D. S. BYSTROV

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

D. S. BYSTROV

INFRARED SPECTRA OF COMPLEXES OF OLEFINS WITH ALUMINUM HALIDES

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The interaction of olefins with aluminum halides has been studied repeatedly. Although in a number of cases it has been shown that, provided the reagents are purified with extraordinary care, aluminum chloride and bromide [1,2] and boron trifluoride [3,4] do not interact with certain olefins, in the presence of small amounts of proton-donor substances—cocatalysts—complexes of olefins with aluminum halides are formed [5,6], about the nature of which almost nothing is known.

Fig. 1. Infrared spectra of complexes of ethylene and its alkyl-substituted derivatives.
1 –ethylene + $AlBr_3$, 2 –ethylene + $AlCl_3$, 3 –propylene + $AlCl_3$, 4 –trimethylethylene + $AlCl_3$, 5 –tetramethylethylene + $AlCl_3$

We investigated the IR spectra of the products of the interaction of aluminum chloride and bromide with ethylene, propylene, tri- and tetramethylethylene, and cyclopentene. (Complexes of cyclohexene with $AlCl_3$, $AlBr_3$, and $SnCl_4$ had been studied earlier [7].) The complexes were obtained by the reaction of the olefin with a layer of aluminum halide sublimed onto a NaCl or KBr plate in a vacuum cell, which made it possible to obtain spectra of the complexes at temperatures down to $-100°$ without exposing them to air. The olefins were purified by low-temperature vacuum distillation; the aluminum chloride used contained impurities of hydrolysis products (in a thick layer one could observe a weak absorption band at 3200 cm^{-1}), which apparently promoted the occurrence of complex-formation reactions. Ethylene, at an initial pressure of 30-50 mm Hg and a temperature of $+20°$, reacted with $AlCl_3$ in 5-10 h; propylene under analogous conditions reacted in 1 h; in the remaining cases, to prevent polymerization of the olefins, the complex-formation reaction was carried out at temperatures of $-50 \div -20°$, by condensation of olefin vapors on a cooled layer of $AlCl_3$, and was completed within several minutes. As a result of the reaction, nonvolatile compounds were formed which could not be removed by evacuation at a pressure of 10^{-3} mm Hg, and which were stable at room temperature in vacuum for at least several days. Their IR spectra are shown

in Figs. 1-3. In all spectra an intense band is observed at 1540-1500 cm^{-1}, which should be assigned to the stretching vibration of the double bond, perturbed by addition of the acceptor. This interpretation is confirmed by analogy with the spectra of olefins coordinated with platinum, in which this vibration is observed at 1500 cm^{-1} ($^{8-12}$). It is interesting, however, to note differences in the spectra of the catalytically active (^{5,6}) complexes of olefins with $AlCl_3$ and $AlBr_3$ and the complexes of olefins with platinum chlorides, which have no catalytic activity.

Whereas in complexes of olefins with platinum the frequencies of the stretching vibrations of CH at the double bond are lowered only slightly, remaining substantially higher than the frequencies of vibrations of aliphatic CH bonds, in complexes of olefins (even ethylene) with $AlCl_3$ and $AlBr_3$ only absorption bands of aliphatic CH bonds are observed in this region of the spectrum. The $\nu \mathrm{C}=\mathrm{C}$ bands in the spectra of complexes of cycloolefins with $AlCl_3$ have very high intensity, considerably exceeding the intensity of other bands of the spectrum in the region below 1600 cm^{-1} (Figs. 2, 3). The relative intensity of the bands at 1500 cm^{-1} in the spectra of platinum complexes of olefins is usually considerably lower (^{10,11}).

Fig. 2. IR spectrum of cyclopentene (1) and of its complex with $AlCl_3$ (2)

The spectra of the complexes of ethylene and its alkyl-substituted derivatives with $AlCl_3$ and $AlBr_3$, with the exception of the bands at 1535 cm^{-1} and at 790-770 cm^{-1}, are very close to the spectra of high-molecular-weight paraffins; evidently, in this case complex formation is accompanied by polymerization, and the observed spectrum belongs not to the initial olefin but to a considerably higher-molecular-weight one. Upon displacement of the hydrocarbon from the complex by the action of strong bases (ammonia, water), a simultaneous decrease in the intensity of the band at 1535 cm^{-1} and of the νCH and δCH bands occurs, which confirms their belonging to a single carrier. In complexes of cycloolefins, the absorption bands in the region below 1500 cm^{-1}, in position and number, correspond approximately to the bands in the spectra of the initial olefins—polymerization in this case apparently does not occur.

Fig. 3. IR spectrum of cyclohexene (1) and of its complex with $AlCl_3$ (2)

In this connection it is interesting to note that the lowering of the frequency $\nu C = C$ in cyclopentene, as compared with cyclohexene, by 30 cm^{-1}, caused by a change in the magnitude of the angle

$$C = ^{C} \tag{13}$$

is retained also in the complexes (1500 cm^{-1} in the cyclopentene complex as against 1535 cm^{-1} in the cyclohexene complex).

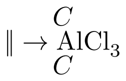
Fig. 4. IR absorption spectra of aluminum bromide. 1—crystalline aluminum bromide (Al_2Br_6), 2—$AlBr_3$ + ethylene, 3—$AlBr_3 \cdot C_2H_5Br$

Figure 2: Fig. 4. IR absorption spectra of aluminum bromide. 1—crystalline aluminum bromide (Al_2Br_6), 2—$AlBr_3$ + ethylene, 3—$AlBr_3 \cdot C_2H_5Br$

To determine the state of the aluminum halide in the complexes with olefins, the change in the spectrum of $AlBr_3$ during complex formation was investigated. As is seen from Fig. 4, the absorption bands at 567 cm^{-1} and 493 cm^{-1}, characteristic of the dimer Al_2Br_6 and observed both in pure aluminum bromide and in the σ-complex with benzene, in which aluminum bromide is present as the ion $Al_2Br_7^-$ (^{14}), disappear on interaction of $AlBr_3$ with ethylene. The spectrum of $AlBr_3$ in the complex with ethylene resembles its spectrum in the complex with ethyl bromide, in which $AlBr_3$ is monomeric (^{15}); this indicates that the olefin complexes studied are indeed coordination compounds, and that the aluminum halide in the complex is monomeric. Against the possible assumption that the spectra obtained belong to vinylaluminum chlorides there is also the fact that in vinyl borofluoride the frequency $\nu C = C$ has the normal value 1629 cm^{-1} (^{16}).

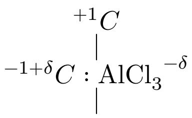
Fig. 4. IR absorption spectra of aluminum bromide. 1—crystalline aluminum bromide (Al_2Br_6), 2—$AlBr_3$ + ethylene, 3—$AlBr_3 \cdot C_2H_5Br$

Of great interest is the question of the nature of the bond between the olefin and the aluminum halide. The closeness of the values of the frequencies $\nu C = C$ in the spectra of aluminum halide complexes and in the spectra of platinum complexes may be interpreted as indicating that aluminum accepts π-electrons, attaching itself symmetrically with respect to the double bond and forming a π-complex



$$\| \rightarrow \overset{C}{\underset{C}{\mathrm{AlCl}_3}} \tag{I}$$

However, the high reactivity of aluminum halide complexes is usually interpreted in favor of the dipolar structure (II) (^{5,17}),



$$\begin{array}{l} \quad {}^{+1}C \\ \qquad | \\ {}^{-1+\delta}C : \mathrm{AlCl}_3{}^{-\delta} \\ \qquad | \end{array} \tag{II}$$

which arises if the pair of electrons occupying the π-bond during complex formation passes to a σ-orbital, which is a hybrid sp^3-orbital of one of the C atoms of the double bond, with which the attached metal halide is also accepted. With such a structure there agrees well the fact of the very high intensity of the valence vibration $\nu C = C$ in the complex, which is difficult (though not impossible) to explain on the assumption of a π-complex structure of the compounds studied.

The question, however, is decided by whether the semipolar bond $\overset{+1}{C}—\overset{-1+\delta}{C}$ can have a force constant sufficiently high to ensure the appearance of the frequency 1535 cm^{-1}. Calculations of the frequency $\nu C = C$ in the complexes, carried out for a group of coordinates including the coordinates of the C and H atoms, directly···

directly bonded to the atoms of the double bond showed that the observed frequency value can be obtained for a force-constant value $K(\mathrm{C} = \mathrm{C}) = 12.5 \div 11.5$ (here and below the force constants are in $1 \cdot 10^6\ \mathrm{cm}^{-2}$), whereas in free olefins $K(\mathrm{C} = \mathrm{C}) = 14.2$ (18). Neglect of the kinematic interaction with the molecule of the added acceptor probably cannot significantly distort the result of the calculation, in view of the comparatively large mass of the Al atom and the very small value of the force constant of the donor-acceptor bond (not more than 3.0). Indeed, replacement of one of the hydrogen atoms of ethylene by chlorine, which has a greater mass than aluminum but also a considerably larger force constant $K(\mathrm{C-Cl}) = 6.0$, leads, at an unchanged value of the force constant $K(\mathrm{C} = \mathrm{C})$, to a shift of the frequency $\nu\mathrm{C} = \mathrm{C}$ by only 25 cm^{-1} (19).

There are very few data on the length, strength, and force constants of semipolar bonds; it is known, however, that the $\overset{+}{\mathrm{N}} - \overset{-}{\mathrm{O}}$ bond in trialkylamine oxides has a stretching-vibration frequency of 990 cm^{-1} and the length of an ordinary single $\mathrm{N-O}$ bond. Addition to the oxygen atom of a proton, which should compensate the negative charge located on the oxygen, leads to a very insignificant change in the stretching-vibration frequency and in the length of the NO bond (20,21).

This would seem to contradict the results of a simple calculation, which shows that the shortening of the bond caused by the electrostatic interaction of two singly charged ions placed at a distance of 1.5 Å should amount to 0.15–0.2 Å, which makes the bond length close to the length of a double bond. The indicated contradiction is evidently explained by the fact that, as a result of inductive displacements of electron density, the actual effective charges on the atoms of a semipolar bond are considerably less than unity.

The considerations set forth lead one to believe that the compounds investigated are built as π-complexes (structure I). The high intensity of the $\nu\mathrm{C} = \mathrm{C}$ band in the spectra of the complexes may be explained by a change in the degree of acceptance of electrons from the double bond when the $\nu\mathrm{C} = \mathrm{C}$ distance changes –this should cause a change in the dipole moment of the donor-acceptor bond with a frequency equal to the vibration frequency $\nu\mathrm{C} = \mathrm{C}$.

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