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The Rate Constant – Reaction Free Energy Dependence for the Electron Transfer Reactions in Solutions. The Way to Interpret the Experimental Data Correctly

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Lev I. Krishtalik. Courtesy of Vasily Ptushenko.

Lev I. Krishtalik left a noticeable mark in electrochemistry and biophysics. His scientific career started in the mid-1940s, when the hardships of wartime were replaced first by hopes for the best, and then by persecution of the numerous segments of the population and many scientific schools in the USSR.

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Fortunately, Lev Krishtalik survived these difficult years, although he had to work for 15 years in the industry, doing science only in his off-duty hours. Even in these hard conditions, he managed to perform an outstanding work on the experimental detection of barrierless electrode reactions (discharge of hydrogen ions). Later, he worked in the Alexander N. Frumkin Institute and contributed substantially to the theory of charge transfer reactions developed by Revaz R. Dogonadze and Alexander M. Kuznetsov and to its experimental confirmation. This was a cutting-edge field in chemistry and led to Rudolph A. Marcus' Nobel Prize in Chemistry in 1992. A little later, Lev Krishtalik developed his views on the catalytical abilities of enzymes.

The work of Krishtalik was well known at the time and his efforts were rewarded with the Frumkin Prize of the International Society of Electrochemistry in 2001. Note that he was a disciple and one of the closest colleagues of Alexander N. Frumkin, although he was never formally his student.

Along with his scientific interests, Lev Krishtalik also had interests and encyclopedic knowledge in different cultural fields, including poetry, music, painting, and architecture. One of his favorite cities was Florence, and the painting "La Catena" with the medieval/renaissance landscape of Florence was always on his bookshelf. His personal memoirs have been recently published (in Russian; https://7i.7iskusstv.com/avtory/krishtalik/).

Lev Krishtalik was a radiant personality. Even in the most difficult moments of his life, he remained friendly to people and grateful to fate.

This is the last manuscript which he worked on in his two or three last years of his life. Unfortunately, his illness did not allow him to publish the paper before his death.

Vasily Ptushenko

Abstract. The relative influences of the reorganization energies of the classical and quantum modes on the maximum position of the rate constant – reaction free energy curve have been studied. In the framework of the continuum electrostatics, the electron transfer reorganization energies in methyltetrahydrofurane solutions for the system biphenylyl – spacer – acceptor were calculated. For different acceptors, the solvent reorganization energy varies from 1.0 to 1.1 eV. When added with the rather small reorganization energies for classical intra-molecular modes we obtain 1.13–1.34 eV. With account of possible errors this coincides practically with the experimental estimate of the energy at the maximum of the rate–free energy curve $\Delta G_{max} \approx -1.2$ eV. Hence, we can conclude that the reorganization of quantum modes does not influence substantially the position of this maximum. To the contrary, in a non-polar solvent isooctane were the solvent reorganization does not play any role the reorganization of the quantum intra-reactants modes becomes determinant. These conclusions agree fully with the results of the general theoretical analysis and should be accounted for in the experimental data interpretation.

Keywords: Reorganization energy, Medium reorganization, Intra-molecular reorganization, Rate maximum.

List of Abbreviations: A – acceptor, BPH – biphenylyl, D – donor, MTHF – metyltetrahydrofurane, Py – pyrenyl, Sp – spacer, Q – benzoquinonyl.

1. INTRODUCTION

One of the fundamental problems of the chemical and electrochemical kinetics is the physical mechanism of the elementary act of the electron transfer, especially in condensed media. This question was intensively studied in many theoretical works (in particular [1-4]; a short review of them is given in Section 2. 1). Electron transfer is connected with some reorganization of the reactant's polar surroundings and reorganization of the molecules inner structure. These two processes are characterized by the corresponding parameters – the medium (solvent) reorganization energy λ_s and the intramolecular reorganization energy λ_v.

The relative contribution of these processes has been many times discussed. In liquid solutions the kinetics of the electron transfer proper can be distorted by kinetics of the mutual diffusion of the reactants. Therefore, most suitable for the comparison of the experimental results with the theory are the systems in which the donor and the acceptor are connected by a rigid linker ensuring a constant distance between the reactants. In the present paper, a typical example of such a system will be considered. In many papers dealing with the problem in chemical and biochemical systems [5-9], it has been a priori accepted that both the parameters – λ_s and λ_v – contribute substantially to the final result. Accordingly, both parameters were found by fitting the experimental data to the theoretical equation derived under the same assumption. The results of such a fitting are not quite unequivocal. Therefore, it is highly desirable to estimate the reorganization energies, both λ_s and λ_v by independent methods. As a vivid illustration of the possible problem the data of [7] can be mentioned. In this paper, the fitting for the system porphyrines – C_2H_4 – quinones in benzene and toluene has been performed with two sets of parameters – the first one $\lambda_s = 0.18$ eV, $\lambda_V = 0.60$ eV and the second $\lambda_s = 0.60$ eV, $\lambda_V = 0.20$ eV. The second set which is physically quite unrealistic gives the results almost so good as the first one. This shows again that one should use parameters obtained from the independent data. To emphasize this conclusion is the aim of the present paper.

Section 2 deals with the theory (2.1) and calculations (2.2); in Section 3, the results described and discussed; in Section 4, the conclusion are presented.

2. THEORY AND CALCULATIONS.

2.1 Theory

In this Subsection, a short description of the most important theoretical results used in this paper is presented.

Marcus [1] was the first who has given, in the framework of a semi-classical theory, the correct exponential dependence of the reaction rate on the reaction free energy ΔG and the reorganization energy λ. Levich and Dogonadze [2] have done a quantum–mechanical analysis of the problem. They have obtained the same exponent and a strict expression for the pre–exponential factor. The final result is

$$k = \frac{4\pi^2 |V(r)|^2}{h\sqrt{4\pi\lambda k_B T}} exp\left[-\frac{(\Delta G+\lambda)^2}{4\lambda k_B T}\right] \tag{1}$$

Here k is the rate constant, $V(r)$ – the distance r dependent electronic coupling matrix element, h – Planck constant, k_B – Boltzmann constant, T - temperature. This equation is valid only at the high-temperature limit, e.g. under condition $\hbar w << k_B T$, where $\hbar w$ is the energy of vibration coupled to the electron transfer.

From Eq.1 follows that the rate constant – reaction free energy dependence presents a symmetric parabola with maximum at

$$-\Delta G_{max}=\lambda \tag{1a}$$

For the purpose of qualitative treatment of results it is instructive to recall the Marcus formula for the medium reorganization energy (2).

$$\lambda_S = e^2\left(\frac{1}{\varepsilon_0}-\frac{1}{\varepsilon_S}\right)\left(\frac{1}{2a_1}+\frac{1}{2a_2}-\frac{1}{R}\right) \tag{2}$$

Here e is the charge to be transferred, ε_o and ε_s are optical and static dielectric permittivities of the medium, a_1 and a_2 are the radii of the spherical reactants, and R is the inter-center distance. This simple analytical solution is obtained for the case of two spherical reactants in an infinite homogenous medium. At a more complex geometry and an inhomogeneous medium one employs the numerical methods of calculation (section 2.2) with the same physical rationale as for derivation of the Marcus Eq.2; hence the latter is suitable for the qualitative discussion.

Dogonadze et al. [3] have considered a more general case when different oscillators are present with a wide range of the frequencies. They have shown the principal difference in the behavior of the intramolecular vibrations that have a high frequency $\hbar\omega >> kT$, i.e. much more than own vibrations of liquid solvent ($\hbar\omega << kT$). Consequently, they are much faster, and hence cannot influence the reorganization energy. It should be noted that the condition of low frequency (condition of the classical behavior) can be fulfilled not only for the solvent but also for some intramolecular movements.

Jortner [4] has presented in an explicit form the expression for the rate constant in the case of the presence of different oscillators.

$$k = \frac{2\pi}{\hbar^2\omega}|V(r)|^2 e^{-S(2\bar{n}+1)}\left(\frac{2\bar{n}+1}{\bar{n}}\right)^{P/2} I_P\left[2S\sqrt{\bar{n}(\bar{n}+1)}\right] \tag{3}$$

where $V(\mathbf{r})$is the electron tunneling matrix element, $\hbar w$ is the energy of the nuclear vibration coupled to electron transfer, S is λ/hw. Here λ is the total reorganization energy equal to the sum of intramolecular (vibrational) component λ_v and the medium (solvent) reorganization λ_s; n is $[\exp(hw/k_B\ T) - l]^{-1}$ where T is the absolute temperature, k_B is Boltzmann constant (it is the thermal population of a mode with vibrational frequency w), $I_P(z)$ is the modified Bessel function, and P is $-\Delta G/\hbar\omega$. This expression calculates the thermally weighted contribution of the Franck-Condon overlap integral from each vibrational quantum level to the rate.

Jortner's Eq.3 also predicts a parabolic k – ΔG dependence but the asymmetric one: at larger ΔG the rate is enhanced due to involvement of exited vibrational levels. The maximum of the rate is determined by the condition

$$-\Delta G_{max}=\lambda_v+\lambda_S \tag{3a}$$

Let us consider the high-temperature limit, e.g. under condition $\hbar w << k_B T$, where $\hbar w$ is the energy of vibration coupled to the electron transfer. This situation usually exists when the reorganization takes place due to the change of the polarization of the surrounding dielectric medium. The latter can be described as a set of the low-frequency phonons. Hence, for this case the Jortner's Eq.3 simplifies to Eq.1

2.2 Calculations

Calculations of the medium reorganization energies are performed in the framework of continuum electrostatics – the approach successfully used for the several intra-protein charge transfers [10]. For the numerical solution of the Poisson–Boltzmann equation the finite difference method was employed [11], the program DelPhi v.4 release 1.0. This program permits to account for the presence of several dielectrics with the different permittivities. To find the reorganization energy one should calculate the dielectric response energy (reaction field energy) upon the simultaneous charging of reactants by +1e and –1e in optical and static dielectric media. Response in the optical medium (dielectric permittivity ε_o) corresponds to the inertialess polarization, and response in the static medium (permittivity ε_s) corresponds to sum of the inertialess and the inertial polarizations. The difference of these responses gives the effect of the inertial polarization, i.e. the reorganization energy.

Parameters

The ±1e charge is supposed to be distributed equally among all of the aromatic hydrocarbons heavy atoms. For quinone molecules, the additional charge appearing upon their reduction were obtained from quantum–chemical calculation by density functional method at the B3LYP/6-311++G(d,p) level. The results are: -0.202e at each of carbonyl oxygen, -0.194e at carbon atoms connected with O, and -0.052e on other C atoms. It should be noted that variation of the charge distribution in reasonable limits result in changes of the reorganization energy by few millielectronvolts.

Electrostatic reorganization energy is often estimated using Eq.2 which accepts the spherical shape of the reactants. In many cases, in particular for large flat molecules this leads to a drastic underestimation of the reorganization energy. For a more realistic description of the reactants' size and shape, the Pauling van der Waals radii of atoms were employed (their more detailed list is given in the PARSE parameterization [12]). Using these radii and partial charges the Poison–Boltzmann equation can be solved numerically.

The probe radius implies the spherical shape (or somewhat similar to that) of solvent molecule. However, the MTHF molecule is a flat one. Therefore, one must use some approximations. As the minimal value the radii of O atom or CH_2 group contacting immediately the reactants, i.e. 2Å. As the approximate maximum effective radius, the radius of a sphere circumscribing the flat figure of tetrahydrofurane was accepted. It equals to 3.2 Å. Calculation of λ_s with these radii gives values differing by 10–12 meV. As the final result for each pair the average figure rounded up to one hundredth of electronvolt was chosen. Its error due to uncertainty of radii hardly exceeds 5–6 meV.

The calculations were performed with the grid size 0.15 Å, box filling 80 %. The salt concentration was accepted formally as 10^{-4} M what allowed to neglect the reorganization of the ionic atmosphere.

The experimental values of the dielectric permittivities, static and optical, for the solvent methyltetrahydrofurane (MTHF) are ε_s=7.0 and ε_o = 1.98 [13]. The permittivities inside the reactants are $\varepsilon_{in} = \varepsilon_s = \varepsilon_o = n^2$ (*n* is the refractive index). because there is no orientational polarization (dipoles reorientation) inside the molecules, The corresponding values for the reactants under study are absent in the literature. They were estimated by comparison with the data on ε_o for the following molecules: benzene 2.25, naphthalene 2.53, phenantrene 2.55. acetone 1.85, vinylmethylketone 1.98, acetylacetone 2.14. Pyren is the next in the series of aromatic hydrocarbons, hence its ε_o can be estimated as ~2.6. For BPH one should expect ε_o higher than for benzene due to the interaction of phenyl groups but this interaction should be substantially weaker than in naphthalene; the estimated ε_o is 2.35. Q is not an aromatic compound but an unsaturated diketone. With the account of additional conjugation the estimate is $\varepsilon_o \approx 2.45$. Further, by computations reason it is more convenient to use a unique value of ε_o for each pair of reactants. These figures are 2.4 for BPH–Q pair, and 2.5 for BPH–Py pair.

Given the approximate nature of these values the calculations with various ε's were performed. The variation in ε_o by 0.1 leads to change of λ_s not exceeding 6–7 meV. Therefore, this approximation seems to be quite acceptable.

3. RESULTS AND DISCUSSION

Among the entire systems donor (D) – spacer (Sp) – acceptor (A), the most suitable for theoretical analysis is the system biphenyl – a spacer of steroidal type– different acceptors that is studied in detail by Miller, Closs, and their coauthors [5, 14–19]. The most data relates to spacer 5-a–androstane. They were used in our analysis.

The advantages of using this and similar spacers are, first, that it provides a constant inter-reactant distance and their orientation. The second advantage is that the long chain of s–bonds excludes any marked electron transfer between the reactants before the reaction starts. Therefore, one can sure use in electrostatic calculations the full integer charges of reactants.

The last remark. In the experiments of Miller et al., reaction was initiated by the pulse of the high-energy electrons. The solutions were without the supporting electrolyte. Hence, in these systems cannot be operative the effect discussed by Kuznetsov [20] for weakly polar media, namely reorganization of ionic pairs formed between the reacting ions and the ions of the background electrolyte.

Below, two typical systems will be considered.

3.1. BPH – Sp – A in MTHF.

For calculations two acceptors were chosen – Py, having the largest size, and Q, having the smallest one; correspondingly, they have the smallest and the largest electrostatic energy of interaction with the dielectric medium. For all the other acceptors the medium reorganization energy has the intermediate value. As described in Section 2.2 the calculations account for the real size and shape of reactants.

The calculated λ_s are for BPH–Sp–Py 1.00 eV, and for BPH–Sp–Q 1.11 eV. Besides medium reorganization there are some other practically classical degrees of freedom.

The first of them is the torsional movement around s – bond connecting two phenyl fragments of BPH; their frequency is estimated theoretically as 55-125 cm^{-1} (reviewed in [21]). Hence, they are classical ones. The corresponding reorganization energy has been estimated experimentally by comparison of the reaction rates with BPH and with 2-(9,9'dimethyl)fluorene having a similar energetics and electronic structures, but for the fluorene derivative the torsional component of λ is absent due to sterical hindrance. Therefore, the difference in rates can be ascribed to $\lambda_t = 0.13 \pm 0.03$ eV [18]. Similar value has been obtained by quantum chemical calculation of two rotamers energy [18].

The second component is the intramolecular low-frequency vibrations. Borrelli and Dormcke [23] have performed *ab initio* calculation of the full benzoquinone vibration spectrum. The main contribution to its reorganization energy is due to five modes with the frequencies near ~440, ~780, ~1140, ~1500, and ~1600 cm^{-1}. The same frequencies were obtained by Fischer and Van Duyne [24] from the data on Raman spectroscopy. It is important that all they are connected with some shift of the polar CO group. The total λ_v due to all vibrational modes is 0,45 eV. The mode with the frequency 440 cm^{-1} behaves practically classically and gives the reorganization energy λ_v= 0.10 eV. The behavior of the mode 780 cm^{-1} is intermediate between classical and quantum ones, nearer to quantum. Fortunately, its full reorganization energy is only 0.01 eV, and hence its contribution to the total classical reorganization energy can be neglected.

In [23], the full analysis of the Mg-porphyrin spectrum was also given. The total vibrational reorganization is about 0.1 eV. Classical vibrations give only 0.0003 eV. In this molecule, all the polar groups are incorporated in a rigid ring structure. Therefore, it is reasonable to accept that in cyclic aromatic hydrocarbons containing no polar groups $\lambda_v \approx 0$.

In total, all the classical components give the $\lambda = \lambda_s + \lambda_t + \lambda_v$. For BPH-Sp-Py λ = 1.13 eV, for BPH-Sp-Q it equals to 1.34 eV. This is rather close to $-\Delta G_{max} = \sim 1.2$ eV found experimentally from the *k* – ΔG curve. With account of the possible errors of two estimates one should conclude that the closeness of the calculated and experimental values is quite acceptable.

Thus, Eq.3a does not describe the experiment satisfactorily while Eq.1a does. This is especially clear for the system including Q where the quantum contribution to the total λ_v equals to 0.35 eV, and the classical one only 0.1 eV. In other words, the reorganization of the solvent (plus other classical components) determines the total reorganization energy. This is fully consistent with the theoretical conclusion by Dogonadze et al. [3]. Jortner [22] also notes that in liquid solvents where exist low-frequency phonons they exert the predominant effect on the reorganization energy.

From this point of view it is interesting that the rates of electron transfer between anion – radical and the neutral reactant and from the neutral reactant and the cation – radical coincide [16] what shows that determining is an electrostatic effect.

The fact that reorganization energy is determined by the solvent and other classical modes does not mean that intra-molecular vibration modes do not influence kinetics, and in particular the shape of the rate – free energy dependence. At $|\Delta G| > |\Delta G_{max}|$, e.g. in the inverted region, the excited vibration levels come into play making *k* – DG curve asymmetric.

3.2. BPH–Sp–A in isooctane.

The data on this system are presented according to [14] at Fig. 1. The dashed curve is tacked from [14]. It is calculated with the following parameters: λ_s = 0.15 eV and λ_v= 0.45eV. Strictly speaking, in the nonpolar solvent isooctane $\lambda_s = 0$. However, with account of the torsional component the accepted value is reasonable for the classical reorganization energy. For the vibrational component the authors quite logical accepted the same value as was obtained previously by fitting the data for the same system in MTHF. However, as it is clear from Fig.1 the agreement of this calculation with the experiment can be hardly considered as satisfactory one. The deviation of the experimental points from the theoretical curve in some cases can be as large as ~ 4 orders of magnitude while for MTHF there is only for one experimental point with the maximal deviation not exciding 0.3 orders. Moreover, the experimental data cannot be described as a bell-shaped dependence. Therefore, it is hardly possible to establish definitely the value of ΔG_{max}.

The reason for that lies, most probably, just in the mechanism of the elementary act of the electron transfer. In absence or at quite small classical reorganization energy the initial and final electronic energy levels can be equalized only at the expense of the excitation of intra-molecular vibrations. Just this idea is accounted for in Jortner equation. However, this equation in fact does not imply the same λ_s and also the same total λ_v for all acceptors. However, as it is shown in Section 3.2 for the different reactants λ_s and, especially, λ_v can be substantially different. This is very likely the reason of the discrepancies between experiment and calculations represented on Fig. 1.

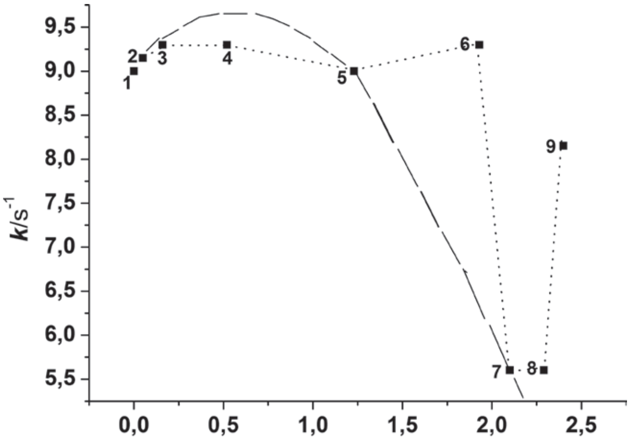

Figure 1. System biphenylyl–spacer–acceptor in isooctane solutions. Dashed line correspond to calculations [14] with the following parameters: λ_s = 0.15 eV, λ_v = 0.45 eV, ω = 1500 cm^{-1}, V = 6.2 cm^{-1}. Dotted line is just a guide for eye that is drawn according to the sequence of the reaction free energies. The symbols indicate experimental data: *1*— 4-biphenylyl, *2*— 2-naphthyl, *3*— 9-phenanthryl, *4*— 1-pyrenyl, *5*— 2-(5,8,9,IO-tetahydronaphthoquinonyl), *6*— 2-naphthoquinonyl, *7*— 2-benzoquinonyl, *8*— 2- (5-chlorobenzoquinonyl), *9*— 2-(5,6-dichlorobenzoquinonyl).

Two additional remarks seem to be proper. First, in the presence of several modes the total λ_v equals to the sum of the corresponding parameters for each mode (the model calculations of Ulstrup and Jortner [25]). Second, there exists a wide set of less effective modes, forming a quasi- continual spectrum important at gradual excitation.

Note also that the difference in the intra-molecular quantum frequencies does not influence the data for MTHF because in polar liquid solvent the location of the rate maximum is determined by the classical reorganization only.

4. CONCLUSION

Nowadays, experimental data processing often uses Jortner formula which implies a substantial contribution of both reorganization energies (of the intra-molecular quantum modes and the classical medium modes) into the total reorganization energy. The latter determines the reaction free energy corresponding to the maximum reaction rate. However, the values of the two reorganization energies are usually taken not from some independent sources but obtained by fitting the kinetic data to Jortner equation. Correspondingly, there is not any attempt to prove the basic condition of a comparable effect of the two reorganization energies.

The specific feature of the approach advanced in this paper is determination of all the parameters not by fitting the kinetic data but basing on the independent experimental data. The medium reorganization energy has been calculated electrostatically. For this purpose, not the simplified Marcus formula implying spherical shape of the reactants but the more general method of the numerical solution of the Poisson–Boltzmann equation was employed. This method allows accounting for the real shape and size of the reactants. The calculations performed for solutions in a polar solvent MTHF show that the medium reorganization gives the predominant contribution to the total reorganization energy. To the contrary, in a non–polar isooctane, the medium reorganization does not play any substantial role, and the intra-molecular reorganization becomes predominant. In the latter case, the shape of the rate – free energy curve is rather complex due to differences in vibration spectra of various molecules. All these results are in agreement with the general theoretical conclusions.

From the above, the algorithm for processing experimental data follows. In the case of reaction in polar solvent one should perform a strict electrostatic calculation of the medium reorganization energy and try to analyze the other possible classical modes. For the reaction in a non-polar medium one should analyze the vibration spectra of the reactants and calculate the corresponding reorganization energies.

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