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# Base-Assisted Electrografting of Aromatic Amines.

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**Abstract:** Contrary to aliphatic amines, aromatic amines have received less attention for the surface modification by oxidation due to the low acidity of their cation radicals. To overcome this limitation, bases are often added in solution to facilitate or make possible the grafting. However, there has only been a modest focus on their impact on the grafting efficiency. Here, the anodic behavior of a series of para-substituted anilines was investigated in the presence of different bases to address this issue. From complete sets of Brønsted acidity/basicity data and H-bond acidity/basicity factors for both para-substituted anilines and bases, a grafting efficiency index was proposed as a practical tool to choose the most suitable base for the grafting. As a proof-of-concept for base-assisted grafting of aromatic amines, two aniline/base systems were tested to modify carbon surfaces at lower potential, compared to the modification achieved from pure aniline solutions.

## Introduction

Since the 1990s, interest in the oxidation of amines was renewed by the possibility for metallic and carbon surfaces to be covalently modified when attacked by an aminyl radical produced by deprotonation of the amino cation radical.<sup>[1]</sup> In this electrografting procedure, the stability of the cation radical (envisioned as the proton loss rate from the cation radical) governs the grafting efficiency of amines. Because of the exergonic deprotonation of the primary aliphatic amine cation radicals by the neutral amines, the resulting cation radicals are only short-lived intermediates in amine oxidations and the primary aliphatic aminyl radicals, produced near to the electrode surface, can be efficiently attached to the surface.<sup>[2]</sup> In contrast, when the charge density at nitrogen is decreased by delocalization, the lifetime of amine cation radicals becomes appreciable, so that the electrochemical oxidation of such amines mostly involves cation radicals. An example is the acidity of the aniline cation radical lower than that of the protonated aniline in water and DMSO,<sup>[3]</sup> which makes endergonic the proton-transfer reaction from the cation radical to the neutral aniline, favoring the formation of coupling products and, in certain conditions, highly condensed coupling products such as polyanilines.<sup>[4]</sup> It is the reason why the covalent attachment of aromatic primary amines to the electrode surface upon oxidation has received less attention and was not reported for a long time. For this last class of amines, an excess of organic base, such as collidine or 3,5-lutidine, is often added in solution to facilitate or make possible the grafting.<sup>[5]</sup> While the effect of a base on the electrochemical oxidation of substituted anilines was widely studied,<sup>[6]</sup> results are discussed on a case by case basis, depending on the electronic effect of substituents expected to exert a strong influence on both the acido-basic properties of the neutral amine and the amine cation radical.<sup>[7]</sup> Although it is well recognized in literature that the base aids in the deprotonation of the amine cation radical, their role in the mechanism of the oxidation of aromatic amine compounds is still being debated.<sup>[8]</sup> Here, in order to clarify the role of the base in the oxidation of aromatic amines, the anodic behavior of a series of para-substituted anilines was investigated in the presence of different nitrogen bases.

## Results and discussion

Complete sets of Brønsted acidity/basicity data and H-bond acidity/basicity factors for both the bases, identified by Roman numerals, and the para-substituted anilines, identified by Greek numerals, permit to rationalize the effect of a base on the oxidation of aniline compounds (see Tables 1 and 2). A salient point of this study is an efficiency parameter to help in choosing the most suitable base for the grafting and proof-of-concept for base-assisted grafting of aromatic amines shall be provided.

**Table 1.** Electrochemical and basicity data in acetonitrile for the nitrogen bases studied.

Base	$\Delta E_{\text{onset}}$ (mV) <sup>[a]</sup>	$\text{pK}_a(\text{BH}^+)_{\text{ACN}}$ <sup>[b]</sup>	$\beta$ <sup>[c]</sup>
(1) Quinoline	-34	12.03	0.645
(2) Pyridine	-55	12.60	0.638
(3) 4-picoline	-73	13.25	0.684
(4) Collidine	-155	14.77	0.731
(5) Morpholine	-255	16.09	0.638
(6) Isopropylamine	-373	18.26	0.716
(7) Piperidine	-421	18.92	0.744
(8) 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)	-622	24.13	1.061

[a] Shift in the onset oxidation potential of the p-bromoaniline (1 mM) measured by cyclic voltammetry at 100 mV.s<sup>-1</sup> in acetonitrile after addition of 5 equivalents of the base B. [b] pK<sub>a</sub> values of the conjugate acid HB<sup>+</sup> of the base B in acetonitrile.<sup>[9]</sup> [c] Basicity factor proposed by Abraham as a scale of solute hydrogen-bond basicity.<sup>[10]</sup>

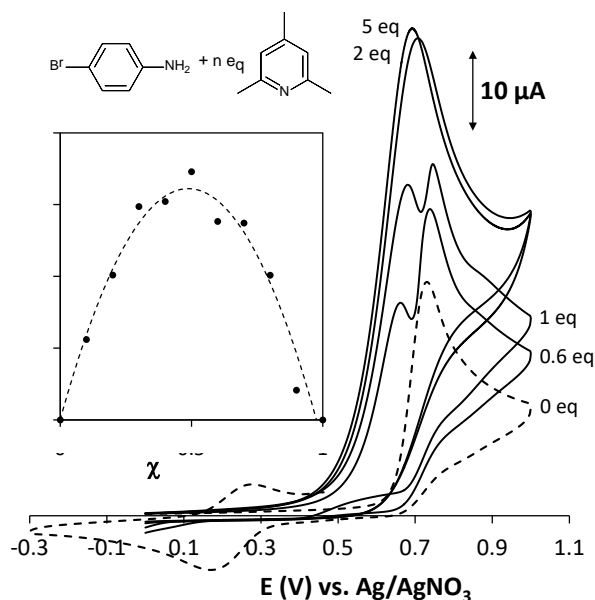
**Table 2.** Electrochemical and basicity data in acetonitrile for the para-substituted anilines studied.

Substituent	$\sigma_p$ <sup>[a]</sup>	$\alpha$ <sup>[b]</sup>	$\Delta E_{\text{onset}}$ (mV) <sup>[c]</sup>	$\text{pK}_a(\text{XPhNH}_3^+)$ <sup>[d]</sup>	$\text{pK}_a(\text{XPhNH}_2^{2+})$ <sup>[e]</sup>
(I) OMe	-0.27	(0.209)	-23	11.86	14.37
(II) Me	-0.17	0.230	-49	(11.45)	9.26
(III) F	0.06	(0.276)	-101	(10.25)	(6.66)
(IV) I	0.18	(0.300)	-146	(9.62)	(3.72)
(V) Br	0.23	0.308	-155	9.43	(4.19)
(VI) CHO	0.42	(0.348)	-183	(8.37)	(1.18)
(VII) CF <sub>3</sub>	0.54	(0.372)	-218	8.03	-0.47
(VIII) CN	0.66	(0.396)	-275	(7.11)	-1.27
(IX) NO <sub>2</sub>	0.78	0.421	-328	6.22	(-2.90)

[a] Hammett coefficients.<sup>[11]</sup> [b] Acidity factor proposed by Abraham as a scale of solute hydrogen-bond acidity;<sup>[12]</sup>  $\alpha$  values in parenthesis are deduced to their dependence with the Hammett coefficients, taking  $\alpha = 0.264$  for the aniline.<sup>[13]</sup> [c] Shift in the onset oxidation potential of para-substituted anilines (1 mM) measured by cyclic voltammetry at 100 mV.s<sup>-1</sup> in acetonitrile after addition of 5 equivalents of collidine. [d] pK<sub>a</sub> values for the protonated forms of para-substituted anilines in acetonitrile;<sup>[14]</sup> data in parenthesis are estimated from a linear Hammett correlation of pK<sub>a</sub> with  $\sigma_p$ . [e] Since the pK<sub>a</sub> values of the para-substituted anilines cation radicals are unknown in acetonitrile, they were calculated from the N-H bond dissociation enthalpies (BDEs) for para-substituted anilines;<sup>[15]</sup> the pK<sub>a</sub> values in parenthesis are deduced to the dependence of the N-H BDE with the Brown  $\sigma_p^+$  constants of the substituents.<sup>[16]</sup> Note that similar values can be deduced to the linear correlation of pK<sub>a</sub> with  $E_{\text{pa}}$ .<sup>[17]</sup>

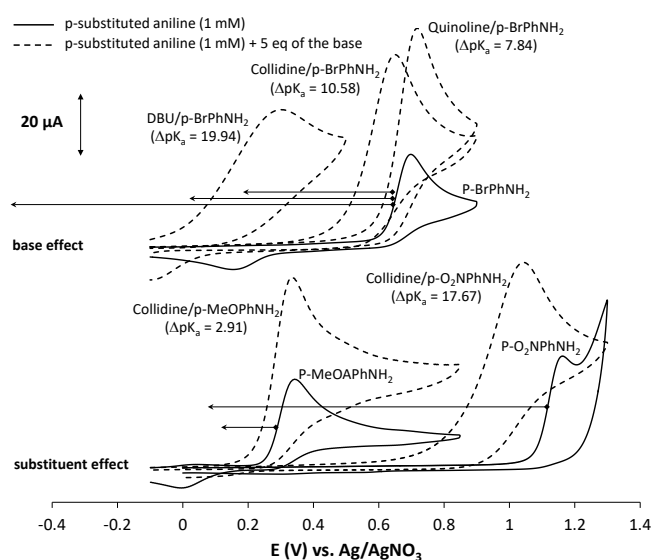
As a starting-point, evidence for the existence of hydrogen bonding between the neutral p-bromoaniline and the collidine has come from cyclic voltammetry and proton NMR

experiments (Figure 1). For the  $^1\text{H}$  NMR characterization of the H-bonded complex, equimolar (50 mM) benzene- $d_6$  solutions of p-bromoaniline and collidine were mixed at constant volume (500  $\mu\text{L}$ ) by varying the molar fraction of p-bromoaniline,  $\chi_{\text{p-BrPhNH}_2}$ , from 0.1 to 0.9. As it is evidenced by partial proton NMR spectra presented in the Figure S1, the peak associated with the  $\text{NH}_2$  protons of p-bromoaniline shifts downfield with addition of aliquots of collidine, indicating the formation of a non-covalent hydrogen bond between p-bromoaniline and collidine. The Job plot analysis presented in the inset of the Figure 1 shows a peak at a molar fraction of p-bromoaniline corresponding to the the formation of a complex of 1:1 stoichiometry.<sup>[18]</sup> Noted that NMR experiments were achieved in a non-polar solvent such as benzene, because the changes in the chemical shift of the amino protons are very small in acetonitrile, which is a competitive hydrogen-bonding solvent.<sup>[19]</sup> The p-bromoaniline (1 mM) was also titrated with collidine by cyclic voltammetry in acetonitrile (Figure 1). In pure p-bromoaniline solution, the irreversible anodic peak obtained indicates that the amine cation radical is unstable in this time scale and underwent an overall deprotonation/dimerization sequence, yielding an electroactive head-to-tail dimer responsible to the reversible system appearing at less positive potential as demonstrated by Bacon and Adams in aqueous media and Farsang in organic ones.<sup>[20]</sup> When collidine is present, an oxidation prepeak (better visible at sub-stoichiometric amounts of the base) appears at a less positive potential than for the pure p-bromoaniline solution and the reduction peak of the oxidized form of the dimer product shifts towards the negative potential due to the more basic medium (not visible in Figure 1). Noted that studies have demonstrated that the dimerization remains the main pathway in the presence of a non-nucleophilic base.<sup>[21]</sup> Further increase in the base concentration produced an increase in the current peak intensity to almost twice because the base replaces the parent p-bromoaniline in the deprotonation step, avoiding the formation of an equivalent amount of the electroinactive p-bromoanilinium ion,<sup>[22]</sup> but no further significant shift in potential is noticed. Such cyclic voltammogram (CV) features were already reported in literature and were attributed to the oxidation of a hydrogen-bonding complex.<sup>[23]</sup>



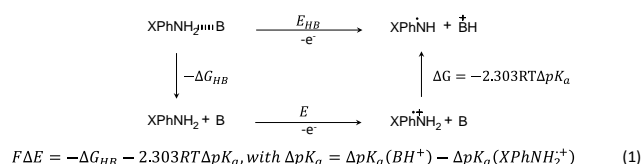
**Figure 1.** Cyclic voltammograms of p-bromoaniline (1 mM) in acetonitrile solutions containing 0.1 M  $\text{Bu}_4\text{NPF}_6$  recorded on a glassy carbon electrode at  $0.1 \text{ V}\cdot\text{s}^{-1}$  with 0, 0.6, 1, 2 and 5 equivalents of collidine. The inset shows a Job plot analysis for the complexation of p-bromoaniline and collidine using  $^1\text{H}$  NMR spectroscopy.

Figure 2 shows the changes in the anodic peak potential and the current peak intensity obtained for different aniline/base pairs in acetonitrile. It should be noted that none of the bases was electroactive in the potential windows studied. In all cases, CVs were recorded first in the absence of the base (solid lines in Figure 2), and then in the presence of 5 equivalents of the base (dotted lines in Figure 2) to make sure that there is a maximum change. In this study, the change in potential was defined as the shift in the onset of the oxidation peak rather than the change in the half-peak potential or the peak potential, because of the changes in the peak shape obtained with some bases. The method used for the determination of the onset potential is described in the Supporting Information and illustrated with the p-bromoaniline/collidine system in the Figure S2. Based on Figure 2 and  $E_{\text{onset}}$  values presented in Tables 1 and 2 for all p-substituted aniline/base pairs studied, some important conclusions can be drawn: i) the onset of oxidation of substituted anilines shifts towards less positive potentials either when the basicity of the base increases or when the acidity of the substituted aniline is exalted by an electron-withdrawing para substituent, suggesting that the amine cation radical of substituted anilines is deprotonated (this assumption is reinforced by the large shift obtained in the presence of DBU); ii) the energetics of the proton-transfer step, estimated from the difference between the  $pK_a$  of the protonated form of the base and the  $pK_a$  of the p-substituted aniline cation radicals (see Tables 1 and 2), gives an overestimated value of the negative shift in potential (indicated by the length of arrows in Figure 2), proving that deprotonation alone is clearly insufficient to account for the potential shifts observed, so that an interaction between aromatic amines and bases is supposed to exist, the energy cost to break it justifying the lower values of the shift in potential.



**Figure 2.** Cyclic voltammograms of different p-substituted anilines (1 mM) / bases (5 equivalents) pairs in acetonitrile + 0.1 M  $\text{Bu}_4\text{NPF}_6$  recorded on a glassy carbon electrode at  $0.1 \text{ V}\cdot\text{s}^{-1}$ .

On the basis of NMR results, the postulated interaction is treated as being mainly a hydrogen bond interaction, so that the thermochemical cycle presented in Scheme 1 provides a simple conceptual framework for thinking about the role of the base on the oxidation of aromatic amines. Noted that all other predominantly electrostatic interactions can be treated by the same conceptual framework. According to these thermochemical concerns, the H-bond formation and the deprotonation have opposite effects on the potential, since a positive shift in potential is required to break the hydrogen bond interaction, while a negative shift results to the energetic deprotonation (see Equation (1) in Scheme 1).



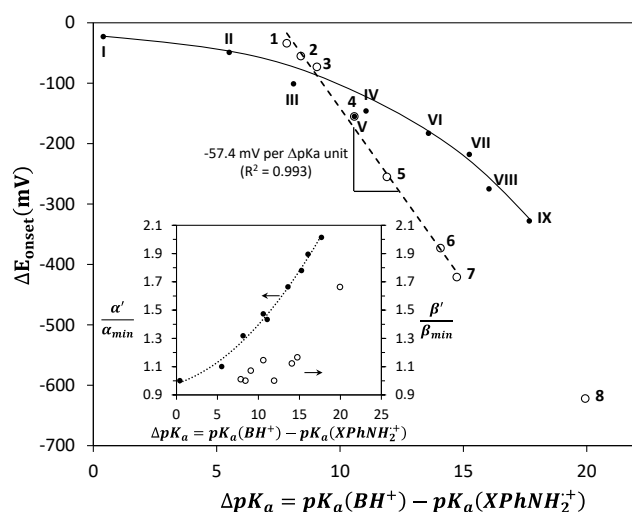
**Scheme 1.** Thermochemical cycle showing the effect of the hydrogen bonding and deprotonation steps on the oxidation potential of aniline compounds.

In parallel to this stepwise mechanism for the electron-transfer-deprotonation process, there is also a possibility for the protonic motion to be concerted to the electronic transfer with a unique transition state.<sup>[24]</sup> Eventually, as in other dissociative electron transfer reactions, a transition between a stepwise and a concerted mechanism may occur, since a large variation of the anodic peak potential and of the peak width is obtained over the extended series of aniline/base pairs studied.<sup>[25]</sup> Nevertheless, the determination of a possible passage from the stepwise to the concerted mechanism requires a detailed examination of the evolution of the anodic peak as a function of the scan rate and this issue will be discussed in a future article. In any case, whatever the mechanism (concerted or stepwise), the increase in the peak width when the base becomes stronger indicates that the electron-transfer step participates more and more significantly in the mixed control of the reaction kinetics as the driving force of the deprotonation step increases, implying that the main factor is the increase of the deprotonation rate constant. Noted that with the strong base DBU the large peak width, uncorrected from ohmic drop, suggests that complete kinetic control by the electron-transfer step is reached and the fact that the ensuing onset peak potential is out of the correlations derived from the scheme 1 (vide infra), may be an indication of a possible transition between stepwise and concerted mechanisms. Since such a transition cannot be excluded, the scheme 1 must be just regarded as a comprehensive thermochemical description of the effect of the hydrogen bonding on a proton-coupled electron transfer redox potential without any regard as the mechanism for the one-electron oxidation of the hydrogen-bonded aniline compounds occurs.<sup>[26]</sup>

Theoretically, quantitative information such as the H-bond strength can be obtained by the Nernst equation when the H-bond donor or acceptor site is electroactive as long as the redox kinetics is fast and reversible. Therefore, the main reservation here is about the irreversibility of the amine oxidation and for this reason, it is of interest for the following discussion, to estimate how the anodic peak potential of substituted anilines deviated from their formal potentials. In seminal work on the mechanism of electrohydrodimerization and its impact on the shape of cyclic voltammograms, the Savéant groups have demonstrated that the peak potential deviate from its formal potential by only 20 mV and 30 mV per decade of scan rate or of their apparent dimerization rate constants for a DIM1 and DIM2 mechanisms under pure kinetic conditions (i.e. in a range of scan rate where no cathodic trace in cyclic voltammetry is observed).<sup>[27]</sup> Furthermore, in a previous study, Amatore et al. explored the impact of a base on the kinetics of the overall dimerization reaction of p-halogenoanilines in DMF.<sup>[21]</sup> Although the dimerization remains the major pathway in the presence of a base, authors have demonstrated that the kinetic of the dimerization reaction can be accelerated and even become irreversible, causing a shift in the anodic peak potential of 30 mV per decade of base concentration. It follows from such kinetic concerns and the above discussions on a possible transition from a stepwise to a concerted mechanism for the electron-transfer and deprotonation steps, that kinetic or mechanism changes may have an impact both on the shape of the irreversible anodic wave and the shift of the peak potential. These effects are assumed to be more and more significant as the base becomes stronger. In the following discussion, we assume that the impact of a base on the dimerization mechanism accounts for a small part of the shift in potential in comparison to the H-bonding interaction or the deprotonation of the amino cation radical, since the apparent dimerization rate constant, typically lower by 5 orders of magnitude than the diffusion limit,<sup>[21,22,28]</sup> implies a maximum potential shift of around 0.15 V. We also assume that there is no passage from stepwise to concerted mechanisms (or vice versa). It is also important to note that while such kinetic concerns complicate the use of absolute potentials, only the change in potential is important in equation (1), which is assumed to be close to the change in the formal potential between the H-bonded and non-H-bonded forms of the substituted anilines, pursuant to the above assumptions. It is clear that

these simplifying assumptions are increasingly irrelevant as the base becomes stronger, as attested by the system with the strong base DBU, which is out of the correlations (*vide infra*).

Figure 3 depicts the shift in the onset potential of the oxidation of *p*-substituted anilines in the presence of nitrogen bases of different strengths with the driving force of the deprotonation step. One important observation is that, with the bases covering the  $pK_a$  range 12.03 – 24.13 in acetonitrile, the variation of the onset potential of the *p*-bromoaniline with the deprotonation reaction exergonicity is close to a Nernstian behavior (open symbols in Figure 3). This becomes even more apparent when the DBU is excluded from the linear fit of data. Conversely, the magnitude of the shift in the onset potential of the oxidation of the *p*-substituted anilines when collidine is present, strongly depends on the nature of the para substituent (closed symbols in Figure 3). While the oxidation peak of the *p*-methoxyaniline undergoes a very small shift because of the low acidity of its cation radical, *p*-substituted anilines are becoming more sensitive to the deprotonation as the electron-withdrawing nature of the para-substituent is increasing. For the strongest ones, the onset potential change parallels what is obtained for the *p*-bromoaniline in the presence of bases, approaching a Nernstian behavior. These results can be partly rationalized by regarding the change in the H-bond acidity  $\alpha$  and basicity  $\beta$  parameters of solutes studied in this work (see the inset in Figure 3). For clarity,  $\alpha$  and  $\beta$  parameters are normalized to their minimum values ( $\alpha_{min}$  is for *p*-methoxyaniline and  $\beta_{min}$  is for pyridine).



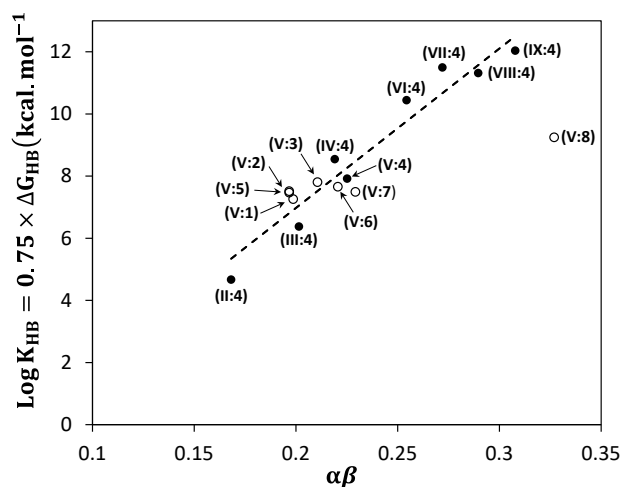
**Figure 3.** Variation of the onset potential of the oxidation of para-substituted anilines (1 mM) in acetonitrile + 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in the presence of nitrogen bases (5 equivalents) with the driving force of the deprotonation of the anilinium radicals. Open symbols are for the *p*-bromoaniline/bases pairs and closed symbols are for the para-substituted anilines/collidine pairs (Roman and Greek numerals refer to the Tables 1 and 2). Note that the solid curve serves just as a guideline for the eye. The inset shows the evolution of the H-bond acidity  $\alpha$  and basicity  $\beta$  parameters with  $\Delta pK_a$ .

In a pioneering work, Abraham et al. have demonstrated that the Gibbs energy of a H-bond interaction (as  $\log K_{HB}$ ) can be expressed by the general equation (2), where  $m$  and  $c$  only depend on the solvent.<sup>[29,30]</sup>

$$\log K_{HB} = m\alpha\beta + c \quad (2)$$

In this  $\alpha\beta$  formalism, it appears that the energies of the H-bond interactions between the *p*-bromoaniline and the bases used in this work are nearly the same, since except for DBU, the  $\beta$  parameter for the other bases is comprised within a very narrow range. It is the reason why the increase in electrochemical potential to make the H-bond interaction broken can be assumed constant, so that the apparent anodic potential shifts in a Nernstian manner with the exergonicity of the deprotonation step pursuant to equation (1). Conversely, because *p*-substituted anilines studied cover a wide H-bond acidity range, deviation to the Nernstian behavior is obtained. On plotting these  $\log K_{HB}$  values versus the product  $\alpha\beta$  for all the H-bond donor:acceptor (i.e. substituted-aniline/base pairs) combinations, there is some linear relationship (Figure 4), that is a good experimental evidence for the dominant H-bonding character in the molecular interaction between aniline and bases. Noted that the deviation obtained with the DBU (see the system **V:8** in Figure 4) is presumably due to a different mechanism for the oxidation of the *p*-bromoaniline in the presence of a very strong base, as it was evoked above. It can also be due

to a singular stoichiometry for the complex **V:8**, since the equation (2) is only applicable to 1:1 hydrogen bonded complexes, or to a deprotonation of the p-bromoaniline becoming energetically accessible with DBU.<sup>[31]</sup>

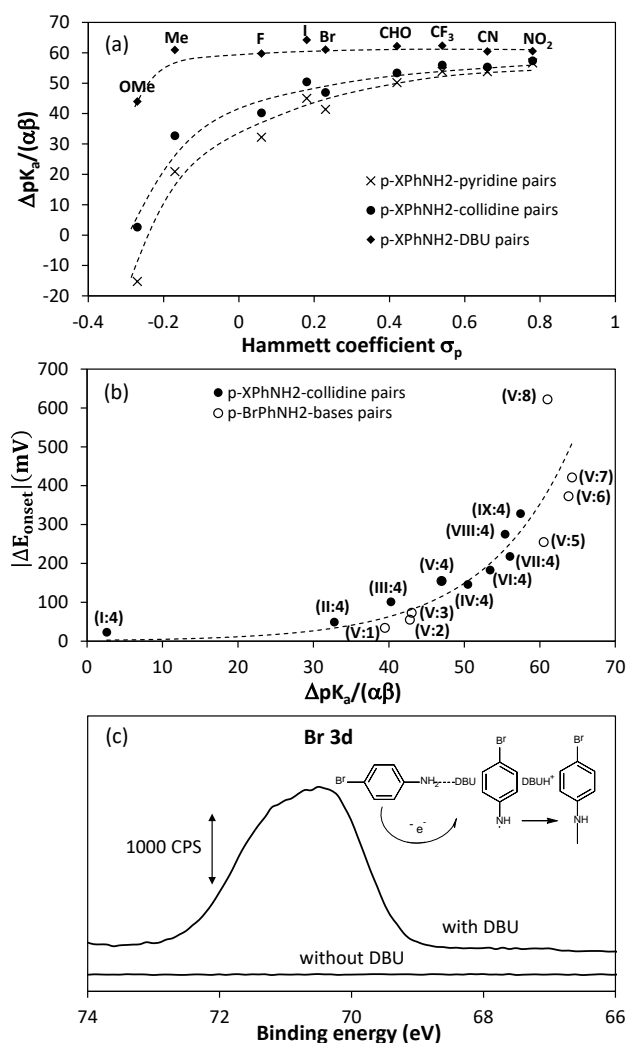


**Figure 4.** Equilibrium constants (as log K values) vs. the  $\alpha\beta$  product for the formation of H-bonded complexes between para-substituted anilines (identified by Greek numerals) and bases (identified by Roman numerals).

These  $\log K_{\text{HB}}$  values correspond to Gibbs energies of the hydrogen bonding interactions comprised between 6 kcal.mol<sup>-1</sup> to 16 kcal.mol<sup>-1</sup> at 293 K. Here, it is important to bear in mind that the amino group can form three H-bonds, in two of them NH<sub>2</sub> is a proton donor and in the third one nitrogen acts as a proton acceptor, so that the  $\log K_{\text{HB}}$  values (and the corresponding Gibbs energies) are for the overall H-bonding interactions. Noted also that, in the  $\alpha\beta$  formalism used in Figure 4,  $\alpha$  values for individual hydrogen atoms were used and the contribution of the nitrogen acceptor sites to the H-bonding interaction was neglected. That being so, the results obtained agree well with the relevant literature, since classical hydrogen bonds (i.e., noncovalent interactions) span energies between 0.2 and 15 kcal.mol<sup>-1</sup>.<sup>[32]</sup>

The correlation in Figure 4 provides an important clue how to treat the impact of a base on the oxidation of aromatic amines, since, in most cases, solvatochromic parameters  $\alpha$  and  $\beta$  provide a reasonable prediction about their initial interactions. So that this study provide us with a unique opportunity to explore the possibility that the overall H-bonding/deprotonation sequence influences the grafting efficiency of aromatic amines, which could help to establish guiding principles to rationalize the choice of the most suitable base for the grafting. Because the base must have both a high  $\text{p}K_{\text{a}}$  value for increasing the driving force of the deprotonation step and, at the same time, a weak  $\beta$  parameter to make easier the breaking of the hydrogen bond, it is possible to obtain an efficiency parameter for the base in the grafting process that we express simply as  $\Delta\text{p}K_{\text{a}}/(\alpha\beta)$ . Noted that for a base makes possible the grafting of an amine, its efficiency parameter must be positive. Figure 5a shows the evolution of this parameter with the Hammett coefficient  $\sigma_{\text{p}}$  of the para substituent (for clarity, only the evolution of the efficiency index for the pyridine, collidine and DBU were showed). Remarkably, this efficiency index asymptotically tends towards the same value whatever the base considered. This constant value is assumed to be characteristic to the solvent as it can be obtained from equations (1) and (2). Figure 5b shows the evolution of the onset potential with the efficiency index of bases in the oxidation of the p-bromoaniline. Importantly, up to an efficiency index of ca. 30 - 40, the bases have practically no effect on the anodic potential, because, for this class of compounds, a certain increase in the driving force of the deprotonation step is required to compensate the energy to provide to break the H-bond interaction. In acetonitrile, conditions making the oxidation of the p-bromoaniline easier are obtained with the DBU. Therefore, as a proof-of-concept for base-assisted grafting of aromatic amines, these conditions were used to modify a carbon surface (Figure 5c).





**Figure 5.** Base-assisted grafting of primary aromatic amines. (a) Variation of the efficiency parameter of the pyridine, collidine and DBU bases in the oxidation of para-substituted anilines with the Hammett coefficient  $\sigma_p$  of the para substituent. (b) Evolution of the onset potential with the efficiency parameter of the collidine in the oxidation of p-substituted anilines (closed symbols) and of the other bases studied in the oxidation of the p-bromoaniline (open symbols). (c) Br 3d core level XPS spectra of glassy carbon surfaces polarized at 0.3 V vs. Ag/AgNO<sub>3</sub> for 5 min in a p-bromoaniline (1 mM) acetonitrile solution containing 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in the absence and presence of 5 equivalents of DBU. Note that the dotted curves serve just as a guideline for the eye.

Importantly, when the modification of a glassy carbon surface was achieved in the presence of DBU, the very exergonic deprotonation of the amino cation radical makes possible the grafting of the p-bromoaniline at very low potential, as evidenced by a strong Br 3d XPS signal for the carbon surface modified at 0.3 V vs. Ag/AgNO<sub>3</sub> for 5 min with DBU in solution, compared to a blank experiment achieved in a pure p-bromoaniline solution (Figure 5c). For information, the survey XPS spectrum for the carbon surface modified with the p-bromoaniline/DBU system is presented in Figure S3. In order to generalize this approach, the p-nitroaniline/collidine system was also tested for the electrografting. This system leads to a situation very similar to that of the oxidation of the p-bromoaniline in the presence of DBU, since in both cases a very exergonic deprotonation step is obtained either by using a very strong base or a very acidic amino cation radical, as it is evidenced in Figure 2 and in the inset of Figure S4. In this system, the collidine is responsible of shifting the peak potential of the oxidation of the p-nitroaniline by around 120 mV towards the less positive potentials, because of the exergonic deprotonation of the p-nitroaniline cation radical. But with the p-nitroaniline/collidine mixture, the H-bond interaction between the NH<sub>2</sub> group and the collidine has a strong antagonist effect on the potential compared to the deprotonation step and a moderate apparent potential shift is obtained. Nevertheless, the net increase in the driving force is sufficient to make possible the grafting of the p-nitroaniline at 1 V vs. Ag/AgNO<sub>3</sub> in the presence of collidine, while this is not the case in the absence of collidine, as it

was evidenced by the presence or the absence of a photoelectron peak at ca. 406 eV ascribed to the nitro group in the N 1s XPS spectrum of carbon surfaces polarized in the presence or absence of collidine (see Figure S5).

In conclusion, this study shows the existence of an interaction between neutral aniline compounds and nitrogen bases that go against the driving force of the deprotonation of the amine cation radicals in the oxidation process of aromatic amines. Prediction of this interaction from H-bond acidity and basicity parameters provides a simple conceptual framework to study how the electrografting of aromatic amines is impacted by a base. An efficiency factor for the base in the oxidation process was proposed as a practical tool to choose the mostly suitable base for the grafting.

## Experimental Section

Electrochemical measurements were made at 293 K in a three-electrode cell containing distilled acetonitrile + 0.1 M nBu<sub>4</sub>NPF<sub>6</sub>. The working electrode was a glassy carbon electrode mirror polished between each measurement. All potential values were referred to the Ag/AgNO<sub>3</sub> system. <sup>1</sup>H NMR experiments were conducted in benzene-d<sub>6</sub>. In the Job diagram, solutions of p-bromoaniline and collidine were prepared with equal concentration (50 mM) and various aliquots of each solution were mixed at constant volume (500 μL). XPS measurements were performed with a Kratos Axis Ultra spectrometer using a Al Kα monochromatic beam working at 1486.6 eV. All spectra were recorded in the constant energy mode at a pass energy of 20 eV.

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**Keywords:** substituted anilines • oxidation • hydrogen bonding • deprotonation • modified electrode

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