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Manifestation of the Dynamic Properties of the Solvent in Electron Transfer Reactions

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Abstract—The ability of the multichannel stochastic model to adequately describe the basic features of the kinetics of thermal electron transfer is demonstrated. It is shown that the solution-controlled regime can be realized in the normal Marcus region, whereas it is almost completely suppressed in the inverted region by the reorganization of high-frequency vibrational modes. The continuous transition between the two regions in the neighborhood of the activationless is quantitatively described. It is found that the dynamic properties of the solvent manifest themselves not only in the dependence of the electron transfer rate on the medium relaxation time τ_L , but also in the free energy gap law, shifting the position of the maximum effective rate constant to higher reaction exergonicities. This shift depends on the longitudinal relaxation time of the medium. In slow solvents, the maximum rate constant of electron transfer can exceed $1/\tau_L$ by several orders of magnitude.

Keywords: vibrational relaxation, medium reorganization, dynamic solvent effect

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INTRODUCTION

The stochastic approach to the description of the kinetics of intermolecular and intramolecular electron transfer (ET) in polar environments, developed in the early 1980s [1–4], enabled to consider the nonadiabatic and solvent-controlled regimes of ET and the transition between them within the framework of a unified model. This approach was a natural development of the Marcus theory of ET, consistently taking into account the formation of the energy barrier separating the states of the reactants and products due to the reorganization of the solvent [5]. In particular, it became possible to relate the dynamics of the delivery of the reactants into the reaction zone (the area of intersection of the terms of the reactants and products, Fig. 1) with the dynamic characteristics of the solvent. The stochastic theory made it possible to demonstrate that, at a sufficiently large electronic coupling constant, V_{el} , the reaction rate is controlled by the dynamic characteristics of the solvent. For Debye solvents, the reaction rate is inversely proportional to the time of longitudinal dielectric relaxation τ_L of the solvent, with its maximum value being $1/\tau_L$. This effect is known as dynamic solvent effect (DSE). For ET reactions, this conclusion was confirmed in a series of experiments [6–9]. A review of earlier experimental studies is presented in [4].

More recent systematic studies of ET have shown that the rate of ET may exceed the upper limit $1/\tau_L$, defined by the stochastic theory, by a factor of 50 to 1000 [10–13]. Furthermore, the experimental depen-

dences of the ET rate on the solvent relaxation time turned out to be much weaker than predicted by the theory.

An analysis showed that the dynamic solvent effect of the solvent was observed only for ET reactions occurring in the normal Marcus region. For reactions proceeding in the activationless or Marcus inverted region, the effect is virtually absent [14]. This implies that the mechanisms of ET in the normal and inverted regions should have significant differences. Thus, these experiments have raised the question about the mechanisms of the suppression of DSE in the inverted region.

This prompted the authors of [14] to conclude that the stochastic theories of ET based on the assumption of the decisive role of the solvent reorganization and all the modifications thereof taking into account the reorganization of intramolecular modes [15–24] are applicable only in the normal Marcus region. Given that, in the activationless and inverted regions, the ET rate may be significantly greater than the upper limit $1/\tau_L$, that is not limited by the dynamics of the solvent, it was suggested to describe the kinetics of ET by using approaches based on calculating the rate within the framework of Fermi's "golden" rule [14]. In this approach, the dynamic properties of the medium do not appear, and the reorganization of all the classical vibrational degrees of freedom is described in terms of the averaged Franck–Condon factors [25]. Thus, to describe the kinetics of ET in the normal and inverted (including activationless) regions, different models are