CHEMISTRY

V. F. LAVRUSHIN and N. N. VERKHOVOD

1957

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

CHEMISTRY

V. F. LAVRUSHIN and N. N. VERKHOVOD

HALOCHROMISM OF PHENYL- AND CYCLOHEXYLCARBINOLS

(Presented by Academician A. N. Nesmeyanov, April 9, 1957)

In studying the phenomenon of halochromism of carbinols of various structures ([1–3]), we established that acid solutions of these compounds give two types of absorption spectra. Carbinols containing phenyl radicals are characterized by complex absorption curves comprising three or more absorption bands, whereas the curves of tertiary cyclohexanols and aliphatic alcohols possess only one absorption band and a broad inflection in the near visible spectrum.

Fig. 1. Triphenylcarbinol: 1 –in conc. H_2SO_4. Cyclohexyldiphenylcarbinol: 2 –in C_2H_5OH, 3 –in conc. H_2SO_4. Dicyclohexylphenylcarbinol: 4 –in C_2H_5OH, 5 –in conc. H_2SO_4

In this connection it was of interest to study the absorption spectra of acid solutions of aromatic carbinols as the benzene rings in their molecules are replaced by cyclohexane rings. For this purpose we undertook a comparative study of the absorption spectra of triphenylcarbinol, cyclohexyldiphenylcarbinol, dicyclohexylphenylcarbinol, tricyclohexylcarbinol, methyldicyclohexylcarbinol, and dicyclohexylcarbinol.

Triphenylcarbinol. The absorption spectra of a sulfuric-acid solution of triphenylcarbinol have been studied repeatedly ([4,5]). According to our data ([2]), the absorption curve of this solution (Fig. 1, 1) has four absorption bands: I – $\lambda = 4200$ Å, $\varepsilon = 50000$; II –$\lambda = 2900$ Å, $\varepsilon = 3100$; III –$\lambda = 2600$ Å, $\varepsilon = 4000$; and IV –$\lambda = 2280$ Å, $\varepsilon = 16000$.

Cyclohexyldiphenylcarbinol in ethyl alcohol solution has an absorption curve with one band, whose maximum is located at $\lambda = 2530$ Å and $\varepsilon = 7762$. The curve of the sulfuric-acid solution has a complex outline and is composed of three absorption bands (Fig. 1, 3): I –$\lambda = 393$ Å, $\varepsilon = 467$; II –$\lambda = 266$ Å, $\varepsilon = 398$; III –$\lambda = 230$ Å, $\varepsilon = 15140$.

Figure 2

Figure 2: Figure 2

In contrast to the curve of triphenylcarbinol, here the band in the visible spectrum is considerably less intense and has a broad inflection on its long-wavelength edge. In the place of the second band of triphenylcarbinol, the curve rises gently upward over a broad region of the spectrum and ends in the middle and

in the short ultraviolet by two absorption bands characteristic of aromatic carbinols ([2]).

Dicyclohexylphenylcarbinol in alcoholic solution also absorbs in the ultraviolet region of the spectrum and has one absorption band with a maximum at $\lambda = 2680$ Å and $\varepsilon = 3311$. In concentrated sulfuric acid it forms an orange-yellow turbid solution, which after heating for 15 min on a water bath becomes completely clear. The absorption curve of the sulfuric-acid solution extends over a broad region of the spectrum and includes five bands (Fig. 1, 4): I $-\lambda = 442$ Å, $\varepsilon = 316$; II $-\lambda = 398$ Å, $\varepsilon = 776$; III $-\lambda = 317$ Å, $\varepsilon = 851$; IV $-\lambda = 267$ Å, $\varepsilon = 2818$; V $-\lambda = 237$ Å, $\varepsilon = 8128$. The first two long-wavelength bands are located in the region of the broad long-wavelength band of triphenylcarbinol. The other two bands are shifted somewhat toward the visible spectrum. The shortest-wavelength band almost coincides with the band of triphenylcarbinol.

Tricyclohexylcarbinol, on interaction with concentrated sulfuric acid, at once gives a yellow color. The solution becomes completely transparent upon heating on a water bath for 10 min. In ultraviolet rays such a solution possesses bright light-green fluorescence.

Fig. 2. Tricyclohexylcarbinol: 1 –in conc. H_2SO_4, 2 –after dilution with C_2H_5OH. Methyldicyclohexylcarbinol: 3 –in conc. H_2SO_4, 4 –after dilution with C_2H_5OH. Dicyclohexylcarbinol: 5 –in conc. H_2SO_4, 6 –after dilution with C_2H_5OH.

The absorption curve of the sulfuric-acid solution (Fig. 2, 1) differs sharply from the above curves of carbinols containing phenyl radicals in their composition. In the region 5500–3800 Å there is a gently sloping bend, after which follows a broad absorption band with a maximum at $\lambda = 3050$ Å and $\varepsilon = 8913$.

Methyldicyclohexylcarbinol with concentrated sulfuric acid forms a yellow turbid solution, which becomes completely clear upon brief heating on a water bath. Under ultraviolet illumination it shows intense light-green fluorescence.

The absorption curve of the sulfuric-acid solution (Fig. 2, 3) consists of a gently sloping long-wavelength branch and a broad absorption band with a maximum at $\lambda = 3000$ Å and $\varepsilon = 6300$.

Dicyclohexylcarbinol also forms with concentrated sulfuric acid a yellow turbid solution, becoming completely clear after heating for 10 min on a water bath. In ultraviolet rays it displays intense light-green fluorescence.

The absorption curve of the sulfuric-acid solution of this carbinol (Fig. 2, 5), like those of the other cyclohexylcarbinols, has a long-wavelength bend extending into the visible region of the spectrum and one broad absorption band with a maximum at $\lambda = 3090$ Å and $\varepsilon = 7079$.

Thus, as a result of the study carried out of the absorption spectra of solutions of phenyl- and cyclohexylcarbinols in concentrated sulfuric acid, it was found that triphenylcarbinol, cyclohexyldiphenylcarbi-

···nol and dicyclohexylphenylcarbinol have absorption spectra of one type, with complex absorption curves that differ from one another in the number of absorption bands. For sulfuric-acid solutions of tricyclohexylcarbinol, methyldicyclohexylcarbinol, and dicyclohexylcarbinol, absorption spectra of another type were obtained, characterized by a simpler form of the curves, with a single absorption band.

The appearance of color upon interaction of all the carbinols studied by us with concentrated sulfuric acid, and its disappearance when the acid solutions are diluted with water, indicate that in this case we are dealing with the typical phenomenon of halochromy.

The phenomenon of halochromy of triphenylcarbinol has been well studied ([6]) and represents an acid–base interaction reaction:

$$(\mathrm{Ph})_3\mathrm{COH} + 2\mathrm{H_2SO_4} \rightleftharpoons [(\mathrm{Ph})_3\mathrm{C}]^+ + 2\mathrm{HSO_4^-}.$$

Since other phenyl- and cyclohexylcarbinols behave toward sulfuric acid like triphenylcarbinol, it should be assumed that their interaction with the acid proceeds in an analogous manner:

$$\mathrm{CyC(OH)(Ph)_2} + 2\mathrm{H_2SO_4} \rightleftharpoons [\mathrm{CyC(Ph)_2}]^+ + 2\mathrm{HSO_4^-} + \mathrm{H_3O^+}$$

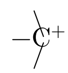
$$(\mathrm{Cy})_2\mathrm{C(OH)Ph} + 2\mathrm{H_2SO_4} \rightleftharpoons [(\mathrm{Cy})_2\mathrm{CPh}]^+ + 2\mathrm{HSO_4^-} + \mathrm{H_3O^+}$$

$$(\mathrm{Cy})_3\mathrm{COH} + 2\mathrm{H_2SO_4} \rightleftharpoons [(\mathrm{Cy})_3\mathrm{C}]^+ + 2\mathrm{HSO_4^-} + \mathrm{H_3O^+}$$

$$(\mathrm{Cy})_2\mathrm{C(OH)CH_3} + 2\mathrm{H_2SO_4} \rightleftharpoons [(\mathrm{Cy})_2\mathrm{CCH_3}]^+ + 2\mathrm{HSO_4^-} + \mathrm{H_3O^+}$$

$$(\mathrm{Cy})_2\mathrm{CHOH} + 2\mathrm{H_2SO_4} \rightleftharpoons [(\mathrm{Cy})_2\mathrm{CH}]^+ + 2\mathrm{HSO_4^-} + \mathrm{H_3O^+}$$

The different number of bands on the absorption curves of carbinols containing phenyl radicals in their composition depends on the number of these radicals and has already been observed by us earlier ([2]) in the study of the halochromy of aromatic carbinols. It is interesting that in the case of carbinols not containing phenyl radicals, the absorption curves, in their form and position, almost coincide with one another and with the curves of tertiary cyclohexanols and aliphatic alcohols ([1,3]). This, in our opinion, is additional confirmation that the curves of all these compounds belong to the carbonium ion



since the radicals bound to it do not absorb ultraviolet light.

Kharkov State University
named after A. M. Gorky

Received
9 IV 1957

REFERENCES CITED

1. V. F. Lavrushin, N. N. Verkhovod, P. K. Movchan, DAN, **105**, 723 (1955).
2. V. F. Lavrushin, ZhOKh, **26**, 2697 (1956).
3. V. F. Lavrushin, N. N. Verkhovod, ZhOKh, **26**, 2704 (1956).
4. L. C. Anderson, *J. Am. Chem. Soc.*, **52**, 4567 (1930).
5. C. S. Schoepfle, J. D. Rian, *J. Am. Chem. Soc.*, **54**, 3687 (1932).
6. L. P. Hammett, *Physical Organic Chemistry*, N. Y., 1940, p. 54.

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