



# Mechanism and kinetics of electrochemical reduction of tert-butyl bromide molecule - improvement of theoretical model



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## ABSTRACT

In the present article the earlier formulated theoretical model of the adiabatic electrochemical reduction of the tert-butyl bromide molecule [1] is improved. The potential energy profiles describing dissociation of the C-Br bond in the neutral molecule and in the anion, which in the previous work were based on quantum calculations performed in vacuo, are replaced with new ones, derived from similar calculations, but taking into account solvent (dimethyl sulfoxide) effects. The modified two-dimensional potential energy surfaces were introduced into the simulation program and the rate constants were re-examined for three different values of the solvent reorganization energies  $\lambda$ : 0.624, 1.0 and 1.41324 eV. The results are found to differ significantly from those reported previously, exhibiting now better agreement with experimental estimates for the activation energy and the transfer coefficient  $\alpha$ . New values of  $\alpha$  calculated in the interval of overpotentials  $\eta = 1.3$ –1.45 V are found to decrease with  $\eta$  from 0.262 to 0.237 when  $\lambda = 0.624$  eV, from 0.305 to 0.273 when  $\lambda = 1$  eV, and from 0.332 to 0.308 when  $\lambda = 1.41324$  eV (the latter obtained approximately). The transfer coefficient is shown to decrease also with the temperature, but this effect is much weaker than reported in our previous study [2]. Some trends found in our results are explained by the saddle point avoidance phenomenon.

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## 1. Introduction

Reactions of the type  $RX + e \rightarrow R \cdot + X^-$ , where R is an alkyl or perfluoroalkyl group and X is a halide atom, were widely investigated in the past by the group of Savéant [3–8], both at the experimental and theoretical levels. According to those studies, the reduction of alkyl halides is a typical example of the concerted processes, in which the electron transfer to the molecule and the C-X bond rupture occur at the same time. Savéant proposed a simple theoretical model allowing to study the kinetics of such reactions [5]. An important part of this theory was an assumption, that the reductive bond cleavage is described sufficiently well by the Morse potential. The results however were not very satisfactory—the transfer coefficients  $\alpha$  calculated for the tert-butyl bromide with different versions of this model were found from 0.31 [5] to 0.33 [7], thus significantly higher than the earlier reported experimental values of 0.2 [3], and also more recent 0.27 [8]. A similar, although less pronounced relation between

theoretical and experimental  $\alpha$  values, was found for tert-butyl iodide. As stated by the authors, the discrepancy between computed and measured results could be due to the peak widening resulting from the overlap of the reduction waves associated with two competitive processes:  $RX + e \rightarrow R \cdot + X^-$  and  $R \cdot + e \rightarrow R^-$ . Although Savéant introduced some corrections to the theoretical model [7], the resulting  $\alpha$  of 0.33 for tert-butyl bromide was even higher than the previous estimate.

In our recent theoretical works on the adiabatic electrochemical reduction of tert-butyl bromide [1,2] we obtained much lower values of the transfer coefficient, varying for a given electrode overpotential  $\eta = 1.3$  V (corresponding to experimental conditions) from about 0.2 to 0.25. The transfer coefficient was shown there to depend not only on the overpotential, but also on the solvent viscosity and temperature. In those works the reaction was studied by molecular dynamics simulation in a two-dimensional model potential. The latter described the concerted electron transfer to the molecule and bond-breaking process on the basis of the Anderson-Newns-Schmickler model of the interfacial electron transfer, combined with the potential energy curves obtained from quantum calculations, where the energy for the neutral molecule  $(CH_3)_3CBr$  and anion  $(CH_3)_3CBr^-$  was scanned with respect to the C-Br distance.

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In [1] the quantum calculations for the molecule and anion were performed in vacuo, assuming that the existence of a minimum on the anion's curve, corresponding to a weakly stabilized form of  $(\text{CH}_3)_3\text{C}\cdots\text{Br}^-$ , can be ignored. However, the presence of a solvent may influence not only this region, but generally the shape of both potential energy profiles and, consequently, also the activation energy for the bond-breaking process. In a very recent study of one of us on the reduction of the  $\text{CF}_3\text{I}$  molecule [9] two models derived from two sets of quantum calculations, one in vacuo, and the second in the presence of a solvent, were compared. It was shown that the inclusion of the solvent effect in the quantum calculations via the polarizable continuum model (PCM) strongly influences the reaction kinetics and is crucial for achieving agreement with experimental data.

The main goal of the present article is to verify whether this correction is of similar importance for the proper modelling of the electrochemical reduction of tert-butyl bromide. New potential energy profiles for the systems  $(\text{CH}_3)_3\text{CBr}$  and  $(\text{CH}_3)_3\text{CBr}^-$  in the presence of dimethyl sulfoxide (DMSO) were constructed and used to obtain the corrected PES. The rate constants and transfer coefficients obtained with the new model are compared to our previous results reported in [1,2] and to experimental values of Savéant [3,8].

## 2. Method of calculations

The theoretical model used in the present work is only a modification of that described in detail in a series of our earlier works [1,2,9–11], therefore only its most important features are given below. The key element of the model is the two-dimensional adiabatic potential energy surface derived from the model Hamiltonian proposed in its general form by Schmickler, Koper and Voth [12,13]. The model Hamiltonian in general takes into account the electronic states in the metal and in the reactant and their interaction, the reorganization of the solvent and the intramolecular changes of the reactant.

This multi-dimensional description is further simplified by using several assumptions. The slow solvent modes are represented by a single generalized coordinate  $x$ , which is normalized such, that  $x=0$  corresponds to the oxidized state in equilibrium, while  $x=1$  to the reduced state. The solvent response is then characterized by the solvent reorganization energy  $\lambda$ . In our previous work this parameter was set to a constant value of 0.624 eV, which at the room temperature corresponds to  $25k_B T$ , and the same value will be used in the present study. However, a much higher value of 1.11 eV was used in the work of Savéant [7]. Therefore, to investigate the effect of  $\lambda$  on the results, we performed an additional series of simulations using  $\lambda = 1$  eV.

An additional, third value of  $\lambda = 1.41324$  eV tested in our work was estimated from energies of solvation in this reaction obtained from our quantum calculations. The solvation energies were calculated as differences between the total energies in DMSO (PCM) and in vacuo. For the t-BuBr neutral molecule, t-Bu• radical and  $\text{Br}^-$  anion we obtained the DMSO solvation energies of  $-0.1005$ ,  $-0.01246$  and  $-2.9146$  eV, respectively. As expected, the largest contribution comes from the solvation of the bromide anion. This value was verified by comparing it to experimental data for the solvation energy of  $\text{Br}^-$  in DMSO, which can be obtained from its hydration free energies and the free energy of transition of this ion from water to DMSO, available in the literature [14–17]. However, the results obtained in this way are rather uncertain and range from  $-2.88$  to  $-3.3$  eV. Our calculated solvation energy equal to  $-2.915$  eV is within this range and is in good agreement with  $-2.98$  eV obtained from the estimates of Marcus [15,16]. The final value for the reorganization energy of  $\lambda = 1.4132$  eV was then

calculated by multiplying the absolute value of the difference in solvation free energies of products  $|\text{dG}_{\text{solv}}| = 2.8266$  by the Pekar factor  $C = 1/\varepsilon_\infty - 1/\varepsilon_0$  ( $\varepsilon_\infty$  and  $\varepsilon_0$  are the optical and static dielectric constants), which for DMSO is approximately 1/2.

Another approximation used in our model is related to the strength of interaction between the molecule and the electrode, characterized by energy broadening of the antibonding state of the reactant,  $\Delta$ . Although in principle this parameter depends on the electronic energy, in our model it is assumed to be constant (the wide-band approximation) and in all simulations was arbitrarily set to 0.01 eV. This value is sufficiently high to assure that the reaction is adiabatic, but still so small that it has a negligible effect on the energy of activation.

Another simplification was introduced by Koper and Voth [12] to the description of the bond dissociation upon reduction. It is assumed, that this part of Hamiltonian can be written as an effective switching function:  $H_{bb} = (1 - n_a)V_i + n_aV_f$ , where  $V_i$  and  $V_f$  are potential energies of the initial and final state of the reactant, respectively, and  $n_a$  is the occupation number of the antibonding orbital.

The resulting adiabatic potential energy has the following general form:

$$E(x, y) = \bar{\varepsilon}_a \langle n_a \rangle + \lambda x^2 + \frac{\Delta}{2\pi} \ln \left( \frac{\bar{\varepsilon}_a^2 + \Delta^2}{\varepsilon_a^2 + \Delta^2} \right) + V_i(y) \quad (1)$$

where the first term contains the electronic energy  $\bar{\varepsilon}_a$ :

$$\bar{\varepsilon}_a(x, y) = \varepsilon_a - 2\lambda x + V_f(y) - V_i(y) \quad (2)$$

and the occupation number is defined as:  $\langle n_a \rangle = (1/\pi) \text{arc cot}(\bar{\varepsilon}_a/\Delta)$ .  $\varepsilon_a$  is the energy of antibonding orbital of the neutral molecule in solution, calculated with respect to the Fermi level of the metal as:  $\varepsilon_a = \lambda - e_0\eta$ , where  $\eta$  is an overpotential;  $y$  is the C-Br bond stretching calculated with respect to its equilibrium value in the neutral particle. Note, that for reduction processes overpotentials are negative, but throughout the article for simplicity minus sign is omitted.

In our previous work [1] the potential energies of the reactant,  $V_i$ , and the product,  $V_f$ , were obtained by fitting analytical functions to the quantum points obtained in vacuo for the molecule  $(\text{CH}_3)_3\text{CBr}$  and anion  $(\text{CH}_3)_3\text{CBr}^-$ . The quantum calculations were performed at B1LYP/6-311G(d) level [18–21]. The curves were constructed by scanning the energy of the particle with respect to the increasing C-Br bond length. For each frozen distance C-Br the structure was optimized. In the optimization some constraints were imposed on the geometry, namely the C-C bonds and C-C-C angles were assumed to be equal, the methyl groups were allowed to rotate independently, but the corresponding C-H bonds, H-C-H and H-C-C angles in the three groups were kept the same.

The same strategy and method B1LYP/6-311G(d) were used in the present work in the quantum calculations with the PCM solvent model. As solvent dimethyl sulfoxide was used, which is characterized by a relatively large dielectric constant of 46.826. All calculations in the present work were performed with the Gaussian 09 package [22].

To new results of the quantum calculations were fitted analytical functions  $V_i$  and  $V_f$  in the following form:

$$V_i(y) = A_1 \exp(-A_2 y) + A_3 \exp(-A_4 y) + A_5 \exp(-A_6 y) + A_7 \quad (3)$$

$$V_f(y) = B_1 \exp(-B_2 (y - d_s)) + B_3 \exp(-B_4 (y - d_s)) + B_5 \exp(-B_6 (y - d_s)) \quad (4)$$

Both potentials are functions of a variable  $y$ , which is the relative C-Br distance, defined as:  $y = d_{\text{C-Br}} - d_0$ . Here  $d_0$  is the equilibrium

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