LETTERS TO THE EDITOR

# PROPERTIES OF TETRACYANOETHYLENE COMPLEXES WITH AZOLES

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UDC 541.49:547.772.781.79:543.422

Ultraviolet and IR spectroscopy and dielcometry have shown that tetracyanoethylene (TCE) reacts with imidazole (I), 1-methylimidazole (II), benzimidazole (III), 1-methylbenzimidazole (IV), 3,5-dimethylpyrazole (V), 1,3,5-trimethylpyrazole (VI), and 1-methyl-1,2,4-triazole (VII) in dioxane, methylene chloride, and dichloroethane to give charge-transfer complexes (CTC), which display new bonds associated with complexing in their electronic spectra; $\lambda_{max}$ values are observed at 300, 400, and 418 nm for I and II and at 400 and 418 nm for III-VI in all of the investigated solvents; at 365 nm for VII in methylene chloride and dichloroethane and at 400 and 418 nm in dioxane. The dielecometric method of isomolar series [1] was used to determine the compositions of the complexes and to investigate their polar properties. It was found that azoles I-VII react with TCE to give 2 : 1, 1 : 1, and 1 : 2 complexes. In the case of the TCE-I and TCE-II systems, two complexes (2 : 1 and 1 : 2) exist in equilibrium, and the form of the curve of the dependence of the polarization on the composition makes it possible to assume that the mixture also contains a 1 : 1 complex, which, being less polar than the 2 : 1 and 1 : 2 complexes, does not display a maximum on the dielecometric curve.

The stability constants [2] for the 1 : 1 TCE complexes change in the following order: 208.3 (I), 210.1 (II), 39.5 (III), 21.4 (IV), 4.6 (V), 3.7 (VI), and 2.6 (VII). From the character of the changes in the stability constants it was observed that the stabilities of the complexes follow the trend of the basicities of the azoles, and highly basic azoles I and II react with TCE to give compounds that have not only high stabilities but also substantial heats of formation and polar properties; this can be associated with an ionic structure. Thus the heats of formation determined from the UV spectral data in dichloroethane are as follows: 15.67 for TCE-I, 12.57 for TCE-II, 13.25 for TCE-IV, 9.14 for TCE-V, and 6.86 kcal/mole for TCE-VII. The dipole moments in dioxane for the 1 : 2 and 2 : 1 complexes for the TCE-I and TCE-II systems, respectively, are 7.87 and 11.54 and 7.37 and 11.08 D.

A complex of one molecule of imidazole and two molecules of TCE was isolated in the solid state. On the basis of the character of the shifts of the bands in the IR spectrum of the complex as compared with the free components it was concluded that coordination of one of the acceptor molecules is realized with the nitrogen atom of the pyridine type.

## LITERATURE CITED

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2. K. B. Yatsimirskii, Zh. Neorgan. Khim., 1, 2306 (1956).

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Rostov State University, Rostov-on-Don. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, p. 1292, September, 1974. Original article submitted December 26, 1973.