SPECIFIC SOLVATION OF PYRYLIUM CATIONS

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Electrochemical methods, which have been successfully used for the study of the specific solvation of organometallic cations, have not been applied to purely organic cations. We have investigated the oscillopolarographic reduction of 2,4,6-triphenyl- (I) and 2,4,6-trimethylpyrylium (II) perchlorates in a series of aprotic solvents (with an $NaClO_4$ base electrolyte and a dropping mercury electrode relative to a saturated calomel electrode at 20°C). It was found that the reduction potentials of these substances (E_r) depend substantially on the electron-donor properties of the solvent. Thus the $-E_r$ values (in volts) for salt I change in the following order: CH_3CN, 1.59; CH_3SOCH_3, 1.45; $[(CH_3)_2N]_3PO$, 1.42; $(CH_3)_2NCHO$, 1.32; $[(CH_3)_2N]_2CO$, 1.32; pyridine, 1.11. The following order was obtained for salt II: CH_3CN, 0.98; $(CH_3)_2NCHO$, 0.83; $[(CH_3)_2N]_2CO$, 0.79.

Thus in the cases under consideration complexing lowers the reduction potential, and the degree of decrease in this value, as compared with its value in an inert solvent, may serve as a measure of the specific solvation of the cations. For most of the pyrylium salts, acetonitrile is a solvent of this type. In more basic solvents the observed E_r values depend not only on the inherent electron affinity of the cation but also on the degree of its specific solvation. It follows from a comparison of the data obtained that the observed effect is manifested to a greater degree if the cation itself is reduced with greater difficulty. Easily reduced cations (2,6-triphenyl- and 2,6-di-tert-butyl-4,2-carboranylpyrylium) are reduced at the same potential (−0.32 and −0.18 V, respectively) in both acetonitrile and dimethylformamide.

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