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The spontaneous decarboxylation of strong carboxylic acid – carboxylate mixtures and the use of carbon surfaces to trap the released free radicals

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ABSTRACT

The mechanism of the spontaneous decomposition of a mixture of 4-nitrophenylacetic acid ($NO_2BzCOOH$) with its respective tetrabutylammonium carboxylate in acetonitrile (NO_2BzCOO^-) was analyzed using cyclic voltammetry, atomic force microscopy, nuclear magnetic resonance and electronic structure calculations. This reaction is favoured by the high acidity of the carboxylic acid and occurs following a decarboxylation loop where the carboxylate anion has the function of reductant whereas the acidic proton of the carboxylic acid acts as oxidant. This redox reaction allows the generation of hydrogen as well as an acyloxy radical, that after cleavage, yields 4-nitrobenzyl radicals that have the possibility to react either in solution to produce 4-nitrotoluene or react with a carbon surface to produce a covalently modified layer with 4-nitrobenzyl groups.

1. Introduction

The use of carbon materials as electrode substrates is considered very attractive because of their good electrical and mechanical properties, low cost compared to noble metals, wide potential window and because many electrografting reactions have been studied on these materials. In the last decades, several electrochemical methods of covalent modification of carbon surfaces have been developed and reviewed [1–3]. The modification procedures have been attributed to the attack of electrochemically generated organic free radicals on the sp^2 carbon atoms existing on the basal or edge sites of the carbon surfaces. Due to the strong nature of the chemical binding mode with the surface, the stability of the covalently modified electrodes is higher than in the case of physically immobilized layers. This difference makes important the covalent grafting for robust applications in the field of sensors and biosensors [4–7], nanoscience [8,9], protection against corrosion [10,11], molecular electronics [12], electrocatalysis [13] and energy storage [14,15].

Until now, the most widely used and documented method to prepare grafted carbon surfaces involves the electrochemical reduction of aryldiazonium salts on carbon electrodes in acetonitrile solutions [16,17]. However, the attachment of organic moieties on these surfaces is also possible following alternative strategies based on the reduction or oxidation of other molecules bearing different functional groups [1–3]. Regardless of the grafting procedure, the covalent attachment of organic moieties on different carbon substrates can be performed on glassy carbon, highly oriented pyrolytic graphite (HOPG), carbon fibers and carbon felts [1]. In the particular case of carbon powders, in which the electrochemical procedures cannot be easily implemented, the grafting of surfaces and carbon powders using diazonium salts generated in situ has been widely demonstrated for different carbonaceous substrates [18–24]. In most of the examples available, aryl and alkylamines have been used as the chemical precursors for this chemical grafting procedure. Alternatively, the covalent attachment of organic groups without electrochemical induction has also been reached on metallic and carbonaceous materials just by dipping the electrodes into concentrated solutions amino-compounds in acetonitrile [25].

In the case of the electrochemical oxidation processes, the oxidation of tetrabutylammonium salts of carboxylic acids in

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acetonitrile has shown that arylmethyl [26,27], quinones [28], ferrocene [29] and aliphatic chains containing alkene, alkyne and ester terminal groups [30,31] can also be attached on the carbon electrodes. The decarboxylation of the precursor carboxylate has been performed directly by electrochemical induction, however, similar to the case of the non-electrochemical grafting from diazonium salts generated in situ, decarboxylation could be also developed in the bulk solution when an oxidant reagent is present together with the carboxylate. In this context, we recently showed that decarboxylation process occurs in mixtures of trichloroacetic acid with tetrabutylammonium trichloroacetate in acetonitrile [32]. This spontaneous reaction involves the formation of a hydrogen bonding association complex between the acid and carboxylate, which promotes an intramolecular one-electron exchange. In this reaction, the carboxylate loses an electron to yield a highly instable acyloxy radical which is rapidly decomposed into carbon dioxide and the trichloromethyl radical. The electron loss of the carboxylate is used to reduce the acidic proton of the trichloroacetic acid, allowing formation of hydrogen and the regeneration of the carboxylate. Even though the dimerization of trichloromethyl radicals is possible, the sole reaction product detected was chloroform, which is the result of the reaction between trichloromethyl radical and the released monoatomic hydrogen. The equivalent reactions with mixtures of acetate/acetic acid was not possible (or extremely slow), allowing to conclude that the decarboxylation mechanism is favoured by the high acidity of the easily reducible proton of trichloroacetic acid.

Upon the hypothesis that mixtures of strong carboxylic acids with its respective conjugated base allow the formation of free radicals, in this work, the mixture of 4- nitrophenylacetic acid with its respective carboxylate was tested to modify glassy carbon surfaces without any electrochemical induction. Thus, 4-nitrobenzyl groups represent an appropriate system to test the covalent attachment of 4-nitrobenzyl radicals on electrically non-connected glassy carbon electrodes. Cyclic voltammetry was used to monitor the reaction behaviour whereas electronic structure calculations were used to determine the thermodynamic and kinetic reliability of the different reaction steps.

2. Experimental

Anhydrous acetonitrile (99.8%) was used as the solvent. Tetrabutylammonium hexafluorophosphate (99%), recrystallized from ethanol and dried under vacuum was the supporting electrolyte whereas 4-nitrophenylacetic acid (99%), was used as received. Tetrabutylammonium hydroxide 1 M in methanol and tetraethylammonium hydroxide 1 M in water were used to prepare *in-situ* the tetrabutylammonium and tetraethylammonium carboxylates. The neutralization reactions were performed in acetonitrile using stoichiometric amounts of the acid and base, where the solvent was previously purged by argon bubbling to avoid carbonate formation. All the chemicals used in this work were purchased from Aldrich Chemical Co. An argon atmosphere was maintained over the solutions during all the experimental runs, which were furthermore performed at room temperature (~25 °C).

A Pyrex glass or Teflon three-electrode cell were used to carry out the voltammetric experiments on an Autolab 302N potentiostat (Metrohm Co.). The working electrode was a 3 mm diameter glassy carbon disk (Sigradur G from HTW), which was polished with 0.05 mm alumina powder and ultrasonically rinsed with distilled water and ethanol before each run. When Highly Oriented Pyrolytic Graphite HOPG (Advanced Ceramics Inc.) was used as working electrode in the Teflon cell, it was cleaved with adhesive type before each experiment in order to obtain a new surface. In all cases, the counter electrode was a platinum mesh and the reference electrode an aqueous Saturated Calomel Electrode (SCE), which was connected to the cell through a salt bridge containing only the solvent and the supporting electrolyte.

Atomic force microscopy (AFM) images of both clean and grafted HOPG samples 10 × 10 mm were obtained using a SmartSPM^{TM}– 1000 atomic force microscope from AIST-NT Inc. (Novato, CA) in contact mode. Silicon cantilevers (AppNano) of 52 μm width, 0.8-8.9 N m^{-1} spring constant and 36–98 kHz resonance frequency in air were used. Typical scan rates around 36–98 kHz were used. Images were processed using the AIST-NT SPM Control Software v. 3.3.78 and the Gwyddion 2.30 software.

The synthesis of the reaction product, 4-nitrotoluene, was carried out by stirring a mixture of 4 mM 4-nitrophenylacetic acid and 4 mM tetrabutylammonium 4-nitrophenylacetate in acetonitrile under argon atmosphere. After 24 h of reaction, the solution was evaporated in a Schlenck tube under vacuum. The residue was extracted from ether-water and the product, recovered from the organic phase, was analysed by ^{1}H and ^{13}C NMR in deuterated chloroform. This product corresponds to 4-nitrotoluene: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 2.45 (s, 3H), 7.3 (d, *J* = 8.7 Hz, 2H), 8.1 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 21.7 (CH_3), 123.6 (2 CH), 129.9 (2CH), 146.0 (C), 146.2 (C). NMR spectra were obtained using a JEOL GSX-270 (270 MHz) spectrometer. Chemical shifts (δ) are in ppm downfield from tetramethylsilane as an internal reference.

All the electronic calculations were performed with Gaussian 09 software [33]. Geometry optimizations and frequency calculations were carried out using the Density Functional Theory (DFT), in particular the M05-2X functional [34] combined with the 6–311 + G(d,p) basis set. All the calculations were carried out in solution, using the solvation model based on density (SMD) [35] and acetonitrile as solvent. The M05-2X functional was chosen because it has proven to be among the best performing functionals for calculating reaction energies involving free radicals [36]. The SMD solvent model was chosen based on its better performance for describing solvation energies of both neutral and ionic species in aqueous and also in non-aqueous solvents, compared to other solvent models [37]. Geometries were fully optimized without imposing any restrictions. Local minima were confirmed by the absence of imaginary frequencies. Thermodynamic corrections at 298.15 K were included in the calculation of relative energies. All the reported data correspond to 1 M standard state.

3. Results and discussion

3.1. Cyclic voltammetry of the 4-nitrophenylacetic acid and its carboxylate

The voltammetric behaviour of both 4-nitrophenylacetic acid ($NO_2BzCOOH$) and its corresponding tetrabutylammonium carboxylate (NO_2BzCOO^-) was first registered in the reduction and oxidation directions (Fig. 1). These experiments were performed with the aim to get a reference to explain the voltammetric features for the mixture of both compounds (Section 3.2).

Fig. 1A shows the reduction pattern for the 4-nitrophenylacetic acid, which presents three cathodic peaks (Ic, IIc and IIIc) in the direct scan and two oxidation peaks (IIIa and IVa) after the potential inversion. A detailed mechanistic analysis of this reduction process is out of the scope of the present work; however the general features of this behaviour can be understood in the context of self-protonation mechanisms that were previously proposed for the reduction of 4-nitrobenzoic acid [38] and 4-nitrophenol [39]. In this context, 4-nitrophenylacetic acid must be reduced at peak Ic according to the global reaction depicted by Eq. (1) (see supporting information), which yield the hydroxylamine derivative NHOHBzCOOH and the carboxylate NO_2BzCOO^-