LETTERS
TO THE EDITOR

Complex Formation of Verdazyl Radicals with Verdazilium Salts

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A number of redox reactions with the participation of stable verdazyl radicals **I** are known to proceed as autocatalytic processes caused by the generation of verdazilium salt **II** [1,2]. We found that compounds **I** and **II** in solution interact with each other to form a complex compound in a molar ratio 1:1. As compound **I** we tested 2,4,6-triphenyl- and 2,3,4,6-tetraphenyl-verdazyl radicals, while as compound **II** the respective bromides and also 2,4,6-triphenylver-dazilium hydroxide. The process of the complex formation was studied by the spectrophotometric method monitoring the change in the long-wave absorption bands of verdazilium cations (in the region of 545–550 nm) and verdazyl radicals (in region of 710–720 nm) in anhydrous acetonitrile and acetone, and also in their aqueous solutions. The choice of these solvents was defined by the good solubility and sufficient stability of verdazilium salts in them. Compositions of the complexes were established by the methods of isomolar series and molar ratios. The initial concentrations of reagents was varied within the range of 1.5×10^{-4} – 0.5×10^{-4} mol l⁻¹.

For the reaction of the complex formation of 2,4,6-triphenylverdazyl radical with 2,4,6-triphenylverdazilium bromide in these solvents the following dependences of the constant of complex formation (K_C ,

l mol⁻¹) on the temperature and the dielectric constant of the medium (dielectric constant of solvents at 20°C is indicated in the parentheses) has been established: acetonitrile pure (37.4) $\ln K_C = -9.13 + 8660.10 T^{-1}$; acetonitrile aqueous (46.6) $\ln K_C = -21.71 + 9538.13 T^{-1}$; (57.3) $\ln K_C = -25.88 + 10885.25 T^{-1}$; acetone pure (21.4) $\ln K_C = -16.74 + 7842.19 T^{-1}$; acetone aqueous (54.1) $\ln K_C = -20.49 + 9177.29 T^{-1}$. The calculation of the equilibrium constant of the process of complex formation was performed by Drago and Frank–Ostwald graphic methods. The dielectric constants of binary solvents were calculated assuming their additivity. The obtained results point to the formation of the moderately stable complexes between the initial components. Small growth of the complexes stability constant with an increase in the solvent polarity is connected apparently with an increase in the degree of dissociation of 2,4,6-triphenylverdazilium bromide in solution.

REFERENCES

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