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Abstract

Full Text

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CHEMISTRY

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ON THE STRUCTURE OF COMPLEX COMPOUNDS OF STANNIC CHLORIDE WITH ESTERS

(Presented by Academician A. N. Terenin, 8 XII 1960)

One of the basic questions in the study of the structure of complex compounds of acids with esters is the question of which oxygen of the ester takes part in bond formation.

Beyer and Villiger ⁽¹⁾, Pfeiffer ⁽²⁾, and Chelintsev ⁽³⁾ believed that the bond in oxonium compounds of esters is formed through the carbonyl oxygen. Kurnakov and co-workers ⁽⁴⁾ attributed this bond to the oxygen of the alkoxy group. J. Kendall ⁽⁵⁾ considered that there were insufficient grounds for deciding the question in favor of either one of the oxygens of the ester. The authors of works devoted to optical studies of the intermolecular interaction of esters with acids ⁽⁶⁻⁹⁾ give preference to addition through the carbonyl oxygen. At the same time, the condensation of esters with aromatic compounds leads not only to alkylation but also to acylation of the latter. The mechanism of such acylation is easier to understand if one assumes that addition of esters to condensing agents occurs through the alkoxy oxygen, since in this case its bond with the acyl group must be weakened.

Fig. 1. Raman spectra of methyl propionate and its mixtures with stannic chloride: *I* –ester; *II* –mixture, 20 mol. % SnCl₄; *III* –25 mol. % SnCl₄; *IV* –33.3 mol. % SnCl₄; *V* –50 mol. % SnCl₄.

Fig. 2 and Fig. 3: Raman spectra

Figure 2: Fig. 2 and Fig. 3: Raman spectra

We have compared the Raman spectra of eleven esters with the spectra of their mixtures with stannic chloride over a wide range of concentrations.

In Figs. 1-3, as examples, the spectra of several esters and their mixtures with stannic chloride are presented.

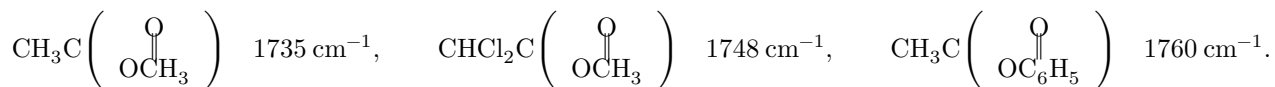
From consideration of Fig. 1 it is evident that, as stannic chloride is added to methyl propionate, i.e., on passing from spectrum I to spectrum V, the intensity of the frequency near 1730 cm^{-1} , belonging to the vibration of the carbonyl group, decreases regularly (spectra II and III) and vanishes at a mixture composition of 33.3 mole % SnCl_4 , corresponding to the compound $\text{SnCl}_4 \cdot 2\text{RCOOR}'$ (spectrum IV). In solutions of stannic chloride in methyl propionate, instead of this frequency (1730 cm^{-1}) a new split frequency of $1610\text{--}1640\text{ cm}^{-1}$ appears, whose intensity increases with increasing concentration of stannic chloride. An entirely analogous change in the spectra is observed in solutions of stannic chloride in methyl formate (Fig. 2) and in methyl acetate (Fig. 3).

Fig. 2. Raman spectra of methyl formate and its mixtures with stannic chloride:

I –ester; II –mixture, 12 mole % SnCl_4 ; III –50 mole % SnCl_4

Fig. 3. Raman spectra of methyl acetate and its mixture with stannic chloride: I –ester; II –6.67 mole % SnCl_4

If it is taken into account that the gradual disappearance of the frequency (1730 cm^{-1}), assigned to the vibration of the carbonyl group of free ester molecules, observed as the concentration of stannic chloride increases, is accompanied by an increase in the intensity of the shifted frequency, then it may be concluded that the latter belongs to the vibration of the $\text{C}=\text{O}$ group in the complex. This gives us grounds to assert that the addition of stannic chloride to the ester molecule takes place at the site of the carbonyl oxygen. Such a conclusion may also be supported by the following consideration. If addition of stannic chloride occurred at the site of the alkoxy oxygen, one would expect an increase in the frequency of the $\text{C}=\text{O}$ group, since it is known that introduction into an ester molecule of acceptor atoms and groups increases the frequency of the $\text{C}=\text{O}$ group:

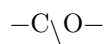


Meanwhile, in the spectra of Figs. 1-3 a lowering of the frequency of the $\text{C}=\text{O}$ group is observed. This lowering is of the same order as the lowering of the frequency of the $\text{C}=\text{O}$ group

in acetone⁽¹⁰⁾, whose addition to stannic chloride through the carbonyl oxygen is beyond doubt.

Thus, the totality of the data permits the conclusion that esters add to stannic chloride through the carbonyl oxygen. Bystrov and Filimonov⁽⁹⁾, on the basis of a study of the infrared spectra of esters with metal halides, arrived unambiguously at the same conclusion. Taking into account that addition of the C=O group to Sn⁴⁺ should lead to a change in the entire ester molecule because of the mutual influence of the atoms in the molecule on one another, it seemed of interest to us to trace, insofar as possible, the change in the frequencies of all bonds in the ester molecule.

In the spectra of mixtures of esters with stannic chloride, the appearance of a new frequency in the region of 1320 cm⁻¹ is observed. Consideration of the literature data^(8, 11, 12) makes it possible tentatively to assign it predominantly to the stretching vibration of the bond



shifted toward higher frequencies. In the case of methyl acetate (Fig. 3), this is illustrated by a considerable shift of the frequency 1252 cm⁻¹ to 1320 cm⁻¹. The increase in frequency in the region from 850 cm⁻¹ to 880 cm⁻¹ (Figs. 1 and 3), which in the literature⁽¹³⁾ is assigned mainly to the vibration of the bond



situated adjacent to the carbonyl group, in all probability indicates its strengthening. In the spectrum of methyl formate (Fig. 2) there is a lowering of the vibration frequency of the O-CH₃ bond^(12, 14) from 910 cm⁻¹ to 884 cm⁻¹. The observed change in the vibration frequencies of bonds in ester molecules under the influence of their addition to stannic chloride can apparently be explained by an intramolecular shift of electronic charges along the bonds⁽¹⁵⁾.

These changes in the Raman spectra make it possible to propose an assumption concerning the structure of the complex compounds of stannic chloride with esters, which may be illustrated by the following scheme:



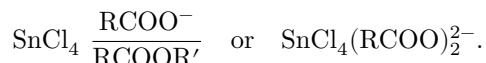
Such a distribution of the electron cloud in the molecule, in particular, should increase the ability of the aliphatic radical of the alkoxy group to split off in the form of an alkyl cation R⁺, i.e., should lead to polarization of the ester molecule and to its electrolytic dissociation. However, an alkyl cation is not capable of prolonged independent existence in solution and is split off only in the presence of molecules with which it can combine. Such particles, capable of accepting

an alkyl cation, are the ester molecules themselves. Therefore the electrolytic dissociation of the complex compounds $\text{SnCl}_4 \cdot 2\text{RCOOR}'$ with splitting off of an alkyl cation occurs in an excess of ester molecules; in this process compounds of the composition $\text{SnCl}_4 \cdot 3\text{RCOOR}'$ and $\text{SnCl}_4 \cdot 4\text{RCOOR}'$ are formed (^{16, 17}).

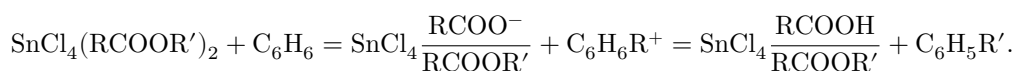
Let us now follow the behavior of the new split band at 1610–1640 cm^{-1} in solutions of stannic chloride in esters as the concentration changes. In Fig. 1 it is clearly seen that the intensity of the high-frequency component of the 1640 cm^{-1} band increases with increasing concentration of the ester (transition from spectrum V to spectrum II), where conditions are created that are favorable for the formation of the compounds $\text{SnCl}_4 \cdot 3\text{RCOOR}'$ and $\text{SnCl}_4 \cdot 4\text{RCOOR}'$, and it tends to disappear when the concentration of stannic chloride is increased (transition from spectrum II to V). On the other hand, with increasing con-

centration of stannic chloride, i.e., in the concentration region in which the compound $\text{SnCl}_4 \cdot 2\text{RCOOR}'$ predominantly exists, an increase in the intensity of the component of the band near 1610 cm^{-1} is observed (transition from spectrum II to spectrum V).

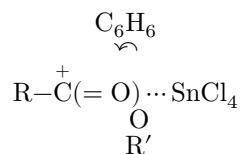
Such behavior of the split band with a change in the concentration of the solutions naturally suggests assigning the frequency near 1610 cm^{-1} to the C=O vibration in the complex compound $\text{SnCl}_4 \cdot 2\text{RCOOR}'$, and the frequency near 1640 cm^{-1} to the vibration of the carbonyl group in the anions



The possibility of detachment of the alkyl cation R^+ in the complex and its interaction with aromatic hydrocarbons implies an ionic mechanism for the alkylation reaction of the latter:



On the other hand, the proposed structure of the complex compound admits that the acylation reactions of aromatic compounds by esters in the presence of stannic chloride proceed through the formation of ternary complexes:



Owing to the interaction of the substance being acylated (electron donor) with the positive carbon atom, the possibility is created for a dynamic displacement of electrons and cleavage of the $-\text{C}-\text{OR}'$ bond.

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