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Oxidation of oxalic acid on boron-doped diamond electrode in acidic solutions

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ABSTRACT

We present results of our theoretical study on the mechanism and thermodynamics of the incineration of oxalic acid $H_2C_2O_4$ on a boron-doped diamond electrode. The reaction is assumed to occur in aqueous solution in several steps, of which the first, the most important, is the generation of the OH radical according to an outer sphere mechanism. The energy balance and barrier for this step as well as for all subsequent steps (OH reaction with oxalic acid leading to creation of HC_2O_4 radical, its C—C bond dissociation and OH reaction with the COOH radical) were evaluated by performing quantum calculations with the MP2 and three DFT methods and the aug-cc-pVTZ basis set. The results indicate that the first step is characterized by a rather low activation energy of 0.25 eV and by a relatively high transfer coefficient of ~0.7. The next process - detachment of H atom from oxalic acid by OH radical – meets an energy barrier of 0.55 eV; for all subsequent steps the activation energies are much smaller. The overall incineration reaction is found to be highly exothermic by ca. 7 eV. Our results are also applicable to similar inert electrodes.

1. Introduction

Prof. Roger Parsons contributed to many areas of electrochemistry, from thermodynamics and double-layer structure to electrode kinetics. Indeed, a negative list of the areas to which he did not contribute would be shorter than a positive list. In any case, one of the topics on which he produced seminal works is the electrochemistry of small organic molecules, in particular of formic acid. So we thought it fit to dedicate an article on the oxidation of oxalic acid, which has two carboxyl groups instead of one, to his memory.

At room temperature the electrochemical window of water, i.e. the range of potential in which it is stable, is about 1.23 V; this limits the classes of reactions which can be studied. However, at special inert electrodes the kinetics of water dissociation is slow, so that in practice this potential range can be extended. Thus mercury allows the study of reactions, in particular metal deposition, at potentials well below the equilibrium potential for hydrogen evolution. This special property forms the basis of polarography, which for many decades was one of the most sensitive analytical techniques, and for which J. Heyrovski received the Nobel prize [1,2]. Boron doped diamond (BDD) plays much the same role for highly anodic potentials, because oxygen evolution is strongly kinetically hindered [3]. Its advent has opened a new potential range for electrochemistry, allowing the generation of highly energetic species [4–6].

An intriguing possibility is the creation of radicals, in particular of the highly reactive OH radical, which can trigger a variety of reactions with organic species [7–14]. A special case is the incineration of organics to CO_2 and water [10–14]. While there are many experimental studies of such reactions at BDD, there is little in the way of theory. Quaino and Schmickler [15] have considered OH generation in alkaline solutions and concluded that on oxygen terminated BDD the reaction takes place according to:

$$OH^- \rightarrow OH + e^-$$

via an outer sphere mechanism, which can be described by Marcus theory. In this work we consider acid solutions, where the mechanism is:

$$H_2O \rightarrow OH + H^+ + e^-.$$

This reaction also takes place without the adsorption of reactants or products, but involves the breaking of a bond, and is therefore more complicated than the mechanism in alkaline solutions. As a special application, we shall consider the subsequent incineration of oxalic acid $H_2C_2O_4$ by the OH radical. For all steps involved, we shall calculate both the reaction free energies and the energies of activation by

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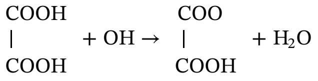
quantum chemical methods. To the best of our knowledge, there is only one work [13] in which the electrochemical incineration of oxalic acid (as well as of two other acids: acetic and formic) was investigated theoretically on the atomic level. For each acid several possible products of incineration were considered and their geometries were optimized in vacuo at the B3LYP/6-311 + + G(d) theory level. The authors discuss the relationship between the difficulty of oxidation of each compound in the frame of their calculations. We shall return to this work below.

There is some discussion in the literature if the oxidation of organic compounds, in our case oxalic acid, is triggered by the generation of the OH radical, or if it proceeds by a direct electron transfer from the acid to BDD with the eventual assistance of OH in subsequent steps [3,5,7,8,11–14,16,17]. In agreement with [16,17], here we investigate the former mechanism, which is supported by the fact that the oxidation of oxalic acid sets in at the potential where OH is generated. It should be stressed that such mechanism can be considered only for inert electrodes with low adsorption properties. As shown in a number of earlier studies [e.g. [18–21]] the reaction path for the oxidation of oxalic acid in acidic solutions on active electrodes, such as Au or Pt, must be very different, as it involves adsorption of intermediates and direct electron transfer to the electrode.

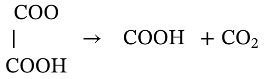
2. Theory

The oxidation of oxalic acid has been well investigated experimentally and discussed extensively by Comninellis [7,8]. Based on experimental evidence, he proposed the following mechanism, which we shall use as the basis of our theoretical study:

$$H_2O \rightarrow OH + H^+ + e^- \qquad (1)$$



$$\begin{matrix}COOH\\ |\\ COOH\end{matrix} + OH \rightarrow \begin{matrix}COO\\ |\\ COOH\end{matrix} + H_2O \qquad (2)$$



$$\begin{matrix}COO\\ |\\ COOH\end{matrix} \rightarrow COOH + CO_2 \qquad (3)$$

$$COOH + OH \rightarrow CO_2 + H_2O \qquad (4)$$

The standard equilibrium potential of step (1) is 2.38 V vs. RHE [22]. It can trigger a number of incineration reactions, which set in near this potential. We consider the oxidation of oxalic acid as a typical example. Comninellis et al. [7,8] discuss if the generated OH is weakly adsorbed on the BDD surface. However, under experimental conditions this surface is passivated, which prohibits adsorption. Also, the fact that OH production takes place at the theoretical potential for an outer sphere process indicates that adsorption plays no role [22]. We note that additionally oxygen evolution can take place in parallel [3].

In the following, we investigate each of these steps individually by quantum chemical calculations. As is always the case in such calculations, there are a fair number of basis sets, approximations, and functionals that can be used. We have applied several quantum methods which we consider to be reasonable options, such as MP2, and a few density functional-based methods (DFT), coupled with the relatively large basis set aug-cc-pVTZ (ATZ). Also, since all reactions 1–4 take place in water, solvent effects have been included by an implicit model, for which we have tested two different variants. Naturally, various methods give somewhat different results, but even though the discrepancies reach 0.5 eV in a few cases, they do not affect any of our conclusions. Therefore, to maintain the integrity of our arguments, in the main body of this article we discuss the results obtained consistently with the same method, namely MP2/ATZ, while the comparison between the various methods can be found in the supplementary information (SI). Their validity was tested by comparing results with both experimental and theoretical data reported in the literature for neutral and ionized water clusters in the gas phase. The changes in ionization potentials, dissociation energies, geometrical parameters, and vibrational frequencies that we observe upon solvation (see Tables S1–S6 in SI) are in line with those reported in refs [23–31].

3. Calculations method

First we focused on reaction (1). There are no naked protons in aqueous solutions, therefore in our quantum chemical studies one additional solvent molecule (H_2O) was included explicitly in the reaction, so step (1) has the actual form:

$$(H_2O)_2 \rightarrow OH + H_3O^+ + e^- \qquad (1)$$

In many earlier works various properties of both the neutral water dimer and of its cationic form were explored both experimentally and theoretically [[23,24,26–29,32–63] and references therein], some of the latter included also assessment of the computational methods used. Nowadays it is routine to use DFT as an inexpensive way to include electronic correlation into quantum calculations. Anderson and Tschumper [32] scrutinized 10 different functionals with respect to the correct description of 10 stationary points on the $(H_2O)_2$ intermolecular potential energy surface (PES). It was shown that for the ground state and the neighboring stationary points the DFT methods perform quite well, although most fail to describe properly the curvature of the PES. Limitations of DFT methods in modeling water clusters were also analyzed by other authors, for example Shields and Kirschner [33], Xu and Goddard [34], Svoboda, Ončák and Slavíček [35,36], Zhao and Truhlar [37]. Based on the results obtained, the methods PBE1PBE, BHandHLYP or X3LYP were indicated as those giving a good description of selected properties of such systems.

However, according to the recent work of Boese [64] not all of them are suitable for reactions involving hydrogen bonds. For a set of 49 systems of various sizes, all containing hydrogen bonds, Boese conducted very extensive tests on the performance of 85 functionals (some including dispersion corrections) combined with 34 different basis functions. The main conclusions of this study were that: the basis set should be of at least triple-ζ with diffuse functions; for small systems, such as the water dimer, inclusion of dispersion corrections increases the error in the DFT calculations of intermolecular interactions; the MP2 theory is superior to any of the DFT methods tested in that work.

Therefore, following this suggestion, as the main technique in our research we used the Møller-Plesset perturbation theory MP2 combined with the aug-cc-pVTZ (ATZ) basis set, which is the Dunning correlation-consistent polarized valence basis set (triple-ζ) including diffuse functions. For comparative purposes we performed analogous calculations with three DFT functionals mentioned above, namely: BHandHLYP, PBE1PBE and X3LYP.

For both the neutral and the ionized water dimer first we performed a number of comparative tests in vacuo and in aqueous solution. In the latter the remaining part of the solvent was described by an implicit model; we tested two approaches: the polarizable continuum model PCM, and the universal solvation model SMD. Using the MP2 and DFT methods listed above the dimer $(H_2O)_2$ and the cation $(H_2O)_2{}^+$ were fully optimized; as the initial structures we used the ground state geometries in vacuo reported in the literature. Some additional PES scans were also performed with respect to intramolecular rotations. The results of these tests are shown in SI.

The procedure used in the present study to evaluate the energy barrier for the reaction (1) occurring without direct adsorption on BDD is similar to that applied earlier by us in the studies on the electrochemical reduction of *tert*-butyl bromide molecule [65,66]. It is thus assumed that close to the surface the electron transfer (denoted below as the process 1a) and the bond dissociation occur simultaneously. The bond breaking process is modeled by two PES constructed as relaxed scans with respect to the dissociating O−H bond in the neutral dimer $(H_2O)_2$ and the corresponding radical cation $(H_2O)_2{}^+$; the latter

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