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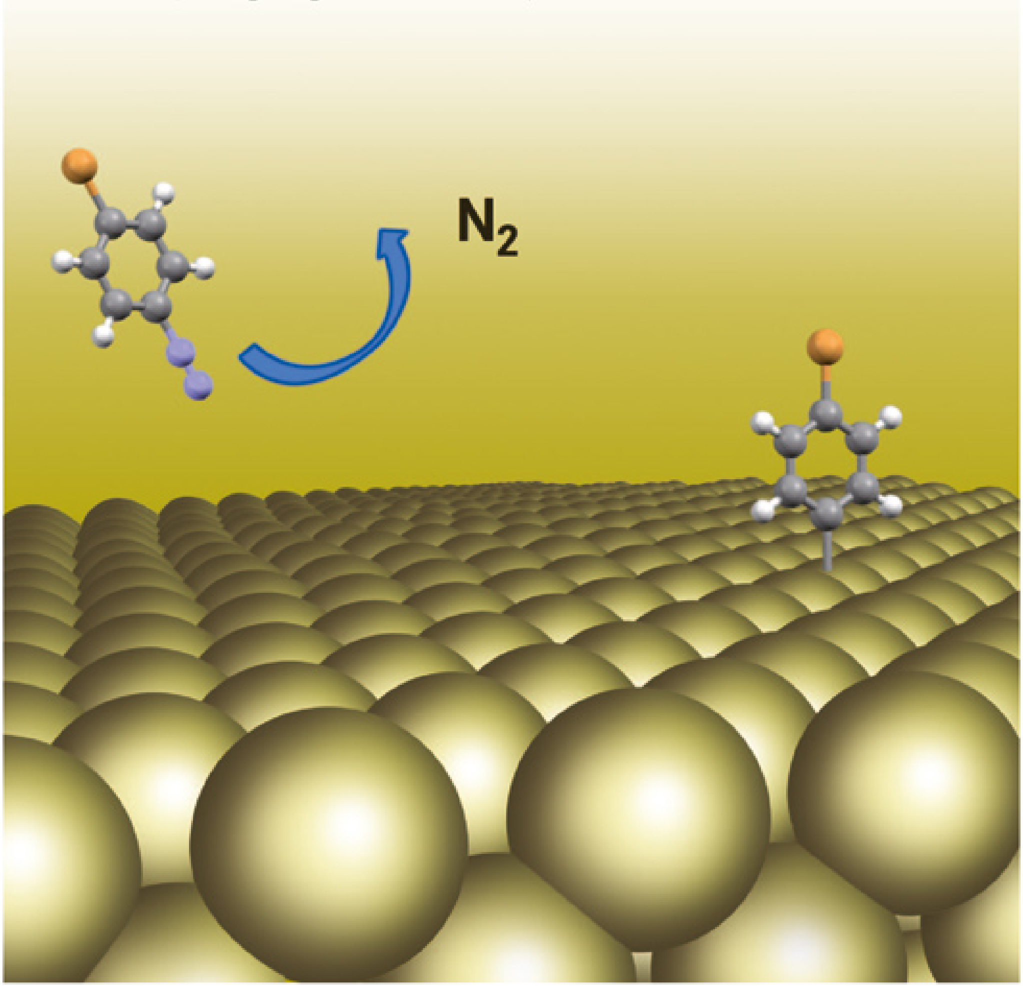
Aryl Diazonium Salts

New Coupling Agents in Polymer and Surface Science



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To Jean Pinson, with gratitude

Contents

Preface

Dear Reader,

The diazotation of compounds has first been described in the mid-19th century by the German chemist Peter Griess. Henceforth, aryl diazonium salts (from the French "diazote", two nitrogen atoms) are commonly used for the synthesis of a large series of organic compounds such as azo dyes, and are thus the object of numerous articles and book chapters or sections. However, the study of the surface and interface chemistry of these salts remained sparse despite its interest in modifying materials surfaces. For example, it was shown in 1958 that the reaction of aryl diazonium salts with mercury electrodes results in electrografting of aryl groups on this liquid metal with formation of phenylmercuric chloride and diphenylmercury (Elofson, R.M., *Can. J. Chem.*, 1958, **36**, 1207–1210, doi: 10.1139/v58-174; see also Chapter 1). Later in 1961, aryl diazonium salts were proposed as coupling agents in histochemistry for the labeling of enzymes (Burstone, M.S., Weisburger, E.K., *J. Histochem. Cytochem.*, 1961, **9**, 301–303, doi: 10.1177/9.3.301).

In modern surface science, Jean Pinson and co-workers described, in 1992, the mechanisms of the reaction between aryl diazonium salts and glassy carbon electrodes resulting in surface-tethered aryl groups. Provided that the functional group, in para position of the diazonium, is reactive, it becomes possible to graft polymers, enzymes, catalysts, etc. Since then, the two last decades (1992–2012) witnessed a quantum jump in the number of publications pertaining to surface chemistry and applications of aryl diazonium salts. The interest in using these compounds obviously lies in their ease of preparation, rapid reduction by a large range of methods and strong aryl-surface covalent bonding. Grafted aryl groups can be used as such in order to impart new physicochemical properties, or can serve as coupling agents for additional species. The applications concern electronics, electrocatalysis, sensors, nanocomposites, drug delivery, to name but a few, as testified by over 3000 articles and reviews, book chapters, and chapter sections. Several processes involving aryl diazonium salts were also patented and industrial products, though not too many, are on the market (see Chapter 14). Despite these extraordinary academic and industrial achievements, there is no comprehensive book dealing with the fundamental aspects of surface and interface chemistry of the diazonium salts and their use as surface modifiers and coupling agents. The book that you are holding in your hands fills this gap in 14 self-contained chapters written by acknowledged experts in their respective fields.

One can distinguish three main parts: fundamental and analytical aspects of diazonium-modified surfaces (Chapters 1–4); applications of diazonium salts in electrocatalysis, polymer science, sensors and biosensors, and electronics (Chapters 5–11). The third part concerns related or alternative organic molecules (e.g. amines, triazenes, vinyl, ethynyl, Grignard reagents) for surface treatment in general (Chapter 12) and for the more applied molecule-silicon electronics, in particular (Chapter 13). The book finishes by a contribution summarizing patents and industrial applications of the surface chemistry of aryl diazonium salts and related compounds (Chapter 14).

Dear Reader, we would like to thank you for choosing our book. As you will appreciate, the surface chemistry of diazonium salts and related compounds has progressed at a remarkable pace. The gap between the academic research on diazonium salt surface chemistry and its industrial applications has already been filled although this topic of surface science and technology is still in its infancy. Whether you are a student, technician, engineer, teacher or researcher; expert or newcomer, it is hoped that the information provided by all contributors will open new horizons.

As an editor, it has been a very exciting experience to collaborate with acknowledged experts from the five continents. I should like to thank them all for kindly accepting my invitations to contribute to this adventure. I am also very much indebted to all reviewers for their guidance. I am grateful to my colleague, Dr. Abderrahim Boudenne (Université Paris Est Créteil, France), for his remarkable help when I started the book project. I must also add here that I, personally, as well as my students, have learned a lot from Professor Jean Pinson. I have enjoyed his teaching of chemical kinetics and magneto-chemistry when I was one of his third year students in 1981 at University Paris 7; it is both and an honor and a privilege to have him as a colleague 30 years later. It therefore gives me great pleasure to dedicate this book to my former professor of chemistry and actual colleague and friend Jean Pinson.

This experience has been intense and exciting over almost 2 years. It would not have been possible to put the book in its final form, in such a short period of time, without the continuous support, encouragement, love, and patience of my daughter Inès, my son Selim, and my wife Heger.

March 2012 *Mohamed Mehdi Chehimi*

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1
Attachment of Organic Layers to Materials Surfaces by Reduction of Diazonium Salts

Jean Pinson

1.1
A Brief Survey of the Chemistry and Electrochemistry of Diazonium Salts

Aromatic diazonium salts ($ArN_2^+ X^-$) are easily synthesized in an acidic aqueous medium (HBF_4) starting from an amine in the presence of $NaNO_2$, and in an aprotic medium (ACN + HBF_4 in ether) in the presence of *t*-butylnitrite or in ACN + $NOBF_4$ [1–2]. As many aromatic amines are available commercially, the preparation of a large number of diazonium salts can be easily carried out. They can be isolated and characterized, but they can be used directly in the solution where they have been prepared [3].

The chemistry of aromatic diazonium salts [1, 4, 5] is dominated by the electrophilic character of the azo group; they react with aromatic amines and phenols to give azo dyes (C-coupling) that are important coloring materials [6]. Aliphatic diazonium salts are extremely unstable and up to now only a few examples of grafting on carbon black involving the diazonium salt of 2-aminoethanesulfonic acid and 4-bromobenzylamine have been reported [1, 7].

As we will see below, when a diazonium reacts with a surface, with a few reported exceptions, the diazonium group is lost and the radical reacts with the surface, therefore grafting involves a homolytic dediazonation step; in this respect the dediazonation reactions are important for discussing the grafting mechanism. This dediazonation can take place heterolytically to give Ar^+ cations, or homolytically to give $Ar^•$ radicals [8]; these spontaneous reactions can be slowed down by reducing the temperature to below 5 °C. The Sandmeyer reaction (1.1) is a first example of an important dediazonation reaction involving a radical; the reduction of the diazonium salt by cupric chloride or bromide ArCl, (Br) gives an aryl radical that abstracts a chlorine (bromine) atom from CuCl (Br) to give ArCl (Br), as shown in the reaction.

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$$ArN_2^+Cl^- + CuCl \rightarrow ArCl + N_2 \quad (1.1)$$

A second important dediazonation reaction of diazonium salts in relation to grafting is the Gomberg–Bachman reaction; in the presence of a base the diazonium group is lost to give radicals that couple to other aromatic groups, dimers and a number of other coupling products are obtained [9, 10]. The Pschorr reaction is the intramolecular reaction of an aryl radical with an aryl group, the radical is produced, for example, by reduction of a diazonium salt by Cu(0) [11]. Merweein reactions also rely on the formation of radicals [12]. Solvolytic dediazonations are another example, they can take place in a heterolytic or homolytic manner, that is, through the intermediacy of an aryl cation or an aryl radical [13–17]; heterolytic dediazonation takes place in solvents of low nucleophilicity (H_2O), while a homolytic mechanism is observed in solvents of increased nucleophilicity (HMPT, pyridine), in a number of solvents, such as MeOH, EtOH, DMSO, both mechanisms can be observed [14]. For example, in ethanol a slow heterolytic mechanism is observed in an acid medium and a 50 times faster homolytic one in a basic medium [14]. For a given solvent, electron-withdrawing substituents in the aromatic ring favor homolytic dediazoniations [14].

In an aqueous acidic medium and in aprotic non-nucleophilic solvents diazonium salts are present, but at neutral and basic pHs [13–17] equilibria between the diazohydroxide and diazoates are established; they are displaced toward the formation of diazoates; equilibrium and rate constants have been measured [13]. In the presence of alcohols, diazoethers Ar–N=N–OEt [13, 18] , and in the presence of amines, triazenes Ar–N=N-(NR_2) are obtained. These derivatives can also be used for surface modification. For example, diazohydroxides can spontaneously dediazonize and the ensuing radical attaches to the surface of gold [19]. Triazenes are interesting because they are transformed into diazonium salts in an acid medium; in 2% HF the oxidized silicon surface is transformed into Si–H and aryldiethyltriazenes are transformed into aryldiazonium salts, followed by spontaneous grafting of the aryl species to the silicon surface [20]. They can also generate aryldiazonium salts in the presence of electrogenerated acid produced by oxidation of hydrazine [21].

Prior to the discovery of the electrografting reaction, the reduction of diazonium salts $ArN_2^+ X^-$ had been investigated in an aqueous medium at mercury electrodes [22]. In an aqueous acidic medium two waves are observed; the first is a one-electron wave, while the overall process involves four electrons on the second wave and leads to phenylhydrazine. The formation of the aryl radical was confirmed by coulometry, on a mercury pool, at the potential of the first wave, that provided, nearly exclusively, phenylmercuric chloride and diphenylmercury by reaction of phenyl radicals with mercury. Note that these mercury compounds can be viewed as the result of electrografting on a liquid metal. The involvement of radicals [23] during the electrochemical reduction (on the first wave) of aryldiazonium salts was also observed through the Pschorr synthesis of phenanthrene [24], and also by electron spin resonance (ESR) in ACN in the presence of a spin-trap [25].

1.2
The Different Methods that Permit Grafting of Diazonium Salts

In this section we describe the many methods that permit the grafting of diazonium salts, on many substrates, through a variety of experimental conditions.

1.2.1
Electrochemistry

This is the first method that was used for grafting (electrografting) diazonium salts [26–29]. Electrochemistry of diazonium salts in an aprotic medium is very simple, a single, broad, one-electron wave is observed at potentials close to 0 V vs SCE as presented in Table 1.1.

The attachment of the ensuing aryl radical (1.2) + (1.3) (Figure 1.1) to the carbon or metal substrate translates in the fast disappearance of the wave due to the blocking of the electrode by the organic layer formed on it. This is, most likely, the reason for the broadness of the wave; the surface is modified while the voltammogram is recorded. Sometimes a prepeak is observed; on gold, it has been

Table 1.1 Some reduction potentials on GC of benzenediazonium salts in ACN.

Diazonium salt	Reduction potential, V vs SCE
4-Nitrobenzenediazonium	+0.20 [27]
4-Bromobenzenediazonium	+0.02 [27]
Benzenediazonium	–0.06 [27]
4-*t*-Butylbenzenediazonium	–0.10 [30]
4-Methylbenzenediazonium	–0.16 [30]
4-Diethylaminobenzenediazonium	–0.56 [31]

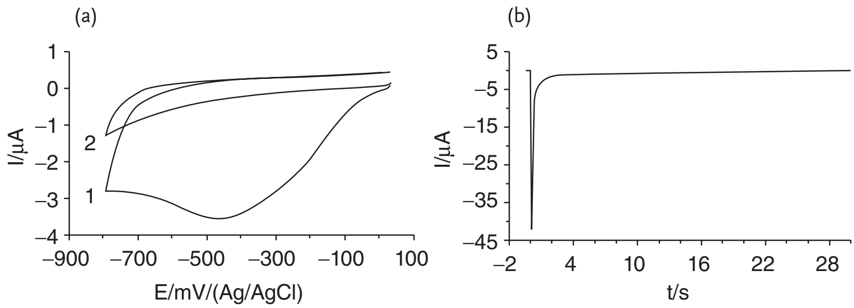

Figure 1.1 (a) Cyclic voltammogram and (b) chronoamperometry of 4-nitrobenzenediazonium (c = 5 mM) in ACN + 0.1 M NBuBF4: 1, first and 2, second scan. Gold electrode (d = 1 mm), $\nu = 100\,\mathrm{mV\,s^{-1}}$, reference Ag/AgCl.

assigned to the reduction on the different crystallographic facets of gold, for example, the diazonium salt $^{+}N_2–C_6H_4–S–C_6F_{13}$ presents three voltammetric peaks on polycrystalline gold at +0.14, +0.03 and ~−0.45 V vs (Ag/Ag$^+$), that are assigned respectively to Au (111), Au (100) and Au (110) + Au (331) [32].

$$\mathrm{ArN_2}^+ + 1\mathrm{e}^- \rightarrow \mathrm{Ar}^\bullet + \mathrm{N_2} \tag{1.2}$$

$$\mathit{Surf} + \mathrm{Ar}^\bullet \rightarrow \mathit{Surf}\text{-}\mathrm{Ar} \tag{1.3}$$

$$\mathrm{Ar}^\bullet + 1\mathrm{e}^- \rightarrow \mathrm{Ar}^- \tag{1.4}$$

The $Ar^\bullet$ radical is responsible for the grafting reaction, its formation and its further evolution are, therefore, important in the context of surface modification. It has been shown, by simulation of the voltammograms, that the reduction of the benzenediazonium cation (1.2) is a concerted reaction, which means that, during the electrochemical reduction at the peak potential, there are no intermediates between the diazonium cation and the radical; this also means that the radical is formed directly on the surface, which is a very favorable situation for the grafting reaction [33]. This radical can be reduced, in turn, to an anion (1.4) that is unfavorable for the grafting reaction. The reduction potential of $Ar^\bullet$ has been measured not only by simulation of the voltammetric curves: $E = -0.64$ V vs SCE [33], but also from the number of electrons consumed at different potentials for the reduction of benzenediazonium, diphenyliodonium and triphenylsulfonium salts, which all provide a phenyl radical upon reduction: $E = -0.95$ V vs SCE [34]. The standard redox potential has been measured by simulation of the voltammograms [33]: $E°(Ph^{\cdot}/Ph^-) = +0.05$ V vs SCE; it has also been calculated by DFT methods: $E°(Ph^{\cdot}/Ph^-) = -0.26$ V vs SCE [35]. These indicate that the reduction of $Ar^\bullet$ is quite easy, which means that during electrografting the potential should not be too negative in order to prevent the reduction of the radical. This is shown by the reduction of different diazonium salts at −1.0 V vs SCE (at a potential where the radical is reduced to an anion), on a mercury electrode, in acetonitrile; azobenzenes were obtained in good yields but no mercury compounds were reported [36].

The formation of the layer can be easily detected, as shown in Figure 1.1, through the disappearance of the reduction wave of the diazonium salt; chronoamperometry is also very characteristic, instead of a decrease in the current according to a Cotrell law, a very sharp decrease is observed due to the fast blocking of the surface.

1.2.2 Reducing Substrate, Homolytic Dediazonation, Reaction with the Substrate

Table 1.1 exemplifies the easy reduction of diazonium salts; if the substrate has reducing capabilities an aryl radical will be formed, close to the electrode, by simply dipping the substrate in the solution of the diazonium salt. In some other examples, where the substrate is less reducing, it is difficult to differentiate a reduction by the substrate from a spontaneous dediazonation. Indeed, a spontaneous homolytic dediazonation is another route for the formation (in solution) of aryl radicals. But the substrate can also react chemically with the diazoniums salt or the aryl cation Ar^+ (and not the radical) and two examples are described in the section on the grafting mechanism.

Metals such as iron and copper can reduce diazonium salts and 4-nitrophenyl layers are obtained by dipping copper, iron, nickel and zinc in a solution of the corresponding salt [37]. The grafting process is in agreement with a redox reaction: grafting is more efficient on zinc than on iron, and even more than on nickel; this trend follows the open-circuit potential order $E_{OCP}(Zn) < E_{OCP}(Fe) < E_{OCP}(Ni)$ and, on a selected metal, grafting is more difficult with less-easily reduced diazonium salts. Benzenediazonium tetrafluoroborate has been reacted in ACN with various metals (Al, Ca, Cr, Cu, Fe, Ga, In, Mg, Li, Na, or Zn), nitrogen evolution was observed, indicating the reduction of the diazonium salt. With copper a ionization-dissolution was evidenced at high concentration and the formation of a complex $[Cu(N_2C_6H_5)(NC{-}CH_3)_3]^+$ was demonstrated [38]. On gold a spontaneous grafting occurs in acidic [19, 39, 40] solution but the mechanism is unclear. These results indicate that the redox properties of both partners (diazonium + metal) are involved in the grafting reaction.

On glassy carbon, the mechanism seems to follow a reductive path as the easily reducible 4-nitro, 4-trifluoromethyl, or 4-bromobenzenediazonium (Ep = +0.20, –0.34, –0.35 V vs SCE, respectively) are grafted spontaneously, but not the diazonium salts of diethyl, amino diphenyl, triphenyl aniline (Ep = –0.42, –0.35 and –0.45 V, respectively) [41] nor *N*,*N*-diethylaminobenzenediazonium (Ep = –056 V vs SCE) [31]. Moreover, a jump in the open circuit potential of the carbon electrode was observed upon addition of the 4-nitrobenzenediazonium salt in solution [41, 42]. These features point to an electron transfer mechanism and to the intermediacy of the aryl radical. Spontaneous grafting of diamond has also been observed [43, 44]; the reaction time necessary to obtain a monolayer (72 h in an ACN saturated solution of 4-nitrobenzenediazonium) [43] is more in agreement with a homolytic spontaneous dediazonation than with an electron transfer from the surface. Carbon nanotubes (CNTs) can also be modified spontaneously [45]. In pure water (where diazoates should be present), the mechanism has been assigned (through a careful kinetic analysis and ESR measurements) to a spontaneous homolytic dediazonation [46].

Spontaneous grafting can also be achieved on hydrogenated silicon, the substrate reduces the diazonium salt to a radical [47], this is described in more detail below. At a scanning electrochemical microscope SECM tip the pH can be modified and fluoride ions transformed into HF that etches the native oxide of a Si wafer, 4-nitrobenzenediazonium can be grafted spontaneously in the holes [48].

1.2.3 Reducing Reagent

As diazonium salts are very easily reduced, a number of reducing reagents can be used. Hypophosphorous acid (H_3PO_2) has been used to functionalize the surface of carbon powder [49–54], polymers (polypropylene, polyethylterephthalate, polyethyletherketone) and inorganic compounds (TiN, SiC, SiO_2, SiOC) [55]. Iron powder has also been used as a reducing agent for the grafting of diazoniums alone or diazonium and vinylics [56]; in this last case, the process is very efficient as even the surface of glass or Teflon can be modified. Gold surfaces have been modified in the presence of ascorbic acid [40]. With these methods, the radical is produced in solution and there should be no limitation to the growth of the layers, but no data about the thicknesses are given.

1.2.4
Neutral and Basic Media

In a neutral aqueous medium diazohydroxides are obtained, they rapidly deprotonate to diazoates that decompose radicals [13]; these radicals react spontaneously with metals [57] and graphene sheets [58]. In basic and neutral media, diazoniums are transformed directly into diazoates; gold surfaces have been modified in this way [19, 40]. Iron oxide magnetite, Fe_3O_4, nanoparticles have been capped by aryl groups, by adding the 2-hydroxyethylbenzenediazonium tetrafluoroborate (BF_4, N_2–C_6H_4–$(CH_2)_2$–OH) directly in the pH 9 solution where the nanoparticles are formed [59]. Carbon nanotubes have been modified spontaneously in a diazoate solution at pH 11 [60]. In these cases, a homolytic dediazonation is known to take place [13, 14].

1.2.5
Ultrasonication

Grafting of various inorganics and polymers (see above) has been achieved under ultrasonication [55]. Diamond nanoparticles have also been modified under ultrasonication by 4-nitrophenyl groups in acidic aqueous solution [44]. ITO has been modified by 4-nitrobenzenediazonium, in water, at different frequencies, the lowest one (20 kHz) was shown to be the most efficient [61]. A mechanism has been proposed, based on the known formation of reducing radicals ($H^•$, $R^•$ from adventitious impurities), these radicals should reduce the diazonium salt [61].

1.2.6
Heating and Microwave

The surface of polyethylterephtalate has been modified by heating an aqueous solution of sulfanilic acid at 70 °C in the presence of $NaNO_2$ [62]; under these conditions a heterolytic cleavage of the diazonium cation should be favored. Thermal reactions, using *in situ* generated aryl diazonium salts, have permitted the derivatization of SWCNTs (single wall carbon nanotubes) at 60 °C in dichlorobenzene for 15 h [45], and MWCNTs (multiwall carbon nanotubes) at 80 °C in concentrated sulfuric acid in the presence of ammonium persulfate and 2,2-azoisobutyronitrile [63]. A microwave-assisted surface modification of CNTs and nanohorns has been described [64–66]. Heating aryldiazonium tetrafluorobo-