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Abstract

Full Text

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Spectroscopic Study of the Complex of Natural Rubber with Titanium Tetrachloride

(Presented by Academician V. A. Kargin, March 13, 1965)

It is known that, under the influence of titanium tetrachloride, cyclization of rubbers occurs (ˆ1). The present study was undertaken in order to clarify the nature of the intermediate products of this process. Natural rubber (NR), treated with boiling acetone for 24 h and then reprecipitated with methanol from a solution in benzene, was used for the investigation. For measurements of the infrared (IR) spectra, an NR film

Fig. 1. IR spectra of an NR film ($d = 0.004$ cm) (1), of the same film + $TiCl_4$ after 5 min (2), after 20 min (3), and one day after preparation of the complex (4)

0.004 cm thick was prepared from a benzene solution at the center of a KBr disk. After thorough drying of the film in high vacuum, several drops of $TiCl_4$ were applied to it. The bright-orange product formed in this process was covered with a second KBr disk, after which its IR spectrum was immediately measured on a UR-10 spectrophotometer. The indicated KBr disks were parts of a cell with a constant thickness of 0.006 cm; in the assembled state the cell was completely hermetic. The IR spectrum of $TiCl_4$ was measured in a KBr cell with a constant layer thickness of 0.002 cm. To measure the electronic spectra, several drops of $TiCl_4$ were added to a 0.02% solution of NR in benzene. The electronic spectra were measured on an SFD-2 spectrometer.

All operations with $TiCl_4$ and with filling the cells were carried out in a hermetic chamber in an atmosphere of dry argon. The IR spectrum of the NR + $TiCl_4$ system (Fig. 1) differs markedly from the spectra of the starting rubber and of pure $TiCl_4$ (Fig. 2): in it a new intense band appears in the region of 1530 cm^{-1}, while the absorption band at 1665 cm^{-1}, assigned to stretching vibrations of the C=C bond in the starting NR, simultaneously disappears. Evidently, this band is shifted into the long-wavelength region by 135 cm^{-1} and its intensity increases. Approximately the same shift of the stretching-vibration band of the

Fig. 2. IR spectrum of TiCl4

Figure 2: Fig. 2. IR spectrum of TiCl4

Fig. 3. Electronic spectrum of 0.02% solution of NR in benzene + TiCl4

Figure 3: Fig. 3. Electronic spectrum of 0.02% solution of NR in benzene + TiCl4

C=C bond was observed in the formation of the π-complex of di-

diphenylethylene and its dimer with $SnCl_4$ (^{2}). According to Terenin and coworkers (^{3}), upon formation of the π-complex of cyclohexene with $SnCl_4$, the frequency of the stretching vibration of the C=C bond decreases by 115 cm^{-1}.

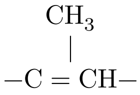
In the electronic spectrum of the NR + $TiCl_4$ system (Fig. 3), an intense absorption band is observed with a maximum in the region of 455 mμ; a band in this region was also observed in the electronic spectrum of the π-complexes of diphenylethylene and its dimer with $SnCl_4$ (^{2}).

These facts indicate that, in the interaction of NR with $TiCl_4$,

Fig. 2. IR spectrum of $TiCl_4$ ($d = 0.002$ cm)

Fig. 3. Electronic spectrum of a 0.02% solution of NR in benzene + $TiCl_4$

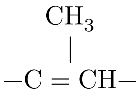
a π-complex is formed first of all. Evidently, as a result of the formation of this complex, the disappearance of the 3040 cm^{-1} band of the stretching vibration of the CH bond in the group



$$\overset{\displaystyle CH_3}{\overset{|}{-C}} = CH-$$

and the shift of the 840 cm^{-1} absorption band of the deformation vibration of this bond (^{4}) into the region 820–810 cm^{-1} are observed. In addition, in the IR spectrum of the NR + $TiCl_4$ system, alongside a very intense band at 500 cm^{-1}, corresponding to the stretching vibration of $TiCl_4$ (^{5}) and evidently due to an excess of $TiCl_4$ in the system, there is also a very intense band in the region of 435 cm^{-1}, which should be assigned to the stretching vibration of TiCl in the $TiCl_4$ molecule incorporated into the complex.

A number of changes in the IR spectrum of the NR + $TiCl_4$ system, in comparison with the spectrum of the initial NR, indicate cyclization of the rubber following the formation of the π-complex: a shift of the 2860 cm^{-1} band to 2880 cm^{-1} is observed; in the region 1670-1640 cm^{-1} a broad absorption band appears with a maximum at 1645 cm^{-1}; the maximum of the 1460 cm^{-1} band broadens and a second maximum appears next to it in the shorter-wavelength region; in the region 1100-1000 cm^{-1} a broad band with several maxima appears. In the region of 800 cm^{-1}, an intense band with two maxima at 820-810 cm^{-1} is observed; upon aging of the system this doublet merges into one broad band with a maximum at 800 cm^{-1}. The appearance of absorption bands in these regions of the spectrum was noted during cyclization of isoprene rubber in works ([6,7]) devoted to the investigation of IR spectra of cyclized rubbers. One component of the doublet in the region of 800 cm^{-1} in the spectrum of the NR + $TiCl_4$ system probably belongs to the deformation vibrations of CH in the group



$$-\overset{\overset{CH_3}{|}}{C}=CH-$$

the frequency of which is shifted from 840 to 820 cm^{-1} owing to complex formation. The other component is due to the emergence of cyclohexene structures in the system. Probably, also because of the cyclization occurring during aging of the system, the maxima of the bands in the regions of 1530 and 820 cm^{-1}, which belong to the perturbed double bonds in the π-complex, gradually become blurred,

and the overall background increases. The bright coloration of the complex in the cuvette is retained for several weeks.

The results of the present investigation indicate that cyclization of NR under the action of $TiCl_4$ proceeds through the formation of a π-complex.

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