On-line electrochemical–mass spectrometry study of the mechanism of oxidation of $N,N$-dimethyl-$p$-phenylenediamine in aqueous electrolytes

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Abstract

The mechanism of electrochemical oxidation of $N,N$-dimethyl-$p$-phenylenediamine (DPD) in aqueous electrolyte solutions in the pH range 1.4–9.7 was studied using on-line electrochemical–mass spectrometry. A radial flow electrochemical cell was used to generate the product stream which was analyzed by a mass spectrometer equipped with an electrospray interface (ESI-MS). It was shown that DPD oxidation in the pH 1.4–9.7 range brings about formation of the Wurster red cation radical, quinonediimine, quinonemonoimine and dimer and trimer products of coupling reactions of DPD with quinonediimine and quinonemonoimine. Coupling reactions were found to be strongly pH dependent. The kinetics of the coupling reaction between DPD and quinonemonoimine were studied at pH 3.6.

Keywords: ESI-MS; EC/MS; Phenylenediamine; Anodic oxidation; Reaction mechanism; Channel flow; Flow cell

1. Introduction

On-line electrochemistry/mass spectrometry (EC/MS) is a relatively new tool in the study of electrochemical transformations of organic substances, though the method has been successfully used for identification of products and intermediates which were produced in electrochemical transformations [1–13].

The goal of the current publication is to expand the range of applications of the EC/MS method by quantitative studies of mechanisms of complex electrochemical reactions. We have monitored the evolution of different products in response to the variation of experimental parameters influencing the rates of chemical reactions, which follow charge transfer reaction. In previous works several authors successfully minimized the transfer time of products from the flow cell to MS [12,14,15]. We have deliberately increased the transfer time by the installation of a relatively large tube in the transfer line leading from the cell to the MS. The transfer line of enlarged volume served as a homogeneous reactor in which subsequent chemical reactions occur. The reactants' residence time in the reactor determined the degree of completion of the reactions. The substance residence time in the reactor was varied in the range 4.3–480 s by selecting tubing of appropriate diameter and length. Use of a chemical reactor of tunable volume enabled us to reach a span of 2 orders of magnitude in the substance residence time while keeping the electrolyte flow rate in a narrow range. Use of a narrow range of electrolyte flow rates is vital since the performance of both the electrochemical flow cell and ESI/MS, is strongly influenced by the liquid flow rate. Increase of flow rate through the cell above the constraint drastically reduces the conversion of the test compound. On the other hand, the use of very low flow rates relocates subsequent chemical reactions from the reactor into the cell. Use of ESI-MS for
quantitative measurements requires application of a standard protocol for ESI operation, which includes constant liquid flow rate, electrolyte concentration, sheath gas flow, spray voltage, etc.

The chemical transformations of the test compound in the cell and in the reactor involved:
(1) electrochemical oxidation of the starting compound;
(2) hydrolysis of the oxidized form of the starting compound;
(3) coupling reactions of the starting compound with its oxidation products.

The electrolyte flow rate, volumes of the flow cell and the reactor were chosen such that hydrolysis and coupling reactions occurred mostly in the reactor. The parameters which were used to influence the subsequent chemical reactions were: (1) concentration of the starting compound in the electrolyte; (2) pH of aqueous electrolyte; (3) degree of conversion of the starting compound in the electrochemical cell; (4) the substance residence time in the reactor.

The experimental setup consisted of an electrochemical flow cell, a reactor of the specified volume in which consecutive chemical reactions occurred, and a mass spectrometer equipped with an electrospray interface. The radial, low volume (0.1 μL), electrochemical flow cell has been described in detail elsewhere [10]. The cell enables controlled potential operation. The desired degree of conversion of the test compound, ranging from 0 to nearly 100%, can be achieved by variation of the electrode potential and the electrolyte flow rate. The reactor of the appropriate volume, which was placed downstream of the flow cell, enabled chemical reactions to proceed for the chosen time. Upon leaving the reactor, the effluent flow was diluted by at least an order of magnitude excess of solvent in order to quench coupling reactions between reactants in the transfer line to the mass spectrometer.

The goal of the current publication is to show the advantages of the proposed configuration of the EC/MS method for studies of complex electrochemical reactions involving subsequent parallel and consecutive chemical reactions. The electrochemical reaction which triggers the chemical reactions is the oxidation of \(N,N'\)-dimethyl-\(p\)-phenylenediamine (DPD) in an aqueous electrolyte. The competitive paths of the reaction mechanism include parallel coupling reactions between unreacted DPD and quinonediimine, the first path, and quinonemonoimine, the second path. The latter is formed by hydrolysis of quinonediimine. The basic transformations of DPD, compound (I), are shown in Schemes 1 and 2. Numbers in brackets represent the masses of ions or protonated molecules. Chemical oxidation of \(p\)-phenylenediamines is well researched due to its application in color photography and hair coloring [16–30]. Information on the electrochemical oxidation of \(p\)-phenylenediamines is more limited [31–41].

Chemical oxidation of \(p\)-phenylenediamines in aqueous electrolytes is a 2-electron process generating quinonediimine (II) [32–37], reaction (a) in Scheme 1. In acidic electrolytes two single electron stages of oxidation were proposed for formation of quinonediimine [19,37,40]. In aqueous solutions compound (II) is deaminated by hydrolysis yielding quinonemonoimines, compounds (III) and (IV), and \(p\)-quinone (V) [21,22,29,38,39], reactions (b), (c), (d), (e), respectively. In acidic solutions hydrolysis reaction (d) dominates over reaction (b).

The disproportionation reaction (f) between the parent diamine and quinonediimine results in the formation of cation radicals (VI) [36]. Diamines and quinonemonoamines undergo coupling reactions with parent phenylenediamines, reactions (g), (h) and (i), (j) yielding corresponding diphenylamines (VIII) and (X) [17,24–26,41]. Compounds (VII) and (IX) are intermediates, which are readily oxidized chemically by excess of the parent quinonediimine or quinonemonoimine. \(p\)-Phenylenediamine (I), or aminophenol (XI), is regenerated as a
result of a chemical oxidation step, reaction (h) or (j). An additional coupling stage (l) followed by chemical or electrochemical oxidation (m) leads to formation of Bandrowski’s base (XIII) [25].

2. Experimental

Fig. 1 shows a schematic of the experimental setup. The electrochemical flow cell consists of two cylindrical Delrin blocks (1) and (2) separated by a 50 μm Teflon spacer (3). A 1.6 mm diameter Pt disk electrode (WE) was pressed into the lower block. The electrolyte flowed in a radial, inward direction. PEEK tubing, frits, crosses, unions, nuts, and ferrules were obtained from Upchurch Scientific (Oak Harbor, WA, USA). Electrolyte containing the test substance was supplied to the working electrode through the annulus formed by the walls of the outer tube (5) (PEEK OD 3.2 mm, ID 1.6 mm) and the inner tube (4) (PEEK OD 1.57 mm). A central aperture in the Teflon spacer (3) allowed passage of the electrolyte towards the center of the disk electrode where it was collected into the axial inner tube (4). The volume of the compartment of the working electrode, which is the volume of electrolyte located between the working electrode and the walls of the central tube (4), was only 0.1 μL. The working disk electrode and the inner tube (4) were coaxial. The channel in the central tube (4) formed a reactor in which subsequent chemical
Finally, dilution of aqueous effluent by a volatile solvent significantly increased the sensitivity of ESI-MS measurements, we have diluted the aqueous effluent of the chemical reactor with an auxiliary stream of methanol acidified by 1% trichloroacetic acid. The addition of acid buffered the ESI stream, so that the hydrolysis of the test substances, which occurred in the ESI, was independent of the cell effluent pH. It enabled us to compare quantitatively the results of electrochemical DPD oxidation obtained in aqueous electrolytes of a wide pH range.

The results of the EC/MS measurements performed with aqueous electrolyte at pH 5 are shown in Figs. 2 and 3. According to previous reports [21,22], using the stopped-flow method, the hydrolysis rate of the quinonediimine, which is a primary product of DPD oxidation, is minimal at this pH. In order to decrease the influence of the auxiliary solvent on chemical transformations of the substances studied in ESI-MS, in this experiment we diluted the effluent only with distilled water.
water. Diagrams “A”, “B”, and “C” in Fig. 2 show mass spectra recorded at different potential values: $E = 0.0 \text{ V}$ – Diagram “A”, $E = 0.25 \text{ V}$ – Diagram “B”; $E = 0.7 \text{ V}$ – Diagram “C”; Diagram “D” – portion of mass spectrum of the flow cell effluent at $E = 0.7 \text{ V}$, Diagrams “E” and “F” – portions of mass spectrum of the flow cell effluent at $E = 0.35 \text{ V}$. Spectra were normalized by the height of the $m/z$ 137 peak at $E = 0.0 \text{ V}$. This presentation gives the relative abundance of the respective ions in the effluent normalized to the concentration of DPD in the feed. Conditions were as follows: Electrolyte flow rate 2 $\mu$L min$^{-1}$, reactor volume 0.5 $\mu$L, DPD concentration 5 mM, pH 5, 0.1 M NH$_4$(CH$_3$COO). The auxiliary liquid, distilled H$_2$O, was supplied at a rate of 90 $\mu$L min$^{-1}$, 1 kV spray voltage was used.
oxidation are subject to fast hydrolysis which results in the formation of compounds undetectable by ESI-MS, calibration of products was virtually impossible. Therefore, the normalized peak heights never sum up to 1. Diagrams ‘B’–‘J’ in Fig. 3 show the potential dependence of the nine most pronounced MS peaks observed in the effluent of the flow cell at pH 5. The curves shown in Diagrams ‘A’–‘J’ were recorded at a scan rate of 1 mV s\(^{-1}\). The diagrams reflect stationary processes since the peak height–potential curves were independent of scan rate in the range 0.25–7 mV s\(^{-1}\).

It is important to mention that in our experiments, products were detected after passing through the reactor, where purely chemical processes occurred. Multistage chemical coupling reactions are relatively slow and for this reason occurred mostly in the reactor. If we neglect chemical reactions in the flow cell, 2 electrons could be removed from each DPD molecule entering the cell. This would result in a complete transformation of DPD into quinonediimine, compound (II). Thus full oxidation of DPD to quinonediimine will completely block subsequent coupling reactions in the reactor since unoxidized DPD is required for coupling, reactions (g)–(n). The maximal yield of the slow coupling reactions can be reached only when the average number of electrons removed from each molecule of DPD entering the flow cell is smaller than 2. For example, to achieve stoichiometry, coupling reactions (j) and (h) require removal of only 4 electrons from 3 molecules of DPD, making the average number of electrons removed from...
the DPD molecule only 1.33. Formation of trimer (XIII) by reaction sequence (a)–(g)–(h)–(l)–(m) requires the removal of 6 electrons from 5 DPD molecules, making the overall number of electrons removed from each DPD molecule only 1.2. To achieve optimal stoichiometry for formation of dimers (VIII), (X) and trimer (XIII), the degree of conversion of DPD into quinone-diimine is therefore 1.33/2 = 0.67 and 1.2/2 = 0.6, respectively. Therefore, the potential dependence of the yield of the particular products of the coupling reactions reflects primarily the change of the ratio of concentrations of quinone-diimine (quinonemonoimine) to DPD with potential. This assumption is substantiated by the simultaneous start of evolution of most of the products at the same potential $E = 0.15$–0.2 V at which DPD oxidation is triggered.

Holding the electrode at potentials below the potentials of the current plateau, leads to the low value of DPD conversion which is required for coupling reactions. Indeed, in Fig. 3 maximal values of the peak heights m/z 269, m/z 270, and m/z 403 were reached at potential readings only slightly above $E_{1/2}$ of the voltammetry curve shown in Diagram “A”. Conversion of DPD into quinone-diimine can be decreased also by the increase of the electrolyte flow rate when the electrode potential is kept within the region corresponding to the current plateau.

According to [9], DPD oxidation on Pt electrode is diffusion controlled. The degree of DPD conversion to quinone-diimine in the radial flow cell at potentials of a radial channel electrochemical cell used in the current study assuming laminar liquid flow [10]. Derivation of Eq. (1) does not take into account any possible coupling reactions which could occur within the flow cell. Calculations by Eq. (1), using the 5 pairs of coefficients shown in Table 1, $D = 1 \times 10^{-3}$ cm$^2$ s$^{-1}$, and $H = 50$ μm, show that at flow rates of 1; 2; 5; and 7 μL min$^{-1}$ conversion reaches 99%; 94%; 71% and 60%, respectively. Formation of dimers and trimer at the optimal stoichiometric ratio between DPD and quinone-diimine (quinonemonoimine) requires DPD conversion values of 1.33/2 = 0.67 and 1.2/2 = 0.6 for dimers and trimer, respectively. On both sides of the optimal DPD conversion value, the yield of the respective coupling products will be smaller than at the optimal conversion value. At low flow rates the potential scan gradually changes the degree of conversion of DPD from 0 to the optimal values for formation of dimers and trimer and then to nearly 1. At flow rates above 7 μL min$^{-1}$, which corresponds to 60% conversion of DPD, we did not observe maxima at curves of potential dependence of the abundance of the dimers m/z 269; m/z 270, and the trimer m/z 403. The respective MS peak heights reached the plateau at potentials close to the potentials of peak maxima observed at lower flow rates. Therefore, in the following experiments we used flow rates below 7 μL min$^{-1}$, which posed a lower limit for residence time in the reactor of 4.3 s.

Measurements presented in Figs. 2 and 3 were performed at an electrolyte flow rate of 2 μL min$^{-1}$. The current value at the plateau region corresponds to ca. 95% conversion of DPD in agreement with the calculations. The reactor volume was 0.5 μL. The potential dependence of the m/z 137 peak, corresponding to DPD, is shown in Diagram “B” in Fig. 3. It is found to be in agreement with the voltammetry curve. In the potential range 0.5–0.7 V, when the current reaches the plateau, the level of the m/z 137 peak falls to approx. 5% of the peak abundance observed at $E = 0.0$ V. Diagram “C” in Fig. 3 shows the potential dependence of the m/z 135 peak. This peak is ascribed to quinonedimine (II), the primary product of DPD oxidation. The potential behavior of this peak corresponds only roughly to the voltammetry curve shown in Diagram “A”. Peak m/z 135 reaches maximal values at $E = 0.7$ V while DPD is virtually exhausted at $E = 0.4$ V. Chemical reactions which consume quinonedimine and unreacted DPD are apparently responsible for the complex potential dependence of this peak. MS peak m/z 136, Diagram “D”, reaches maximal values at potentials when the current plateau is not yet reached, and then decreases, although at $E = 0.7$ V it holds about 50% of its maximal height. Two compounds, Wurster’s cation radical (VI), and quinonemonoimine (IV), are expected to contribute to the m/z 136 peak. The potential dependence of this MS peak helps ascribe it chiefly to Wurster’s cation radical.

<table>
<thead>
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<th>No.</th>
<th>$C^2_i$</th>
<th>λ</th>
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<td>2.43037</td>
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<td>2</td>
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<tr>
<td>5</td>
<td>0.004535869</td>
<td>215.3643</td>
</tr>
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</table>
(VI), which is formed by disproportionation reaction (f). Formation of quinonemonoimine (IV), by quinonediimine hydrolysis, is likely to follow the potential dependence of the quinonediimine MS peak, m/z 135. Therefore, the contribution of quinonemonoimine to the m/z 136 peak is probably smaller than that of Wurster's cation radical, at least at potentials corresponding to maximal peak height.

Diagram “E” shows the complex potential behavior of peak m/z 254. It is probably a superposition of two curves, which describes the potential dependence of formation of two isomers or the same compound but formed by two different reaction routes. In our measurements performed at pH below 3.6, the potential dependence of peak m/z 254 was similar to curves shown in Diagrams “F”, “G”, and “I”. Coupling between quinonemonoimine and DPD by reaction (n) in Scheme 2 is a probable route of formation of compound (XIV) with m/z 254. The route was proposed in [45] as a mechanism of condensation of hydroxy-1,4-benzoquinones with primary amines. The upsurge of peak m/z 254, which occurs at potentials above 0.6 V in Diagram “E”, is probably caused by electrochemical oxidation of one of the dimers.

Formation of oxidized forms of diphenylamines (VII) and (IX), compounds (VIII) m/z 269 and (X) m/z 270, respectively, occurs apparently by coupling reactions of DPD with quinonediimine and quinonemonoimine reactions (e), (f) and (g), (h) [24–26,40,41]. Oxidation of DPD triggers the release of the appropriate ions, however at higher potentials, when DPD is exhausted in the reactor, since aminophenol can be formed only by chemical reduction of quinonemonoimine.

Potential traces of MS peaks corresponding to DPD and major products of DPD electrochemical oxidation at pH 1.4 are shown in Fig. 4. Diagrams “B”–“F”. The corresponding voltammetry curve is shown in Diagram “A” of the same Figure. Diagram “G” shows the full mass spectrum of the effluent of the cell at E = 0.5 V. All traces were normalized by the height of the DPD peak m/z 137 measured at E = 0.3 V when no oxidation of DPD occurs. The spectrum of the effluent at E = 0.3 V is not shown since it is virtually identical to the spectrum shown in Fig. 2, Diagram “A”.

As follows from voltammetry curves shown in Diagrams “A” in Figs. 2 and 3, the half wave potential of DPD oxidation is shifted to positive values with decrease of pH. The mass spectrum of the oxidized products at pH 1.4 is less complex compared to spectra recorded at higher pH. It contains peaks of monomeric compounds m/z 136, m/z 137, m/z 138, and dimeric compounds m/z 254, and m/z 270. Evolution of peak m/z 138 indicates the formation of aminophenol (XI) in the course of DPD oxidation. This peak was not observed in measurements performed at pH above 2.5. Formation of aminophenol (XI) indicates the occurrence of the redox processes in the reactor, since aminophenol can be formed only by chemical reduction of quinonemonoimine.

Fig. 5 shows the dependence of the normalized maximal MS peak heights corresponding to peaks m/z 138, m/z 269 and m/z 270 on the substance residence time in the reactor. 4 mM DPD solution at pH 1.4 was pumped through the cell. Measurements were performed by imposition of a potential ramp (1 mV s⁻¹) from 0.25 to 0.7 V and back. Data shown in Fig. 4, as well as data recorded with reactors of different volumes and different electrolyte flow rates, were used for construction of Fig. 5. When the potential is scanned, the degree of conversion of DPD in the flow cell changes gradually from zero, at the starting potential, to maximal values, approaching 100%, and back, following the voltammetry curve. MS peak readings were taken at the maximum of the particular peak potential dependence. Peak readings were normalized by the height of the DPD peak, m/z 137, measured at potentials at which no DPD oxidation occurred, E = 0.3 V at pH 1.4. This was done assuming that a maximal peak height of the coupling reaction product is attained at potentials when the optimal degree of DPD conversion for the formation of the particular compound was reached.

According to Fig. 5, the height of peak m/z 269 falls sharply with the increase of the substance residence time. At pH 1.4, hydrolysis of quinonediimine by reaction (d) in Scheme 1, decreases its concentration by a factor of approx. 0.5 in 1.6 s (first order rate constant
This implies that in the few seconds after formation, quinonediimine (II) will be eliminated by hydrolysis and for this reason all coupling reactions involving quinonediimine will be quenched. Therefore the level of dimeric compound (VIII) in the effluent will be constant within the time scale of our experiments, regardless of the rate of the coupling reaction (g). In fact, the level of peak \( m/z \) 269 falls with the increase of the residence time. This entails the occurrence of the reaction consuming (VIII), which is most probably hydrolysis. Fast elimination of quinonediimine (II) by hydrolysis in acidic media [21,22,29,30,38,39] suggests that quinonemonoimine accounts for the coupling reactions which occur in the time domain of our experiments (residence time above 4.3 s).

According to Fig. 5, the levels of peaks \( m/z \) 270 and \( m/z \) 138 grow steadily with increase of residence time reaching a plateau at about \( t = 200 \) s. The slow increase of the level of peak \( m/z \) 270 is apparently related to slow formation of the compound (X) by coupling of quinonemonoimine (IV) with DPD, reaction sequence (a), (d), (i), (j). Evolution of aminophenol (XI), \( m/z \) 138,
supports this reaction route. MS peak m/z 138 changes in parallel with the evolution of m/z peak 270. According to Scheme 2, aminophenol (XI) is produced in chemical redox reaction (j), in which quinonemonomine is reduced by dimer (IX). The production rate of aminophenol should be equal to the production rate of dimer (X).

Formation of dimer (X) is most probably controlled by the rate of the coupling reaction (i). Since the concentration of both components is proportional to the starting DPD concentration, the rate of this reaction should be proportional to the squared initial concentration of DPD in the electrolyte. Fig. 6 shows the dependence of the normalized level of peak height m/z 270 on the initial DPD concentration in the electrolyte at pH 1.4. Measurements were staged using the same procedure which was used to construct Fig. 5. The concentration of DPD in the starting electrolyte was varied between 0.22 and 5 mM. Since any particular point in Fig. 5 is normalized by the initial level of the DPD peak, m/z 137, in the particular run (level of DPD at potential when no oxidation occurs). Broken lines are introduced to guide the eye.

Fig. 5. Dependence of the selected MS peaks on the substance residence time in the reactor. Electrolyte was 0.1 M CCl₃COOH, pH 1.4. DPD concentration was 4 mM. Residence time was varied using reactors of different volumes (0.5, 2.8 and 8 L) and by change of electrolyte flow rate within the 1–7 µL min⁻¹ range. Effluent was diluted by a 90 µL min⁻¹ flow of 1% CCl₃COOH in MeOH. Each point represents a curve of the potential dependence of the selected MS peak at a given reactor-flow rate configuration. The maximal reading of the particular peak height observed on the curve is normalized by the maximal height of the DPD peak, m/z 137, in the particular run (level of DPD at potential when no oxidation occurs). Broken lines are introduced to guide the eye.

Fig. 6. Dependence of the normalized level of peak height m/z 270 on DPD concentration at pH 1.4. Measurements were staged using a reactor of 2 µL volume, flow rate 2 µL min⁻¹. Peak height determination and normalization were done similarly to the procedure used to construct Fig. 4.

respectively. Fig. 7 was constructed similarly to Fig. 5. MS peak heights were measured in the potential scan experiments. Maximal particular MS peak readings were normalized to unoxidized DPD peak readings, m/z 137, observed in the run. At this pH, the m/z 269 normalized peak height decreases slightly with substance residence time in the reactor within the whole residence time do-
main. On the other hand, peaks m/z 270 and m/z 403 grow with residence time. Very similar behavior of MS peaks m/z 403 and m/z 269 was observed in measurements performed at pH 7, which are not shown. In electrolyte of pH 7 peak m/z 403 grew almost linearly with the residence time within the time domain 6–240 s, while peak m/z 269 decreased slightly with increase of the residence time. MS peak m/z 270 corresponding to dimer (X) was weak since the formation of quinonemonoimine by hydrolysis of quinonediimine is very slow at neutral pH [22]. Slow growth of peak m/z 403 contradicts the results of [25] obtained with unsubstituted phenylenediamine by \(\text{vis}-\)spectra measurements. According to [25], formation of Bandrowski’s base is controlled by the coupling reaction of quinonediimine and phenylenediamine, reaction (g). The follow up reactions (h), (l) and (m) were considered fast. However, in our experiments with dimethyl-substituted phenylenediamine formation of the dimer (VIII), m/z 269, was virtually accomplished within 6 s, while the peak of trimer (XIII) m/z 403, which corresponds to Bandrowski’s base, grew within 7 min of residence time. This implies that coupling reaction (l) is the limiting step in the current case. According to [25], forming of Bandrowski’s base is controlled by the coupling reaction of quinonediimine and phenylenediamine, reaction (g). The follow up reactions (h), (l) and (m) were considered fast. However, in our experiments with dimethyl-substituted phenylenediamine formation of the dimer (VIII), m/z 269, was virtually accomplished within 6 s, while the peak of trimer (XIII) m/z 403, which corresponds to Bandrowski’s base, grew within 7 min of residence time. This implies that coupling reaction (l) is the limiting step in the current case.

Fig. 8 summarizes the results of EC/MS measurements performed over a wide pH range. The graphs presented here were constructed using data shown in Figs. 5, 7 and data of a series of similar curves of MS peaks dependence on residence time measured in the electrolytes of different pH, which are not shown. The initial concentration of DPD in the electrolyte in all cases was 4 mM. Peak height values were taken for substance residence time \(t = 2.8\) min, which corresponds roughly to the saturation of the m/z 270 peak height. This residence time is much higher than the time required for saturation of peak m/z 269. Particular product peak heights were normalized using the maximal DPD peak, m/z 137, height in each experiment. According to Fig. 8, yields of the compounds (VIII), m/z 269, and (XIII), m/z 403, grow with the increase of pH. The yield of the compound (X), m/z 270, reaches a maximum at approximately pH 2.7 and then declines steadily. This finding is consistent with the pH dependence of quinonediimine hydrolysis reaction (d) rate [22], which produces quinonemonoimine. Formation of quinonemonoimine by hydrolysis of quinonediimine switches the coupling reaction path from reactions (g), (h), which dominate in neutral pH, to (i), (j), which are more prominent in acidic electrolytes. Comparison of results obtained in acidic electrolytes shows that coupling reactions (g), (h), (i), (j), (l), (m) at pH 1.4 do not account completely for the consumption of
quinonedimine and quinonemoiine. Namely, results, presented in Fig. 8, show that the saturation level of compound (X), \( m/z \) 270, at pH 1.4 is more than five times smaller than its level attained at pH 3.6. Formation of compounds (VIII), \( m/z \) 269, and (XIII), \( m/z \) 403, is negligible at pH 1.4, since a change of pH from 1.4 to 9.7 results in more than an order of magnitude growth of levels of both. Therefore at pH 1.4 the concentration level of all products of coupling reactions is at least five times smaller than at pH 3.6. This means that hydrolysis reactions at pH 1.4 are responsible for the loss of at least 80% of compounds detectable by ESI-MS.

We have evaluated the coupling rate constant of DPD and quinonemoiine at pH 3.6 assuming that no side reactions occur at this pH and the rate limiting reaction for formation of compound (X) is reaction (i). We used kinetic data for the compound (X), \( m/z \) 270, evolution shown in Fig. 7. We assumed that the composition of the flow cell effluent at potentials of maximal yield of compound (X) was stoichiometric, namely 2 molecules of quinonedimine per one molecule of DPD; and that all chemical transformations, namely hydrolysis of quinonedimine (d), coupling reaction (i), and chemical oxidation reaction (j) occurred in the reactor. The reaction sequence used to fit \( m/z \) 270 evolution curve was:

\[
(II) \xrightarrow{k_h} (IV), \tag{2}
\]

\[
(IV) + (I) \xrightarrow{k} (IX) \tag{3}
\]

\[
(IX) + (IV) \rightarrow (X) \text{ fast} \tag{4}
\]

The following equations were solved numerically in order to fit experimental points of the dependence of level of MS peak \( m/z \) 270 on the substance residence time, shown in Fig. 7:

\[
d[II]/dt = -k_h[II], \tag{5}
\]

\[
d[IV]/dt = k_s[II] - 2k[IV][I], \tag{6}
\]

\[
d[X]/dt = k[I][IV]. \tag{7}
\]

Here Roman numerals in brackets represent compounds or their concentrations using the convention of Schemes 1 and 2. The hydrolysis rate constant from [21] \( k_h = 0.02 \) s\(^{-1}\) at pH 3.6 was used. The solid line drawn in Fig. 6 shows results of the fit using \( k = 10 \text{ mol}^{-1} \text{ L s}^{-1} \). The theoretical curve was related to axis “Peak Ratio 270/137” using a normalization factor.

4. Conclusions

EC/MS was used to study the complex mechanism of electrochemical oxidation of \( N,N \)-dimethyl-\( p \)-phenylenediamine in aqueous electrolytes in the pH range 1.4–9.7. The multistage mechanism of DPD oxidation,
which includes both parallel and subsequent reactions, was probed by monitoring the evolution of a number of compounds in a single EC/MS experiment. At pH 3.6, at which the DPD oxidation mechanism is less complex, the kinetics of the coupling reaction between quinonomonoimine and DPD were monitored qualitatively and fit numerically by a reaction sequence involving 2 slow stages: (1) hydrolysis of quinonediimine to give quinonomonoimine; (2) second order coupling reaction between quinonomonoimine and DPD. The rate constant of the coupling reaction between DPD and quinonomonoimine was found to be \( k = 10 \text{ mol}^{-1} \text{ L s}^{-1} \).

In order to study the kinetics of relatively slow subsequent chemical reactions, the EC/MS setup proposed in [10], was improved by incorporation of a chemical reactor of a tunable volume between the electrochemical cell and MS. The completeness of subsequent chemical reactions, which was monitored by MS, was varied by change of the substance residence time in the reactor.

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