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Comparison of temperature effect on electroreduction of tert-butyl chloride and tert-butyl bromide—Theoretical study

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ABSTRACT

An effect of temperature on kinetics and mechanism of the reaction $RX + e \rightarrow R^{\bullet} + X^{-}$ is studied using molecular dynamics simulations method for two molecules: t-BuCl and t-BuBr in two different solvent viscosities $\gamma_x = 2\ \mathrm{ps}^{-1}$ and $\gamma_x = 40\ \mathrm{ps}^{-1}$. The potential surfaces used in the simulations are two-dimensional and depend on the solvent generalized coordinate x and the C–X bond elongation y, the latter part based on quantum calculations. For both systems the transfer coefficient α is found to decrease with temperature and this effect is stronger in the more viscous solvent. For $\gamma_x = 40\ \mathrm{ps}^{-1}$ the following α values are reported: at $T = 278$ K 0.234 (t-BuCl) and 0.264 (t-BuBr), while at $T = 398$ K 0.208 (t-BuCl) and 0.222 (t-BuBr). In identical conditions and for the same height of the energy barrier, α(t-BuCl) is always lower than α(t-BuBr). The results are interpreted as an effect of the saddle point avoidance phenomenon.

1. Introduction

In a series of earlier works [1–7] we investigated at a theoretical level various problems related to kinetics of electron transfer reactions, such as the rate dependence on different reaction conditions or adiabacity and non-adiabacity of such processes. Two most recent works [6,7] were focused on adiabatic one-electron reduction of tert-butyl chloride and tert-butyl bromide molecules. These and other similar reactions were studied widely in the past by the group of Savéant using experimental [8,9,13] and also theoretical [10–13] techniques. It was established then, that alkyl halide reactions should be treated as concerted processes, i.e. the electron attachment and the C–X bond rupture proceed simultaneously in one step:

$$(CH_3)_3CX + e \rightarrow (CH_3)_3C^{\bullet} + X^{-} \qquad (1)$$

The theoretical model proposed in those works was based on the Morse potential employed to describe the dissociation process in the neutral molecule and also in the radical anion formed after reduction. The results obtained with this model were compared to experimental data mainly for the t-BuBr and t-BuI molecules, as the measurement for the tert-butyl chloride met some difficulties. The authors noted, that their model properly reproduced experimental results for the tert-butyl iodide, while for the tert-butyl bromide the calculated transfer coefficient was higher than the measured value of 0.2.

Methodology used in our studies was quite different and based on the general model proposed in the work of Koper and Voth [14]. They combined the model of Savéant with earlier work of Schmickler [15] and from this Hamiltonian derived the two-dimensional, adiabatic potential energy surface (PES) as a function of two coordinates: one related to the solvent reorganization and second – to the dissociating bond.

In our approach, instead of the Morse potential used in [14] and also by Savéant, the energy profiles for the bond dissociation processes were derived from quantum calculations. The fitted potentials were combined with the Anderson–Newns–Schmickler Hamiltonian [15–17] yielding also two-dimensional potential energy surfaces. These PESs were used in conjunction with the simulation method of Kast et al. [18,19] to study various aspects of the tert-butyl halides reduction. As shown in [1,4–7], this theoretical scheme allows to perform a very detailed analysis of the reaction rates and transfer coefficient, their dependence on temperature, solvent viscosity and strength of interaction between the reactant and the electrode. It allows also to explore the reaction mechanism with respect to the intramolecular and solvent reorganization. It was not possible to verify our results for the t-BuCl system in [6] by comparing them with measured values of the transfer coefficient, as such do not exist, but its magnitude agrees with general trend observed for other tert-butyl halides. The quality of the model was finally confirmed when it was applied to the t-BuBr molecule [7]: the transfer coefficients obtained for electrochemical reduction of

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this system in different conditions are in excellent agreement with experimental data.

Among various aspects of reaction kinetics is an intriguing problem of the relation between the transfer coefficient α and the temperature T. Experimental measurements [20–22] performed in the past showed that for some reactions α depends on T, while for others it does not, and even very similar compounds exhibit different trends. Theoretical studies of Koper and Voth [14] considering the temperature effects on dissociative reduction, and also other performed for some hypothetical redox reactions [23,24], confirmed the experimental observations that the temperature influence on the α coefficient depends on properties of the reactant and that each system should be analyzed individually.

In the works [6,7] on the two molecules we presented only a few results showing the influence of temperature on the adiabatic reactions studied. In this work I present more thorough analysis of this problem and perform comparison of results obtained in the same conditions for both molecules. It is shown that some trends observed for one molecule are present also for another, but there are also some substantial differences in values and mechanisms of the two reactions.

2. Method

As mentioned already, this work is an extension of our earlier studies on the electrochemical reduction of tert-butyl halides. The model used here was described in detail in our earlier works on this subject, therefore below I present only its general description. From the model Hamiltonian the adiabatic potential surface was derived as a function of two coordinates: the generalized solvent coordinate x known from the Marcus theory, and the C–X (X = Cl, Br) bond stretching coordinate y calculated with respect to the equilibrium C–X distance in the neutral molecule $(CH_3)_3CX$. The coordinate x was normalized such, that $x = 0$ before the electron was transferred to the reacting system, and $x = 1$ after reduction. Thus, on the potential energy surface (PES) the initial state corresponds to the point (0, 0). Following the Marcus theory, the solvent response was represented by only one parameter, namely the solvent reorganization energy λ, which in all our calculations was assumed to be equal 0.624 eV (25 k_BT at the room temperature).

Another very important factor comes from the Anderson–Newns model and describes the strength of interaction between the molecule and the electrode. This is so-called energy broadening of the antibonding state of the reactant, Δ, which generally depends on the electronic energy, but in the wide-band approximation it is assumed to be constant. In this study $\Delta = 0.01$ eV was used, which should be sufficient for the adiabatic outer-sphere electrochemical reduction occurring at a certain distance from the metal surface (no specific adsorption of the reactant).

The adiabatic potential energy of the system is defined as:

$$E(x,y) = \tilde{\varepsilon}_a < n_a > +\lambda x^2 + \frac{\Delta}{2\pi}\ln\left(\frac{\tilde{\varepsilon}_a^2 + \Delta^2}{\varepsilon_a^2 + \Delta^2}\right) + V_i(y) \tag{2}$$

The first term contains the electronic energy $\tilde{\varepsilon}_a$ equal to:

$$\tilde{\varepsilon}_a(x,y) = \varepsilon_a - 2\lambda x + V_f(y) - V_i(y) \tag{3}$$

and the occupation number $\langle n_a \rangle = (1/\pi)\text{arccot}(\tilde{\varepsilon}_a/\Delta)$.

Parameter ε_a in Eqs. (2) and (3) 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 η is an overpotential.

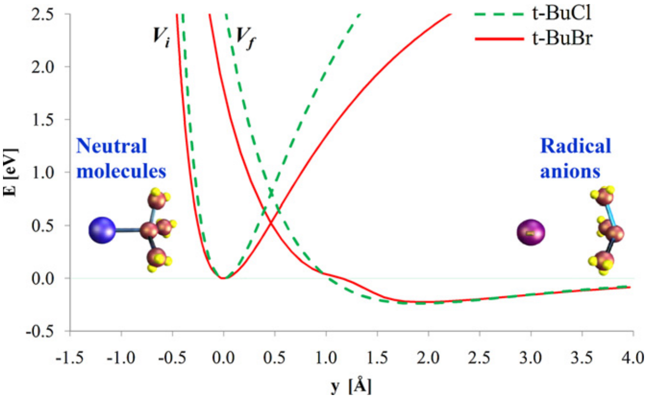

Fig. 1. Comparison of energy profiles describing dissociation of the tert-butyl chloride and tert-butyl bromide molecules and the corresponding radical anions (Eqs. (4) and (5)) and used in construction of the two-dimensional potential energy surfaces.

The potential energies of the reactant, V_i, and the product, V_f, were obtained by fitting analytical functions to the quantum points, as described for t-BuCl in [2] and for t-BuBr in [7]. The quantum calculations for the tert-butyl chloride were performed at the MP2 level using the 6-31G basis set for the tert-butyl part and the 6-31G(d) basis set for the Cl atom or ion. For the t-BuBr system the calculations were performed using the B1LYP density functional combined with the 6-311G(d) basis set used for all atoms. As shown in detail in [2,7], these methods yield good description of properties of these systems, especially the C–X vibrational frequencies in the neutral molecules, which are very important in the present studies. The potentials V_i and V_f for both molecules may be written in the general form:

$$V_i(y) = A_1\ \exp(-A_2 y) + A_3 \exp(-A_4 y) + A_5 \exp(-A_6 y) + A_7 \tag{4}$$

$$\begin{aligned} V_f(y') = {} & B_1\ \exp(-B_2 y') + B_3 \exp(-B_4 y') + B_5 \exp(-B_6 y') \\ & + B_7 \exp(-B_8 (y' - y_{inv})^2) \end{aligned} \tag{5}$$

The variables y and y' are the relative C–X distances, defined as: $y = d_{\text{C–X}} - d_0$ and $y' = d_{\text{C–X}} - (d_1 - d_0)$, where d_0 is the C–X equilibrium distance in the neutral molecule and d_1 is the distance defining the shallow minimum on the anion potential energy profiles shown in Fig. 1. All parameters used in the fitted potentials V_i and V_f are presented in Table 1. As can be seen, the V_f functions for t-BuCl and t-BuBr differ by the last term of Eq. (5), which for the tert-butyl chloride disappears. This part of the potential V_f is responsible for reproducing small irregularities observed on the anionic curve only for the tert-butyl bromide.

Note in Fig. 1, that the energy profiles were shifted such, that at the equilibrium the energies of the initial state (the neutral molecule $(CH_3)_3CX$) and the final state (the radical $(CH_3)_3C^{\bullet}$ and the anion X^- after dissociation) are the same and equal to 0 eV. As discussed in detail in [2,7] for both neutral molecules the fitted functions V_i very well reproduce the C–X bond vibrational frequency, which is very important as it describes the curvature of the potential profile for the neutral molecules. The higher frequency of C–Cl vibrations ($\omega_{\text{exp}} = 570\,\text{cm}^{-1}$ [25]) is manifested in steeper V_i curve for the tert-butyl chloride molecule when compared to the tert-buty bromide ($\omega_{\text{exp}} = 514\,\text{cm}^{-1}$ [25]). The minima on the anionic potential energy profiles reflect formation of the radical anions $(CH_3)_3CX^{\bullet-}$, which are unstable and in solution dissociate fast into the tert-butyl radical and the halide anion. The crossing point of the neutral and anionic curve defines the height of the potential barrier associated with the intramolecular reorganization. It should be mentioned that our functions based on quantum points predict much lower energy barriers than the Morse potentials used in the work of Savéant [10].

To compare the kinetics and mechanism of the reduction (1) for these two molecules, the same reaction conditions should be