of quenching allophanyl cation by ethanol was almost the same as above, but ethyl allophanate was isolated as a crystalline material (mp 191° (lit.[22] 191–192°)).

Acknowledgment. Support of our work by the National Institutes of Health is gratefully acknowledged.

(19) M. Linhard and K. Betz, *Ber.*, **73**, 177 (1940).
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(21) K. H. Slotta and R. Tschesche, *Ber.*, **60**, 295 (1927).
(22) R. Kreher and G. H. Berger, *Tetrahedron Lett.*, 369 (1965).

Electrophilic Reactions at Single Bonds. XVI.[1] $AgSbF_6$ Catalyzed Bromination of Alkanes and Cycloalkanes with Bromine in Methylene Chloride Solution

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Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received May 8, 1973*

Abstract: Anhydrous $AgSbF_6$ in methylene chloride solution catalyzes the electrophilic bromination of isoalkanes and cycloalkanes. Products of bromination are generally affected by silver catalyzed isomerization, as well as elimination and addition reactions.

In contrast to the extensive investigation on vapor phase photobrominations[3] or thermal gas phase brominations[4] of alkanes, only scattered results are available on brominations of saturated hydrocarbons in solution, which could have electrophilic nature. Stetter[5] reported the bromination of adamantane in neat bromine giving 1-bromoadamantane as the major reaction product and the preparation of di-, tri-, and tetrabromoadamantanes by $AlCl_3$–BBr_3 catalyzed bromination.[6] More recently Stetter also reported the reaction of several alkanes, having two adjacent tertiary hydrogens, with neat bromine at elevated temperatures.[7] In this case $\alpha,\alpha',\alpha'',\alpha'''$-tetrabromoalkanes were obtained as stable end products as the result of a sequence of bromination–dehydrobromination reactions. Straight chain unbranched alkanes failed to react even under forced conditions. Using different catalysts (mainly Lewis acids) only tarry reaction products were obtained.

Deno[8] investigated the $FeBr_3$ and $AlCl_3$ catalyzed bromination of cyclopropane, a "bent" σ bonded more reactive cycloalkane.

One of the major difficulties in electrophilic bromination of alkanes arises due to the fact that alkyl bromides formed in the reactions themselves react further in the presence of acid catalyst (which are necessary for the generation of the electrophilic brominating agent) to give a variety of alkylation, condensation, and polymerization products characteristic of the behavior of alkyl halides with Friedel–Crafts catalysts. It seems that only cycloalkanes, such as adamantane, which cannot be readily deprotonated to an olefin, avoid this difficulty.

Recently we reported the reaction of typical electrophiles such as H^+, R^+, NO_2^+, and "Cl^+" with alkanes (σ donors). In these reactions electrophilic substitutions at C–H bonds, as well as electrophilic cleavage of the C–H and C–C bonds, took place. Both reaction types are assumed to proceed *via* a two-electron, three-center bonded carbonium ion type transition state, as shown

(1) Part XV: G. A. Olah and J. J. Svoboda, *J. Amer. Chem. Soc.*, **95**, 3794 (1973).
(2) Postdoctoral Research Investigator, 1970–1972.
(3) (a) P. C. Anson, P. S. Fredericks, and J. M. Tedder, *J. Chem. Soc.*, 918 (1959); (b) B. M. Eckstein, H. A. Scheraga, and E. R. Van Artsdalen, *J. Chem. Phys.*, **22** (1), 28 (1954); (c) M. S. Kharasch, Y. C. Liu, and W. Nudenberg, *J. Org. Chem.*, **20**, 680 (1955); (d) J. D. Backhurst, *J. Chem. Soc.*, 3497 (1959); (e) U. Kh. Agaev, S. D. Mekhtiev, Zh. M. Mekhtieva, and N. F. Aliev, *Dokl. Akad. Nauk Azerb. SSR*, **23** (11), 18 (1967); (f) I. Tabuski, J. Hamuro, and R. Oda, *J. Amer. Chem. Soc.*, **89**, 7127 (1967).
(4) B. H. Eckstein, H. A. Scheraga, and E. R. Van Artsdalen, *J. Chem. Phys.*, **22** (1), 28 (1954).
(5) H. Stetter, M. Schwarz, and A. Hirschhorn, *Ber.*, **92**, 1629 (1959).
(6) (a) H. Stetter and C. Wulff, *Ber.*, **93**, 1366 (1960); (b) G. L. Baughman, *J. Org. Chem.*, **29**, 238 (1964).
(7) H. Stetter and E. Tresper, *Ber.*, **104**, 71 (1971).
(8) N. C. Deno and D. N. Lincoln, *J. Amer. Chem. Soc.*, **88**, 5357 (1966).