D. S. BYSTROV and V. N. FILIMONOV

1960

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

D. S. BYSTROV and V. N. FILIMONOV

CHANGES IN THE INFRARED ABSORPTION SPECTRA OF CERTAIN ESTERS UPON ADDITION TO THEM OF $TiCl_4$, $SnCl_4$, $AlCl_3$, AND $AlBr_3$

(Presented by Academician A. N. Terenin, 9 XI 1959)

The study of the products of addition of electron-acceptor molecules of metal halides to ester molecules is of considerable interest in view of the fact that $AlCl_3$ and certain other metal halides catalyze alkylation and acylation reactions of aromatic compounds with esters (1). In the present work, in order to determine what changes individual valence bonds in ester molecules undergo upon their interaction with metal halides, and to establish the site of addition of the halides to allene molecules, the IR absorption spectra were investigated for the products of addition of $TiCl_4$, $SnCl_4$, $AlCl_3$, and $AlBr_3$ to methyl formate, isoamyl formate, ethyl acetate, and propyl acetate*.

$TiCl_4$ and $SnCl_4$ form with esters of formic and acetic acids stable molecular compounds of composition $R_1COOR_2 \cdot TiCl_4$ and $2R_1COOR_2 \cdot SnCl_4$, whose physicochemical properties have been investigated in considerable detail (3).

The compounds formed in the interaction of formates and acetates with $AlCl_3$ and $AlBr_3$ have been less studied. It is known, however, that mixing ethyl acetate with $AlCl_3$ (4) and $AlBr_3$ (5) at room temperature, even with an excess of aluminum halides, is not accompanied by decomposition of the ester; moreover, the latter can again be isolated from the compound with $AlCl_3$ by decomposing it with ice.

The molecular compounds of metal halides with esters were investigated by us in the solid state and were prepared as follows. A plane-parallel plate of rock salt or fluorite, used as a substrate, was placed in a vacuum cuvette equipped with NaCl windows. A thin layer of metal halide was deposited on the plate in vacuum by condensation of vapors ($TiCl_4$, $SnCl_4$) on a previously cooled surface or by sublimation ($AlCl_3$, $AlBr_3$). Then vapors of the ester under investigation were admitted into the cuvette, where they reacted with the halide layer. (The esters were preliminarily dried with $CaCl_2$.) After pumping off at room temperature the excess, unreacted amount of ester, the plate was moved to the part of the cuvette containing the windows, and the spectrum was recorded. This method of sample preparation made it possible to obtain, for spectral study, the required

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

thin (0.005 mm) layers of molecular compounds, scattering little light, without exposing them to air and without dispersing them in a medium that reduces light scattering. At the same time, however, it precluded the possibility of controlling the composition of the compounds formed.

An IKS-14 IR spectrometer with NaCl and LiF prisms was used to obtain the spectra. The spectral slit width was usually 15-20 cm^{-1}.

* Preliminary data indicating the addition of metal halides to the carbonyl group of ethyl acetate were published by us in paper (2).

The frequencies of the maxima of the absorption bands of the molecular compounds of ethyl acetate and methyl formate that we investigated are given in Tables 1 and 2. There, for comparison, are also given the vibrational frequencies of gaseous and liquid ethyl acetate and the principal frequencies of the free methyl formate molecule. In Fig. 1, as an example, transmission spectral curves are presented for gaseous ethyl acetate and for the same ester after addition of $TiCl_4$. In Figs. 2 and 3 a schematic representation is given of the spectra obtained by us for the molecular compounds of propyl acetate and isoamyl formate, as well as of the corresponding gaseous esters.

Fig. 1. Absorption spectra of ethyl acetate: 1—gaseous ethyl acetate; 2—$CH_3COOC_2H_5 + TiCl_4$

Comparison of the absorption spectra of the molecular compounds with the spectra of the pure esters shows that addition of metal halides to all the esters investigated by us leads to the disappearance in the spectra of these compounds of the two most intense absorption bands, located at 1770-1750 and 1250-1200 cm^{-1}. The first of these bands ($\nu C = O$) is associated mainly with the stretching vibration of the carbonyl group; the second,

Fig. 2. Position of the absorption maxima of gaseous propyl acetate and of the molecular compounds of propyl acetate with $TiCl_4$, $SnCl_4$, and $AlBr_3$

designated as $\nu\overset{\|}{C}-O$, in the case of acetates belongs chiefly to the antisymmetric stretching vibration of the group $\begin{matrix}C\\O\end{matrix}\!>C=$, and in the case of formates—to the stretching vibration of the bond $\overset{\|}{C}-O$ (7,8). At the same time, two new strong absorption bands appear in the spectra of the addition products, with maxima at 1635-1600 and 1360-1300 cm^{-1}.

Fig. 3. Position of absorption maxima of gaseous isoamyl formate and molecular compounds of isoamyl formate with TiCl4 and SnCl4

Figure 3: Fig. 3. Position of absorption maxima of gaseous isoamyl formate and molecular compounds of isoamyl formate with TiCl4 and SnCl4

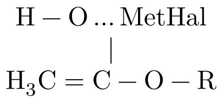
Such a change in the vibrational spectra cannot be explained by addition of the metal halides to the oxygen atom of the alkoxy group of the ester molecules. Indeed, in this case one would naturally expect

a slight change in $\nu C = O$ and a lowering of the vibration frequency $\nu C = O$. On the other hand, the disappearance of absorption bands in the region 1770-1750 cm^{-1} and the appearance instead of them of new bands shifted by 120-160 cm^{-1} toward lower frequencies agrees well with the assumption that metal halides add to the carbonyl group of ester molecules. The new absorption bands in the region 1635-1600 cm^{-1} may in this case be assigned to the vibration of the carbonyl group, perturbed as a result of the addition to it of an electron-acceptor agent. The position of these bands

Fig. 3. Position of the absorption maxima of gaseous isoamyl formate and of the molecular compounds of isoamyl formate with $TiCl_4$ and $SnCl_4$

approximately coincides with the position of the C=O bands in the molecular compounds of $AlBr_3$ and $SnCl_4$ with acetone (1635-1625 cm^{-1}) (9) and of $AlBr_3$ with acetaldehyde (1660 cm^{-1}) (2), formed as a result of the addition of metal halides to the carbonyl groups of organic molecules.

It should be noted that the disappearance of absorption bands at 1770-1750 cm^{-1} in the case of ethyl and propyl acetate can also be explained by the transition of these esters into the enol form upon addition of metal halides to them:



$$\begin{array}{c} \mathrm{H-O\ldots MetHal} \\ | \\ \mathrm{H_3C=C-O-R} \end{array}$$

The absorption bands at 1635-1600 cm^{-1} could in this case be assigned to vibration of the C=C bond. This assumption, however, seems to us unlikely, since molecular compounds of formates, which cannot pass into the enol form, exhibit absorption bands with maxima at the same frequencies. In addition, in the spectrum of the molecular compounds of ethyl acetate there are no frequencies characteristic of CH groups located at a double bond.

The new intense absorption bands in the region 1360-1300 cm^{-1} should evidently be regarded as absorption bands of $\nu C - O$, shifted toward higher frequencies. The strong shift of these bands apparently indicates a considerable strengthening of the $C - O$ bond as a result of weakening of the adjacent double bond. In the case of methyl formate, it is also possible to trace a lowering of the vibration frequency of the O—CH_3 bond from 925 to 885-865 cm^{-1}, caused, in all probability, by a decrease in the strength of this bond.

The increase in the frequency of $\nu C-O$, as well as the lowering of the vibration frequencies of the C=O bond, indicates addition of metal halides to the carbonyl group. Thus, investigation of the infrared spectra makes it possible to decide unambiguously the question of the site of addition of metal halides to ester molecules.

$AlCl_3$ and $AlBr_3$ generally cause a stronger shift of the absorption bands of esters than do $TiCl_4$ and $SnCl_4$, which is in agreement with the greater catalytic activity of the aluminum halides. Especially —

···the absorption spectrum of propyl acetate undergoes considerable changes upon addition of $AlBr_3$ to it (see Fig. 2).

Table 1

Frequencies of the ethyl acetate molecule (cm^{-1})

Literature data (^{6})	$CH_3COOC_2H_5$ gas	$CH_3COOC_2H_5$ liquid	$CH_3COOC_2H_5$ + $TiCl_4$	$CH_3COOC_2H_5$ + $SnCl_4$	$CH_3COOC_2H_5$ + $AlCl_3$	$CH_3COOC_2H_5$ + $AlBr_3$
$\nu C=O$	1770 s.	1745 s.	1625 s.	1633 s.	1620 s.	1610 s.
δCH_2, CH_3	1463 sl.	1458 sl.	1450 m.	1475 m.1425 m.	1485 m.1455 m.	1490 m.1455 m.
δCH_3 acyl.	1375 m.	1377 m.	1392 m.	1388 m.	1393 m.	1395 m.
$\nu C\|-O$	1245 s.	1250 s.	1335 s.1160 sl.	1325 s.	1345 m.1163 sl.	1348 m.1165 sl.
	1100 sl.1058 m.930 sl.852 sl.785 sl.	1100 sl.1050 m.940 sl.918 sl.850 sl.785 sl.	1045 m.1010 m.850 m.812 m.	1100 sl.1045 m.1008 m.855 m.815 sl.	1100 sl.1045 m.1007 m.840 m.820 m.	1105 sl.1045 m.1010 m.845 m.810 sl.

Table 2

Frequencies of the methyl formate molecule (cm^{-1})

Literature data (7)	$HCOOCH_3$ (7)	$HCOOCH_3$ + $TiCl_4$	$HCOOCH_3$ + $SnCl_4$	$HCOOCH_3$ + $AlCl_3$	$HCOOCH_3$ + $AlBr_3$
$\nu C = O$	1754	1635 s.	1632 s.	1635 s.	1630 s.
δCH_3	146514541445	1435 m.	1440 m.	1442 m.	1437 m.
δCH	1375	1372 m.	1375 m.	1385 m.	1378 m.
$\nu C\|-$	12071168	1308	1322	1346 s.1175	1355
$O\delta CH_3$		s.1180 sl.	s.1170 sl.	sl.1100 sl.	s.1100 sl.
$\delta CH\nu O-$	1032925767	885 m.811	1000 m.883	978 sl.870	865 sl.830
$CH_3\delta OCO$		m.	m.812 m.	m.828	sl.780 sl.
				m.798 m.	

The authors express their deep gratitude to Academician A. N. Terenin, under whose supervision the present work was carried out.

Scientific Research Institute of Physics
Leningrad State University
named after A. A. Zhdanov

Received
2 XI 1959

REFERENCES

[1] Ch. Thomas, *Anhydrous Aluminum Chloride in Organic Chemistry*, IL, 1940.
[2] A. N. Terenin, V. N. Filimonov, D. S. Bystrov, *Izv. AN SSSR, ser. fiz.*, **22**, 1100 (1958).
[3] N. S. Kurnakov, E. B. Shternina, *Izv. AN SSSR, OKhN*, 1936, 467; N. S. Kurnakov, N. K. Voskresenskaya, *Izv. AN SSSR, OKhN*, 1937, 797; Yu. A. Lysenko, O. A. Osipov, E. K. Akopov, *ZhNKh*, **1**, 535 (1956); Yu. A. Lysenko, O. A. Osipov, *ZhOKh*, **28**, 1724 (1958).
[4] D. N. Kursanov, R. R. Zel' vin, *ZhOKh*, **9**, 2173 (1939).
[5] U. Takegami, U. Shingu, *Bull. Inst. Chem. Research, Kioto Univ.*, **24**, 84 (1951); *Chem. Abstr.*, **47**, 12276 (1953).
[6] B. Nolin, R. N. Jones, *Canad. J. Chem.*, **34**, 1392 (1956).
[7] J. K. Wilmshurst, *J. Mol. Spectr.*, **1**, 201 (1957).
[8] S. A. Francis, *J. Chem. Phys.*, **19**, 942 (1951).
[9] V. N. Filimonov, D. S. Bystrov, A. N. Terenin, *Optics and Spectroscopy*, **3**, 480 (1957); A. Terenin, V. Filimonov, D. Bystrov, *Zs. Electrochem.*, **62**, 180 (1958).

Note: Figure translations are in progress. See original paper for figures.