The Methyl Fluoride—Antimony Pentafluoride Complex

By JEAN-YVES CALVES and RONALD J. GILLESPIE*
(Department of Chemistry, McMaster University, Hamilton, Ontario, Canada)

Summary It is shown by ^{19}F and ^{1}H n.m.r. spectroscopy that the complex MeF–SbF_5 does not exist in solution in SO_2, as the solvent is methylated with the formation of CH_3OSO^+, but it can be obtained in SO_2F_2 as a stable species which undergoes neither intramolecular nor intermolecular exchange on the n.m.r. time scale.

THE formation of a MeF–SbF_5 complex has been postulated to explain the strong methylating ability of solutions of MeF–SbF_5 in SO_2 and SO_2ClF.[1] However, the ^{1}H n.m.r. spectra of such solutions showed only a singlet that could be attributed to a deshielded methyl group and no proton–fluorine coupling. In order to explain the absence of this coupling a rapid intramolecular fluorine exchange in the MeF–SbF_5 complex was proposed. A later investigation of the ^{19}F n.m.r. spectra of these solutions[2] showed the presence of the SbF_6^- and $Sb_2F_{11}^-$ ions and the formation of the fluxional molecules $MeSbF_6$ and $MeSb_2F_{11}$ was proposed to account for these spectra and the absence of H–F coupling.

We have now reinvestigated solutions of MeF and SbF_5 in SO_2, SO_2F_2, and other solvents. The ^{19}F n.m.r. spectrum of a solution of SbF_5 and excess of MeF in SO_2F_2 is given in the Figure. The ^{1}H n.m.r. spectrum of the same solution at −90 °C showed simply a deshielded doublet (δ 5·80; J 41 Hz) in addition to the doublet (δ 4·50; J 46 Hz) due to the excess of MeF. The magnitude of this splitting strongly suggests proton–fluorine coupling and the ^{19}F spectrum is completely consistent with the formation of the simple donor–acceptor complex (I). Thus, in addition to the solvent peak and the quartet signal due to excess of MeF the ^{19}F spectrum, at −145 °C, consists of a double doublet attributed to the four fluorine atoms F_e coupled to F_a (J 94 Hz) and to F_b (J 48 Hz), a quintet due to F_a coupled to the four atoms F_e (J 94 Hz), and a complex spectrum due to F_b. The latter in principle consists of a quartet of quintets due to coupling with the four atoms F_e and the three protons which, because of the similarity of the two coupling constants [J (F_b–H) 41 Hz; J (F_b–F_e) 48 Hz], is complex and not fully resolved. The coupling between F_a and F_b appears to be negligible as is also the case for the similar fluorine atoms in $Sb_2F_{11}^-$. In the ^{1}H spectrum two doublets are observed, one due to free MeF (δ 4·50; J 46 Hz) and the other to the complexed MeF (δ 5·80; J 41 Hz). At −80 °C there is no exchange between free and complexed MeF. In addition a very weak spectrum due to $Sb_2F_{11}^-$ was observed.

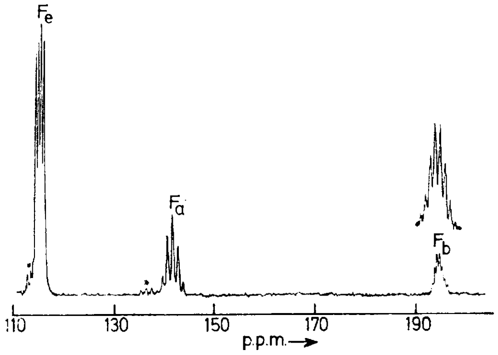
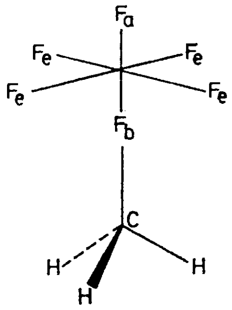


FIGURE. The ^{19}F n.m.r. spectrum (at −145 °C) (F-on-Sb region only) of a solution of MeF–SbF_5 in SO_2F_2 (reference: $CFCl_3$). * $Sb_2F_{11}^-$.

In contrast in SO_2 as solvent the ^{19}F n.m.r. spectrum shows only the lines due to $Sb_2F_{11}^-$ plus that of excess of MeF if it is present and the spectrum of the MeF–SbF_5 complex is not observed. Peterson[3] has recently given evidence that in solution in SO_2FCl the ion $MeOSO^+$ is formed by the reaction of an SbF_5–MeF mixture with SO_2. We have recently obtained a white crystalline material from a solution of MeF and SbF_5 in SO_2 which has been shown by an *X*-ray crystallographic examination of its structure,[4] to be the salt $MeOSO^+Sb_2F_{11}^-$. The absence of proton–fluorine coupling is thus quite understandable as the MeF is converted quantitatively into the $MeOSO^+$ ion.



(I)

In conclusion it may be stated that solutions of SbF_5 and MeF in SO_2 do not contain the MeF–SbF_5 complex as previously supposed. This complex, if formed initially, rapidly and quantitatively methylates the solvent to give the $MeOSO^+$ cation. However SO_2F_2 is not methylated and the complex MeF–SbF_5 may be obtained in this solvent as a stable species which does not undergo either intramolecular fluorine exchange at low temperature as previously supposed or intermolecular exchange with excess of MeF.

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[2] J. Bacon and R. J. Gillespie, *J. Amer. Chem. Soc.*, 1971, **93**, 6914.

[3] P. E. Peterson, personal communication.

[4] R. J. Gillespie, F. G. Riddell, and D. R. Slim, to be published.