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PHYSICAL METHODS OF INVESTIGATION

Coordination Modes and Reaction of Acetic Anhydride with Tantalum Pentafluoride

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Abstract—The composition and structure of compounds formed upon the reaction of equimolar amounts of TaF_5 and MeC(O)O(O)CMe in CH_2Cl_2 and upon dissolution of the fluoride in an anhydride excess have been studied by ^{19}F NMR (293–183 K). It has been found that, in both cases, the anhydride is fluorinated to form MeC(O)F (a quartet at 47.7 ppm, J_{FH} = 18 Hz) and the $MeC(O)O^-$ anion. In the spectra of the reaction mixture in CH_2Cl_2, the signals of pentafluoro complexes are assigned to the TaF_5[OC(Me)OC(O)Me] adduct and the $TaF_5[OC(O)Me]^-$ anion; on the basis of the chemical shifts of the singlets, they are assigned to the $TaF_4[OC(Me)OC(O)Me]^+$ and $TaF_2[OCOC(O)Me]_2^{3+}$ cations in which the anhydride acts as a chelating ligand. Upon the direct reaction of the reagents in an anhydride excess, the spectra at low temperatures show, in addition to the signal of the tetrafluoride cation, the signals of the hexafluorotantalate ion TaF_6^- and four trifluoroacetate complexes. Close relative concentrations of the latter enable the suggestion that they form chain or cyclic structures. It is believed that, in these structures, the acetate group has monodentate and bridging coordination modes, while chelating coordination mode seems to be less probable.

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Carboxylic anhydrides RC(O)OC(O)R can be considered analogues of bidentate bases, such as RC(O)XC(O)R, $R_2P(O)XC(O)Y$, and $R_2P(O)XP(O)R_2$ (X = CH_2, NH; Y = R, NR_2). Upon their reaction with highest fluorides of Group IV–VI transition and main-group elements, hard Lewis acids, they can be coordinated mono- or bidentately and act as bridging or chelating ligands, depending on the ratio of components; in addition, in the presence of a mobile hydrogen atom, they can be substituted for fluoride ions to produce HF [1–5]. Since $CH_3C(O)OC(O)CH_3$ is known to be one of the most active acylating agents, it was of interest to study how this property would affect the character of reactions with highest fluorides of d^0 transition metals. To study the interaction of carboxylic anhydrides with pentafluorides, the products of the reaction of $CF_3C(O)OC(O)CF_3$ with SbF_5—two dimeric mixed-ligand complexes—have been isolated and studies by X-ray crystallography [6, 7]. In one of them—$Sb_2(O_2CCF_3)F_9$, fluoride ion and $CF_3C(O)O^-$ anion act as bridges; in the other—$Sb_2O(O_2CCF_3)_2F_6$, bridges are the oxygen ion and two $CF_3C(O)O^-$ anions [6, 7].

In the present work, the products of the reaction of MeC(O)OC(O)Me with TaF_5 have been studied by ^{19}F NMR. TaF_5 was synthesized by fluorination of the metal with elemental fluorine in a quartz system. The anhydride was dried over P_2O_5, and distilled two times. The reaction was carried out under different conditions: by adding a solution of L in an inert polar solvent (CH_2Cl_2) to a weighed portion of pentafluoride under CH_2Cl_2 or by introducing TaF_5 directly into cooled acetic anhydride. All operations are carried out in a dry glove box in a nitrogen atmosphere. The ^{19}F NMR spectra were recorded on a Bruker AC-200 in the temperature range 290–183 K. Chemical shifts were referenced to CCl_3F. Negative values corresponded to upfield shifts of the signals.

The addition of a solution of L in CH_2Cl_2 to a TaF_5 sample under CH_2Cl_2 at room temperature led to the complete dissolution of the pentafluoride. The ^{19}F NMR spectrum of the resulting solution (Fig. 1) showed three signals. Quartet D at 47.7 ppm and J_{FH} = 18 Hz reflected, in our opinion, the formation of an organofluorine compound, acetic fluoride MeC(O)F, and strong narrow line B at 94 ppm and a broad exchange signal at 70 ppm were assigned to tantalum fluoride complexes.

With decreasing temperature, the exchange signal was split, and the spectrum at 223 K (Fig. 1) showed new resonance signals. Two strongest broad signals A and A' at 106 and 66 ppm with an intensity ratio of 1 : 4 and two weak signals at 62 and 88 ppm (the latter had a doublet fine structure) with the same intensity ratio were indicative of the presence of two tantalum pentafluoride complexes in the solution. The formation of

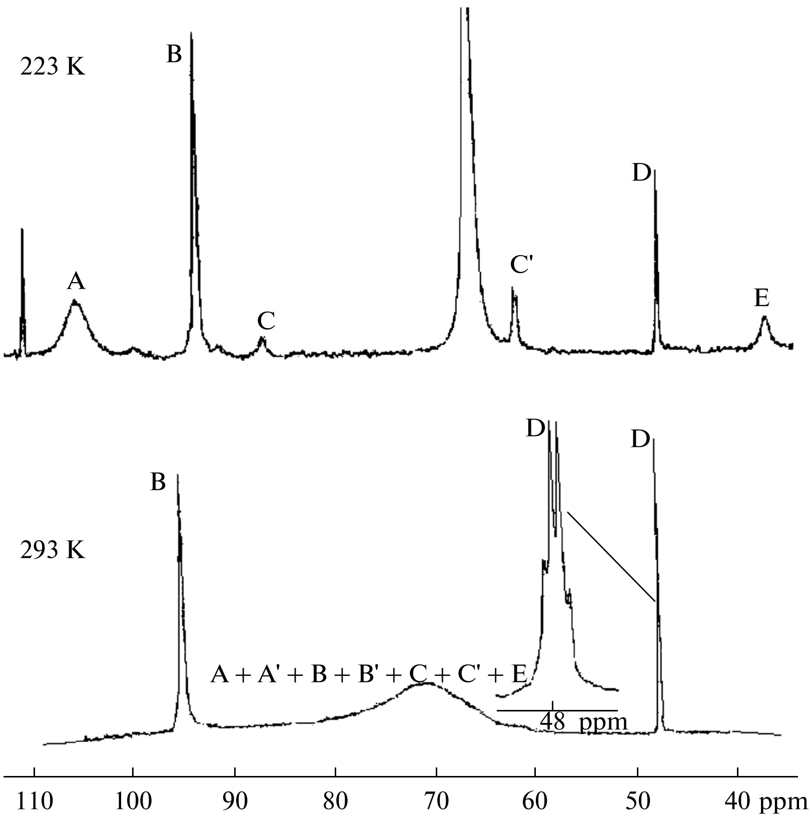
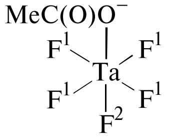


Fig. 1. ^{19}F NMR spectrum of an equimolar solution of MeC(O)OC(O)Me and TaF_5 in CH_2Cl_2: A and A'—F^1 and F^2 in $[TaF_5OC(Me)O]^-$, B—$\{[\eta^2\text{-}OC(Me)OC(Me)O]TaF_4\}^+$, C and C'—$F^1$ and F^2 in $TaF_5OCMeOC(O)Me$, D—MeC(O)F, and E—$[TaF_6]^-$.

$CH_3C(O)F$ as a result of the fluorination of acetic anhydride by the scheme

$$OCMeOC(O)Me + F^- = MeC(O)F + MeCO_2^-$$

allows us to suggest that one of these complexes can be the tantalum pentafluoride complex with acetate ion $[TaF_5OC(Me)O]^-$ (**1**) and the other, the adduct of TaF_5 with anhydride molecule $TaF_5OCMeOC(O)Me$ (**2**). The weak upfield signal at 38 ppm has been assigned to the hexafluorotantalate ion $[TaF_6]^-$ present in solution in low concentration.



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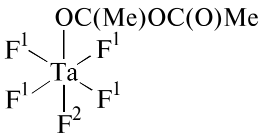

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To confirm the formation of a fluoroacetate complex, a suspension of TaF_5 in CH_2Cl_2 was prepared to which finely ground crystals of anhydrous MeCOONa or freshly distilled glacial acetic acid were added. After magnetic stirring of the suspension for 1 h, the ^{19}F NMR spectra showed signals at 70 and 118 ppm with a 4 : 1 intensity ratio assigned by us to $[TaF_5OC(Me)O]^-$. Since these shifts were close to those of the most intense signals A and A' observed in the spectra of the reaction products (Fig. 1), the latter were assigned to complex **1** and the weakest signals C and C', to complex **2**.

The lack of fine structures of the ^{19}F resonance lines of complex **1** at low temperatures points to a high exchange rate, which can be caused by the presence of the second donor site, the oxygen atom of the free C=O group of the ligand capable of coordination to the central tantalum atom to form an intermediate seven-coordinate pentafluoride complex. In the latter the acetate ion acts as a chelating ligand and forms an unstable four-membered chelate ring.

As for the strong line at 94 ppm narrow at room temperature, which had no fine structure down to the freezing point of the solution, it was assigned on the basis of its chemical shift to the tetrafluoride tantalum cation $\{[\eta^2\text{-}OC(Me)OC(Me)O]TaF_4\}^+$ (**3**) with the bidentately coordinated ligand. This assignment is supported by the fact that the signals of the previously studied analogous tantalum chelates $[\eta^2\text{-}(MeC(O)CHC(O)Me)TaF_4]$ [5] and $[(\eta^2\text{-}MeC(O)NC(O)Me)TaF_4]$ [4] are observed in the same range of ^{19}F NMR chemical shifts. Nonequivalence of the equatorial and axial fluorine atoms was observed only for the former complex with decreasing temperature to 198 K, which is evidence of the fast intramolecular exchange of fluorine atoms

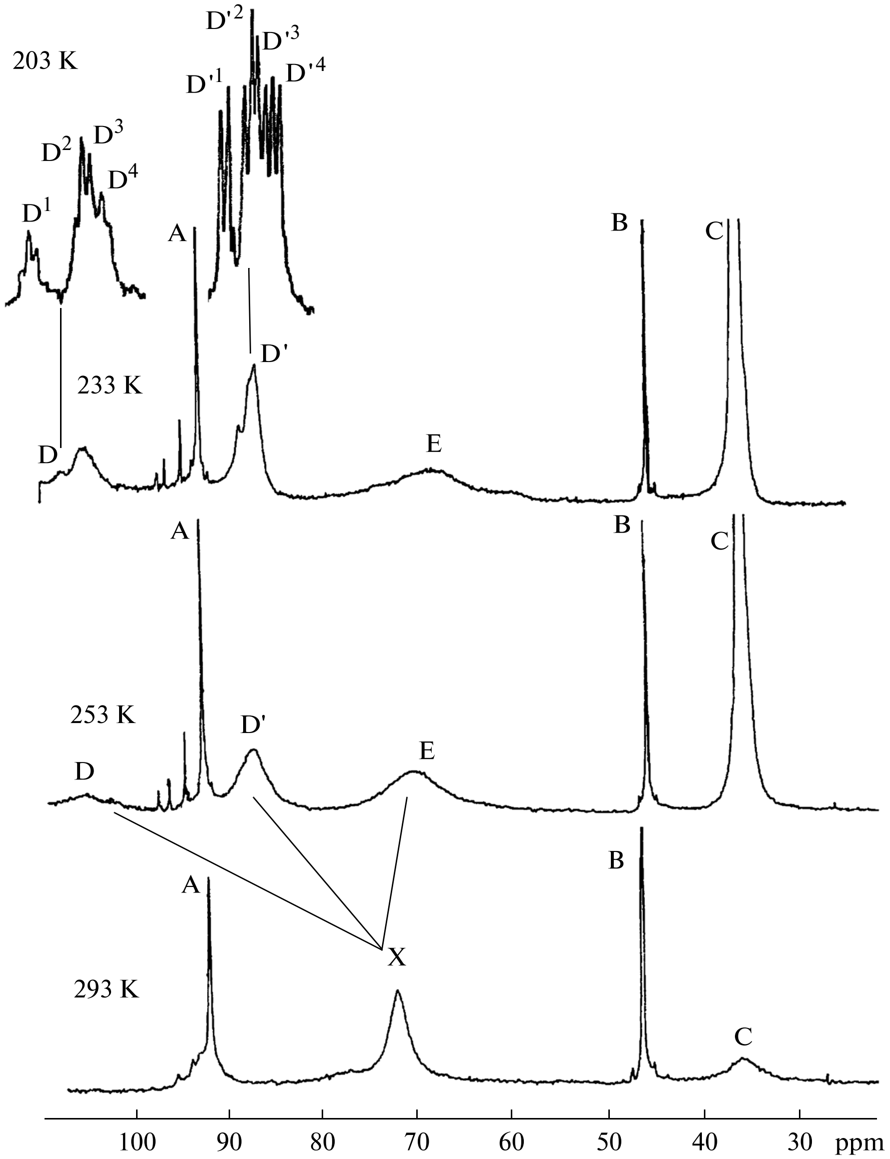
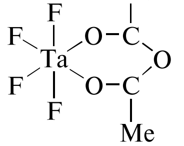


Fig. 2. ^{19}F NMR spectrum of a solution of TaF_5 in a MeC(O)OC(O)Me excess: A—$\{[\eta^2\text{-OC(Me)OC(Me)O]TaF}_4\}^+$; B—$CH_3C(O)F$; C—$[TaF_6]^-$; D^1 and D'^1—F^1 and F^2 in dimer **6**; D^2, D^3, D^4 and D'^2, D'^3, D'^4—F^{1a}, F^{1b}, F^{1c} and F^{2a}, F^{2b}, F^{2c} of oligomer **5**, respectively; E—exchange signal of $TaF_5OCMeOC(O)Me$ and $[TaF_5OC(Me)O]^-$.

through the pseudorotation mechanism, i.e., though the change of positions of nonequivalent fluorine atoms caused by rotation of the chelating ligand. The singlet in the lowest field at 111 ppm was assigned by us to the *trans*-$\{TaF_2[MeC(O)OC(O)Me]_2\}^{3+}$ complex (**4**).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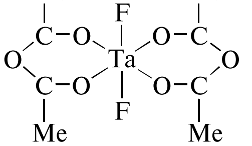
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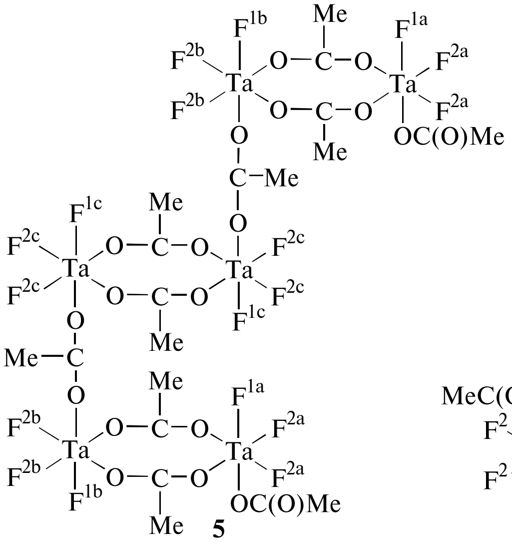
The reaction carried out under more severe conditions (without an inert solvent by dissolving TaF_5 in an acetic anhydride excess) led to products of somewhat different composition. The ^{19}F NMR spectrum of this solution at 293 K (Fig. 2) showed, in addition to the narrow signals of tetrafluoride cation **3** (A) and MeC(O)F (B), a weak and broad signal of the $[TaF_6]^-$ anion (C) and an exchange signal X, which split into a number of separate signals with decreasing temperature. With a decrease in temperature, new signals appeared, and the hexafluorotantalate signal intensity sharply increased; hence, the corresponding complexes are involved in intermolecular exchange of fluoride ions with $[TaF_6]^-$.

With decreasing temperature to 203 K, broad signals D and D' with the intensity ratio 1 : 2 (Fig. 2) were split and showed fine structure so that four triplets and four doublets (Fig. 2, D^{1-4}, D'^{1-4}) with the 1 : 2 ratio were observed, which pointed to the existence in solution of four trifluorotantalum complexes. The formation of MeC(O)F in the reaction of acetic anhydride with TaF_5 can be evidence of the presence of acetate ions $MeCO_2^-$ in solution. In our opinion, these ions are located in the inner coordination sphere of the tantalum cations together with the fluorine ions. Similar chemical shifts and relative intensities of the doublets and of the triplets enable the suggestion that the trifluoro complexes corresponding to these signals have the same composition of the coordination sphere and differ in the coordination modes of the ligand. For example, acetate ion can be terminal or can form one or two acetate bridges between tantalum cations. Close relative intensities of the signals of the same type allow us to assume that the corresponding complexes are involved in oligomeric chains or rings with bridging and terminal acetate groups (**5**, **6**).



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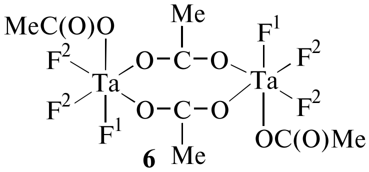

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The chelate coordination of the acetate ion seems to be less probable.

Thus, both in methylene chloride and in the absence of the solvent, in the reaction with TaF_5, acetic anhydride is not only monodentately or bidentately coordinated to tantalum ion forming a chelate ring and substituting for fluoride ions, but is also fluorinated by TaF_5 with cleavage of the oxygen bridge and formation of MeC(O)F and acetate ion. Upon the direct reaction of the components, there are considerable amounts of trifluoro acetate complexes in solution constituting oligomeric chains or rings with bridging and terminal coordination of acetate ions.

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