Highly Reactive Diazenyl Radical Species Evidenced during Aryldiazonium Electroreduction

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We report the experimental reassessment of the commonly admitted concerted reduction mechanism for the diazonium electroreduction. Ultrafast cyclic voltammetry was exploited to demonstrate the existence of a stepwise pathway and real-time spectroelectrochemistry experiments allowed to visualize the spectral signature of an evolution product of the phenyldiazenyl radical intermediate. Unambiguous identification of the diazenyl species was achieved by radical trapping followed by X-ray structure resolution. The electrochemical generation of this transient under intermediate energetic conditions calls into question our

comprehension of the layer structuration when surface modification is achieved *via* the diazonium electrografting technique as this azo-containing intermediate could be responsible for the systematic presence of azo bridges in the nanometric films.

TOC GRAPHICS
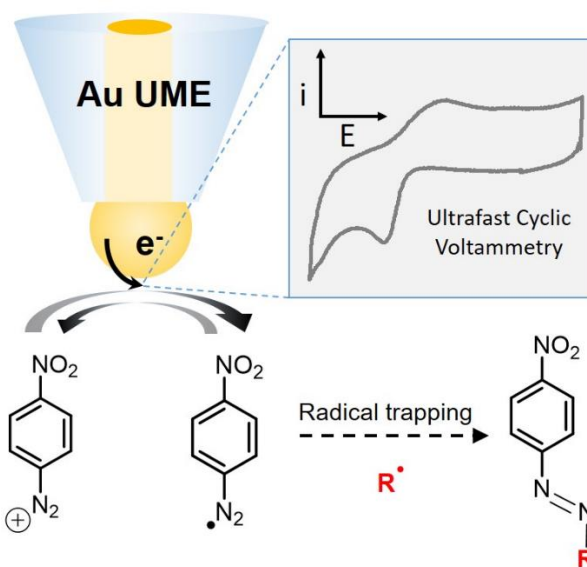
KEYWORDS. Diazonium, Stepwise mechanism, Concerted mechanism, Spectroelectrochemistry, Radical trapping, Grafting.

In 1992, J. Pinson et coll. reported the very first example of carbon modification exploiting the aryldiazonium electroreduction.[1] This new grafting approach, based on the production, and subsequent grafting of reactive aryl radicals, was to become one of the most popular methods to functionalize a broad range of substrates in a very simple way.[2–8] However, the fine description of the layer structuration remains to be developed. Indeed, even if the carbon-substrate bond is now evidenced, nitrogen is systematically detected in the nanometric films in a non-negligible proportion .[9–13] XPS, Raman and TOF-SIMS investigations all converged towards the presence of azo bridges,[14,15] but our scientific community has not yet proposed any alternative mechanistic

explanation for their formation.[5,14,16–18] This led us to take a step back and reconsider the sequence that served as a basis for the electrografting technique understanding. Electrochemical reduction of the diazonium compounds has been extensively investigated since the 50's.[19–21] The main objective was to determine whether the electron transfer was coupled to the decomposition into aryl radical and dinitrogen (concerted), or involved an aryldiazenyl radical intermediate (stepwise) (Scheme 1). Several electrochemical investigations on series of para-substituted diazonium have tilted the balance in favour of a stepwise mechanism versus a concerted one by establishing a strong dependence between their reduction potential and the hammet's constant of the substituents.[20,22] Following those first steps, studies were carried out by thermo- and photolysis of azo compounds in the early 70's but did not succeed in discriminating between concerted and non-concerted decomposition mechanisms.[23–25] The existence of the diazenyl radical transient remained a subject of debate because of conflicting CIDNP (Chemically Induced Dynamic Nuclear Polarization) and ESR (Electron Spin Resonance) interpretations until 1978,[25–28] date on which important evidence of the radical trapping was obtained from the photolysis decomposition of a series of unsymmetric diazene compounds.[29] The development of pulsed radiolysis/photolysis and time-resolved ESR techniques in the 80's definitively confirmed the relative persistence of the aryldiazenyl radical and gave access to decay constants ranging from 10^5 to 10^6 s^{-1}.[30–34] However, first, this intermediate has never been trapped from a diazonium decomposition and second, the highly energetic conditions used to evidence the stepwise decomposition are not transposable to the low driving force exploited for the diazonium electroreduction. Indeed, the driving force typically applied for electrochemical reduction at the peak potential is about 0.07 eV while it is on the order of 3.20 eV when solvated electrons are the reducing species (corresponding to -3.10 V/SCE). In this context, Savéant has worked on the energetic aspect of the bond

breaking/formation associated to electron transfers in the early 2000's and stated that the mechanism of a bond cleavage passes from stepwise to concerted as the driving force becomes lower and lower.[35,36] Since this work, the scientific community considered the existence of the sole concerted mechanism in the diazonium electroreduction process.[14,37] Therefore, the grafting technique has been developed and improved with the idea that only aryl radicals can be grafted. In a work published in 2010 focused on the chemical reduction of the nitrobenzene diazonium in homogeneous medium, the trapping of the aryl radical by a ESR active scavenger has strengthened the consensus within the scientific community regarding the reduction of the diazonium salts *via* the sole concerted mechanism.[38]
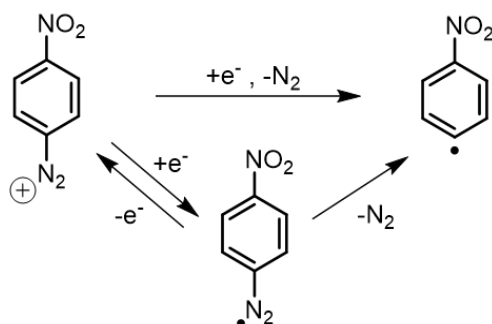
Scheme 1. Concerted (top) *vs* stepwise (bottom) mechanism for the diazonium electroreduction.

Herein, we experimentally reconsider the mechanistic approach of the diazonium electroreduction to collect evidences of the existence of a stepwise pathway, without rejecting a competing concerted route. The objective is tobridge the gap between polarographic studies that suggest a stepwise mechanism without, however, evidencing the diazenyl radical intermediate, and high energy experimental conditions that evidenced its formation. The 4-nitrobenzene diazonium cation (4-NBD), which widely served as a benchmark for the scientific community to develop the surface functionalization *via* the diazonium reduction, was used in the present work.[18,39,40] The

first step consisted to evidence *in-situ* the mechanistic pathway involved in the reduction of the 4-NBD under usual electrografting conditions. Examination of the cyclic voltammetric response is a convenient means to distinguish the stepwise mechanism from a concerted one.[36] The simplest case is when the cyclic voltammogram becomes chemically reversible upon raising the scan rate. Indeed, as shown in Figure S1, the simulated CVs performed in similar experimental conditions to those previously reported[37] do not allow to discriminate between the two mechanisms unless the dissociation rate of the diazenyl radical formed in a stepwise mechanism is lower than the values already reported for similar species.[36] Then, for a reduction, the presence of a reverse anodic trace at high scan rate is the signature of the radical or radical anion. Using ultramicroelectrodes (UME), very high scan rate can be reached, corresponding to lifetimes in the submicrosecond range for the reduced intermediate.[41–43] A voltammetric study was carried out on a gold ball UME with increasing scan rate in the presence of 4-NBD (Figure 1a and Figure S2). For low scan rate, no reversibility of the signal was observed. The rise of an anodic reversible voltammetric process was evidenced at a scan rate of 8080 V.s^{-1} (Figure 1b), unambiguously demonstrating the existence of a stepwise pathway. To circumvent the electrode passivation issue possibly occurring at low scan rate and accurately estimate the diazenyl radical lifetime, the ultrafast cyclic voltammetric experiment was simulated in 1D using COMSOL Multiphysics software (V 5.5) (Table S1, Figure S3 and S4). The simulated curves for various dissociation rate constants of the species issued from the diazonium reduction at the very same scan rate are presented in the inset of Figure 1b. From the ratio of the peak intensity i_{ox}/i_{red} with i_{ox} and i_{red} corresponding to the intensity of the anodic and the cathodic peak respectively, we estimated a dissociation rate constant k_d of 0.9×10^4 $\pm 0.5 \times 10^4$ s^{-1} for the species probed experimentally (Figure S4).[36] Compared to the values reported

in the literature from radio- and photolysis experiments, ranging from 4×10^4 to 10^7 s^{-1}, this value is in the low range (*vide supra*).[34,44]

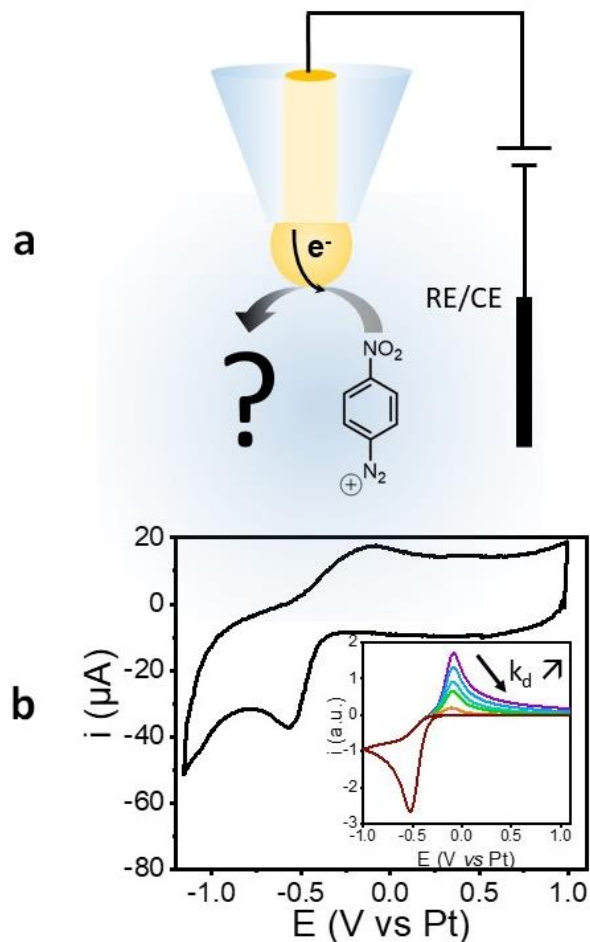**Figure 1.** a) Cyclic voltammetry of the 4-NBD at gold ball UME. b) Experimental and simulated (inset) cyclic voltammograms recorded at 8080 V.s^{-1} in a 0.3 M nBu$_4$NPF$_6$ acetonitrile solution containing 5 mM of 4-NBD.

In a second step, we attempted to identify the aryldiazenyl radical. However, obtaining a sufficient concentration and a continuous production of the diazenyl radical allowing its characterization is challenging because the grafting process usually leads to the electrode passivation within few seconds due to the formation of multilayers.[45] To circumvent this issue and

minimize the radical polymerization, a grafting control technique recently reported was exploited. This approach involves the use of a redox reducer activated at an electrode to induce the diazonium reduction in the diffusion layer of the electrode, as illustrated in Figure 2a.[46,47] Employing this strategy, the mediated diazonium electroreduction was monitored in real-time using an ultra-sensitive spectroelectrochemical bench recently developed by our group to probe electrochemically generated species in the visible range.[48] In this work, the dissolved atmospheric dioxygen was exploited as a redox mediator since its reduced form (superoxide anion O_2^{-}) does not absorb in the wavelength range of interest. The chronoamperometric reduction of 4-NBD was monitored by absorption spectroelectrochemistry using the following potential program: 30 s at +0.5 V, followed by a 15 min electroreduction step at -0.9 V, and a 5 min final step at +0.5 V (details in the Supporting Information).
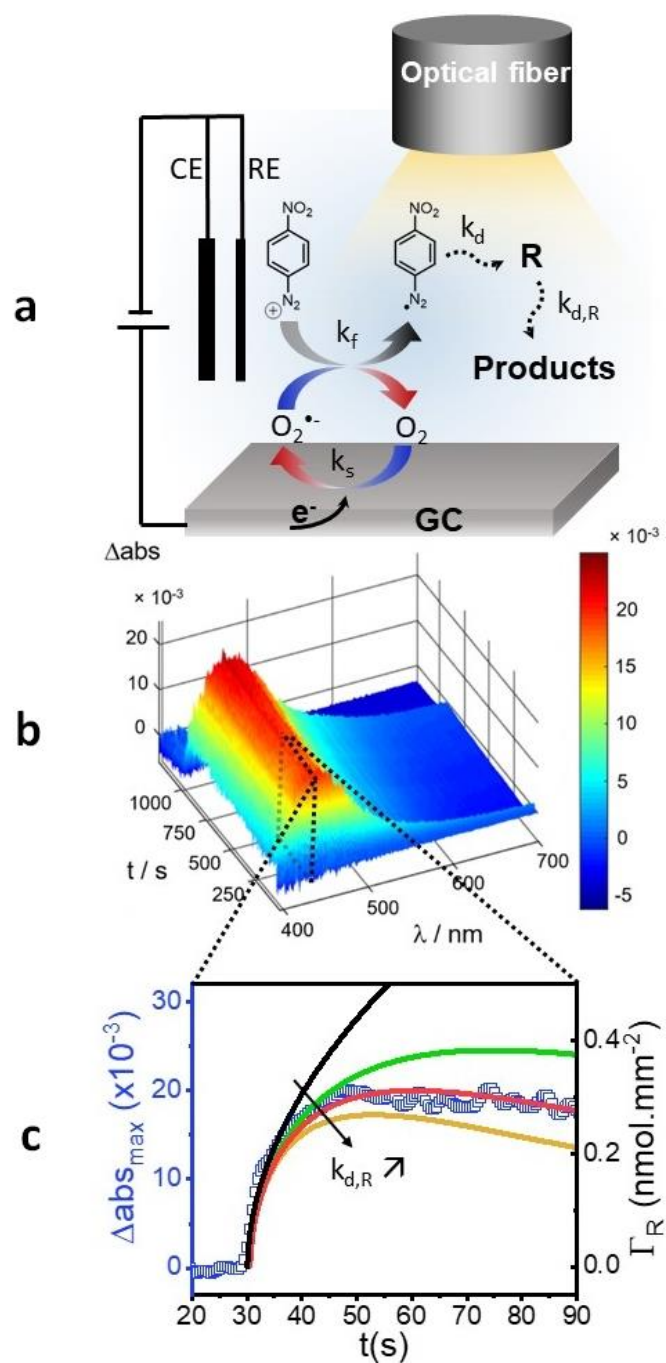
Figure 2. a) Mediated 4-NBD electroreduction under spectroelectrochemical monitoring, b) dynamic chronoabsorptogram recorded on GC electrode in the presence of 1 mM 4-NBD in acetonitrile nBu4NPF6 0.1 M. c) Experimental ΔAbsmax over time (blue circles) and simulated

concentration evolution of the secondary product for a dissociation constant $k_{d,R}$ of 0 (black), 0.02 (green), 0.03 (red) and 0.04 s^{-1} (yellow) obtained from 1D simulations considering a first order reaction.

The chronoabsorptogram presented on Figure 2b shows the appearance of an absorption band ΔAbs with a maximum located at $\lambda_{max} \sim 450$ nm for the whole reductive step duration (*i.e.* -0.9 V). The ΔAbs value returns close to its original value when the potential is shifted to +0.5 V. The absence of absorption signal after the positive potential shift confirms that the visualized absorption signal corresponds to the spectral signature of a dissolved species and not to any grafted moieties. This point was confirmed by the current-time curve presented in Figure S5, which exhibits an absence of electrode passivation. To further understand the origin of this species, the whole mechanism of the reduction process shown in Figure 2a was simulated versus time in 1D (Table S2 and Figure S6). Firstly, the theoretical concentration profile of the nitrophenyldiazenyl radical under our spectroelectrochemical analysis conditions was simulated. Using the dissociation rate constant of the diazenyl radical sepcies k_d determined above, the simulation drives to a rapid decrease of its apparent concentration profile over time, that is in contradiction with the quasi-constant ΔAbs$_{max}$ value observed in Figure 2b. While being in fair agreement with the simulated spectra obtained by TD-DFT calculation ($\lambda_{max} \sim 500$ nm, see Figure S7), the observed absorption spectrum is thus unlikely the signature of the diazenyl radical moiety. This spectrum can neither be attributed to the nitrophenyl anion nor radical, characterized by an absorption signal in the UV domain (Figure S7). Additionally, the experimental absorption band cannot be associated to the diazenyl radical attack on the superoxide anion or the acetonitrile molecules as the very same experimental spectra were obtained in DMSO or exploiting ferrocene as reducer instead of $O_2^{\cdot-}$ (Figure S8).

Among the considered structures expected under electroreduction conditions, TD-DFT calculations showed that absorption bands in the visible range are likely attributable to delocalized dimer radicals such as those produced from nitrophenyl and/or nitrophenyldiazenyl radical attacks (Figure S7). A close examination of the non-accumulating process observed for this species (*i.e.* quasi-constant ΔAbs value for the reduction step) agrees with its progressive disappearance with time as shown from the simulations of its concentration (Figures S9 and S10), considering, as a first approach, a first order dissociation rate constant $k_{d,R}$ (Figure 2c). Noteworthy, $k_{d,R}$ value extracted here ($k_{d,R} = 0.03 \pm 0.01$ s^{-1}) that reflects the decomposition rate of the species is also in good agreement with the decay rate of Δabs$_{max}$ once the potential is shifted to +0.5 V as shown in Figure S11. This result, coupled to the large FWHM observed experimentally, suggests that spectroelectrochemical spectra might be attributed to several coupling intermediate species. Even if at that point our measurement cannot fully establish the species detected, it reveals that mediated electroreduction is an interesting pathway to continuously produce intermediate species in solution while preserving the integrity of the electrode surface.

To confirm the existence of the reactive diazenyl radical, we speculated that it should be possible to form and isolate a stable compound by radical trapping. To this end, N-terbutyl-alpha-phenylnitrone (PBN), that is widely used as a radical scavenger in chemical and biological studies, was employed.[49] Typically, in the presence of free radicals, PBN undergoes a coupling on the benzylic sp^2 carbon, giving rise to a stable nitroxyl radical derivative. PBN adducts can also lead to a spontaneous decomposition to form 2-methyl-2-nitrosopropane (MNP), also known as an efficient radical scavenger.[50] In order to obtain a sufficient amount of coupling product, the sustainable production of radicals was ensured by exploiting the mediated diazonium electroreduction strategy described in Figure 2a on a large area glassy carbon electrode. In a cell

containing 2 mM of 4-NBD and 10 mM of PBN, a potential of -0.9 V was imposed to a 1 cm^2

glassy carbon electrode for 20 minutes. After electrolysis, numerous products, likely formed by

multiple radical reactions, were evidenced by UV absorption on thin layer chromatography.

Colored products, likely coming from the diazenyl coupling, were separated from the bulk, leading

to the detection of two main products, one of which was isolated (details in the Supporting

Information). The structure of compound 1 was deduced from a mass spectrometry analysis

(Figure S12) and corresponds to the expected coupling product between the nitrophenyldiazenyl
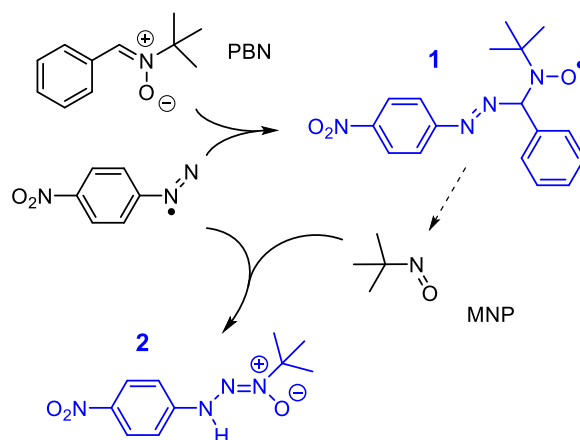
radical and the radical scavenger PBN (Figure 3).

Figure 3. Radical trapping of the nitrophenyldiazenyl radical by the PBN scavenger, followed by

the decomposition of the PBN adduct **1** into MNP scavenger, leading to the MNP adduct **2**.

Structure of **1** was deduced from mass spectrometry and structure of **2** was resolved by X-ray

diffraction.

  The structure of the second product (compound 2, Figure 3), isolated as orange crystals, was

resolved by X-ray diffraction (Supporting Information). The zwitterionic structure corresponds to

the coupling of the 4-nitrophenyldiazenyl radical with the 2-methyl-2-nitrosopropane (MNP). The

existence of compounds 1 and 2 unambiguously demonstrates that a diazenyl radical intermediate

is produced subsequently to the 4-NBD reduction as suggested from the cyclic voltammetry experiments.

The results presented in this work shed new light on the diazonium electroreduction mechanism. The strategy based on the combination of UFCV, spectroelectrochemistry and radical trapping, allowed evidencing the formation of the diazenyl radical and thus the existence of a stepwise mechanism pathway. The strategy illustrated herein in the case of the mediated 4-NBD reduction could be further deployed to decipher the reduction mechanism of other aryldiazonium compounds. Besides, in the context of surface modification by diazonium electrografting, the existence of the diazenyl radical could have a direct impact on the film structuration. Indeed, the direct coupling of this intermediate on the surface, if demonstrated, could be responsible for the presence of azo bridges usually identified in the nanometric films and play a major role in the structure/properties relationships understanding.

ASSOCIATED CONTENT

Supporting Information. Experimental details for electrode treatment, ultrafast cyclic voltammetry, spectroelectrochemistry, radical scavengering and X-ray diffraction ; Cyclic voltammetry simulations ; Spectroelectrochemistry current-time curves ; Spectroelectrochemistry simulations ; DFT calculations and TD-DFT simulated spectra; Spectroelectrochemistry control experiments ; LDI mass spectra. Crystallographic data for the compound 2 have been deposited with the Cambridge Crystallographic Data Centre with the deposition number CCDC 2151044. These data can be obtained free of charge from CCDC, www.ccdc.cam.ac.uk.

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