

# Electrochemistry as a Tool for Studies of Complex Reaction Mechanisms: The Case of the Atmospheric Aqueous-Phase Aging of Catechols

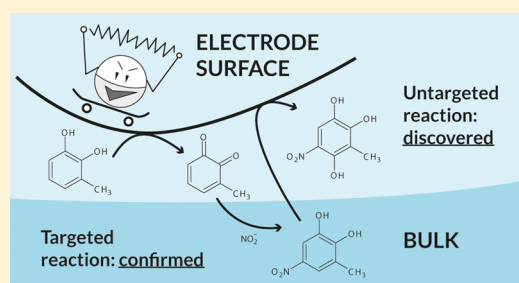
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## Supporting Information

**ABSTRACT:** The ultimate goal in the understanding of complex chemical processes is a complete description of the underlying reaction mechanism. In the present study and for this purpose, a novel experimental platform is introduced that builds upon electrochemistry capable of generating reactive intermediate species at the electrode surface. The atmospherically relevant nitration of catechols is taken as a case example. First, we confirm the recently proposed nitration mechanism, advancing the understanding of atmospheric brown carbon formation in the dark. We are able to selectively quantify aromatic isomers, which is beyond the limits of conventional electroanalysis. Second, we identify a new pathway of nitrocatechol hydroxylation, which proceeds simply by oxidation and the addition of water. This pathway can be environmentally significant in the dark aqueous-phase formation of secondary organic aerosols. Third, the developed methodology is capable of selectively detecting a wide range of nitroaromatics; a possible application in environmental monitoring is proposed.



## INTRODUCTION

Aqueous-phase secondary organic aerosol (aqSOA) formation, in which nonradical oxidations rather than radical reactions are presumably paramount, has been attracting increasingly more attention.<sup>1–3</sup> One of the generally established strategies to obtain greater insight into a complex reaction mechanism is to start the reaction from the anticipated intermediate stage and follow the formed reaction product(s).<sup>4–7</sup> Electrochemically assisted electron transfers can be coupled with irreversible homogeneous chemical reactions, which is known as an electron-transfer chemical reaction mechanism (EC mechanism).<sup>8</sup> In this sense, electrochemistry provides versatile means to perform research and has been entering numerous related disciplines.<sup>9–15</sup> Such an approach can be of vital importance not only in the fundamental understanding of any chemical process in which redox transition is present but also in the optimization of (industrially) important redox reactions.

In the field of atmospheric chemistry, however, the employment of electrochemistry is underutilized. One good example in which electrochemistry could be effectively used is the nitration of the emerging atmospheric pollutant, 3-methylcatechol (3MC; 3-methyl-1,2-dihydroxybenzene). Specifically, dark methylnitrocatechol (MNC) formation has been observed in ambient air, being related to the atmospheric aqueous phase.<sup>16</sup> Very recently, a mechanism of 3MC nitration in the dark has also been proposed but has not been unequivocally confirmed.<sup>17</sup> An exact description of the underlying mechanism would thus significantly contribute to

the fundamental understanding of various poorly investigated atmospheric processes such as aqSOA and light-absorbing brown carbon (BrC) formation in the dark.<sup>18–20</sup> This would further allow appropriately predicting impacts of atmospheric pollution on the ecosystem and climate change.

In general, the nitration of aromatic compounds in mildly acidic aqueous solutions has been considerably less investigated than under more aggressive conditions (i.e., at extremely low pH). Although aromatic nitration is essential in natural and biological environments and nitration under mild reaction conditions is also advantageous in other applications, the underlying mechanisms have been only rarely studied.<sup>21–23</sup> We developed a novel experimental platform combining the advanced utilization of electrochemistry (as an analytical and preparative technique) and state-of-the-art analytical techniques and applied it to explore the underlying mechanism of dark 3MC nitration in the aqueous solution, representative of the atmospheric aqueous phase.

In this work, we first confirm the existence of 3-methyl-o-quinone (3MoQ) in the homogeneous reaction system by complementarily using high-pressure liquid chromatography with mass spectrometric detection (HPLC-MS/MS). The following electrochemical generation of 3MoQ and its

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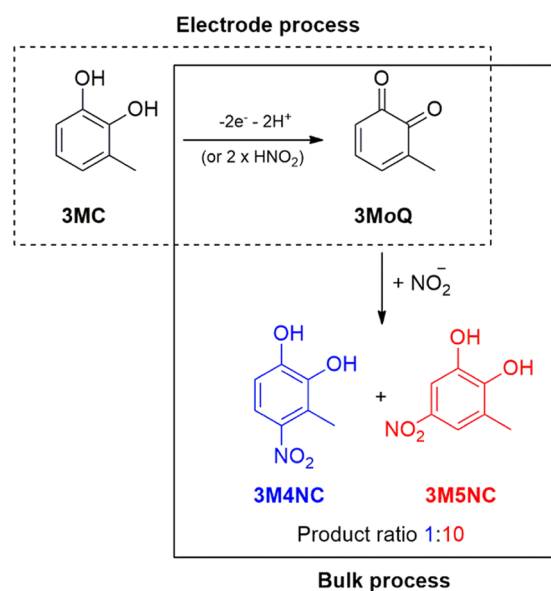
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homogeneous reaction with nitrite ions ( $\text{NO}_2^-$ ) in bulk allowed us to confirm the proposed reaction mechanism of dark 3MC nitration in the aqueous phase (Scheme 1).

**Scheme 1. Schematic Representation of the Main Dark Nitration Pathway of 3-Methylcatechol (3MC) in Aqueous Solutions of  $\text{HNO}_2/\text{NO}_2^-$  Adapted from Our Recent Paper<sup>17 a</sup>**



<sup>a</sup>In present work, oxidation by  $\text{HNO}_2$  is prevented and the conversion of 3MC to 3-methyl-*o*-quinone (3MoQ) is electrochemically assisted, whereas the coupled nitration to 3-methyl-5-nitrocatechol (3M5NC) and 3-methyl-4-nitrocatechol (3M4NC) occurs by  $\text{NO}_2^-$  in the bulk. The applied EC mechanism confirms the recently proposed nitration pathway.

Moreover, we were able to quantify in situ the formed regioselective nitrated products, 3-methyl-4-nitrocatechol (3M4NC) and 3-methyl-5-nitrocatechol (3M5NC), in real time. At the end of this study, we demonstrate that the unprecedented ability to electrochemically differentiate between aromatic isomers could be further exploited in routine environmental monitoring. Finally, we were also able to identify a not-yet-considered, nonradical mechanism of nitrocatechol hydroxylation in the dark, which could be very important in natural systems. With all this, we demonstrate the exceptional capability of electrochemistry to (i) assist in studying the already identified atmospheric and other aqueous-phase chemistry in more detail and (ii) seek novel, not-yet-discovered pathways of aqSOA formation and aging.

## METHODS

**Electrochemical Experiments.** A one-compartment glass electrochemical cell was used to perform the experiments. All experiments were performed in phosphate buffer pH 6.5, when necessary saturated with nitrogen using a gas purging system (i.e., cathodic experiments). Ag/AgCl was always used as a reference electrode and a platinum rod was a counter electrode. Unless stated otherwise, a glassy carbon (GC) disk electrode ( $A = 0.0314 \text{ cm}^2$ ) was used as the working electrode. Before every experiment, the electrode was polished with an alumina slurry of particle size  $0.05 \mu\text{m}$  (Buehler micropolish II). In the case of long-term potentiostatic electrolysis, a GC

rod electrode ( $A = 3.8 \text{ cm}^2$ ) was the working electrode. An Autolab station (model PGSTAT204) was used to control the experiments and analyze the data.

**HPLC-UV/VIS Analysis.** An ultimate 3000 UHPLC system (Thermo Fisher Scientific) equipped with a UV-vis diode-array detector was used for the determination of primary nitration products (3M4NC and 3M5NC) and validation of the developed electrochemical methodology. The separation of the positional isomers was achieved on an Atlantis T3 column ( $3.0 \times 150 \text{ mm}^2$ ,  $3 \mu\text{m}$  particle size; Waters) with an isocratic elution by acetonitrile/0.1% formic acid (30:70, V/V). For the detection of secondary reaction products (hydroxylated 3M5NC (hydroxy-3-methyl-5-nitrocatechol, 3M5NC-OH) and oxidative cleavage products of 3M4NC), a different chromatographic method was used. Separation was assured on a Hypersil GOLD aQ column ( $2.1 \times 150 \text{ mm}^2$ ,  $3 \mu\text{m}$  particle size; Thermo Scientific) with isocratic elution by methanol/50 mM ion-pair reagent for LC-MS dibutylammonium acetate-DBAA (10:90, V/V).

**LC-MS/MS Analysis.** The same UHPLC system was used for intermediate/product identification, this time coupled with a triple quadrupole/linear ion trap mass spectrometer (4000 QTRAP LC-MS/MS System; Applied Biosystems/MDS Sciex, Ontario, Canada). In the course of MS parameters optimization, a wide parameter space including ionspray voltage, declustering potential, and entrance potential was examined. Several collision energies were screened in the MS/MS experiments to confirm the identity of 3MoQ. All experiments were performed in a negative ionization mode.

Reagents and details on the employed analyses are given in Section 1 of the Supporting Information (SI).

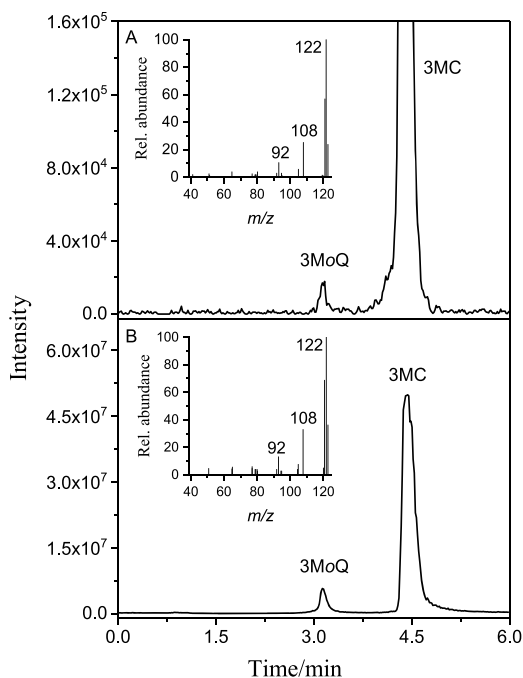
## RESULTS AND DISCUSSION

In our recent paper, we proposed a new pathway of catechol nitration in the atmospheric waters and demonstrated that it could contribute significantly to the burden of atmospheric BrC.<sup>17</sup> The results of the experimental modeling study suggested that, in the first step of 3MC nitration in the dark,  $\text{HNO}_2$  oxidizes 3MC to the corresponding 3MoQ. Further on, 3MoQ was believed to undergo a conjugated addition reaction with  $\text{NO}_2^-$ , forming two isomeric MNC. A schematic presentation of the proposed nighttime nitration pathway is shown in Scheme 1. It was, however, not confirmed in any other way than by the modeling that 3MoQ is involved in the MNC formation.

Although the existence of a quinone species has already been confirmed in similar reaction systems,<sup>24–27</sup> this does not suffice for the unambiguous confirmation of its direct involvement in the catechol nitration. Quinones could be formed as side products in the reaction mixture. Therefore, an original experimental approach is applied to unequivocally resolve the role of quinone intermediate in the naturally relevant nitration of catechol. In general, we first confirm the existence of 3MoQ in the reaction mixture and then seek additional evidence for its involvement in the nitration of 3MC.

**3-Methyl-*o*-quinone in the Reaction Mixture.** Because of the adjacent carbonyl oxygens, the formed *o*-quinone is unstable, and it is very difficult to isolate it in a pure form.<sup>28,29</sup> As the reference compound is not commercially available, we synthesized 3MoQ according to Albarran et al.<sup>30</sup> using 3MC and hexachloroiridate(IV) (henceforth referred to as syn-3MoQ). HPLC-UV/VIS analysis of the standard solution and the reaction mixture showed that the two chromatographic

peaks are identical (Figure S1), and the subsequent LC-MS/MS analysis further confirmed the identity of 3MoQ in the reaction mixture (Figure 1). For details on resolving this complex identification, the reader is referred to SI Section 2.

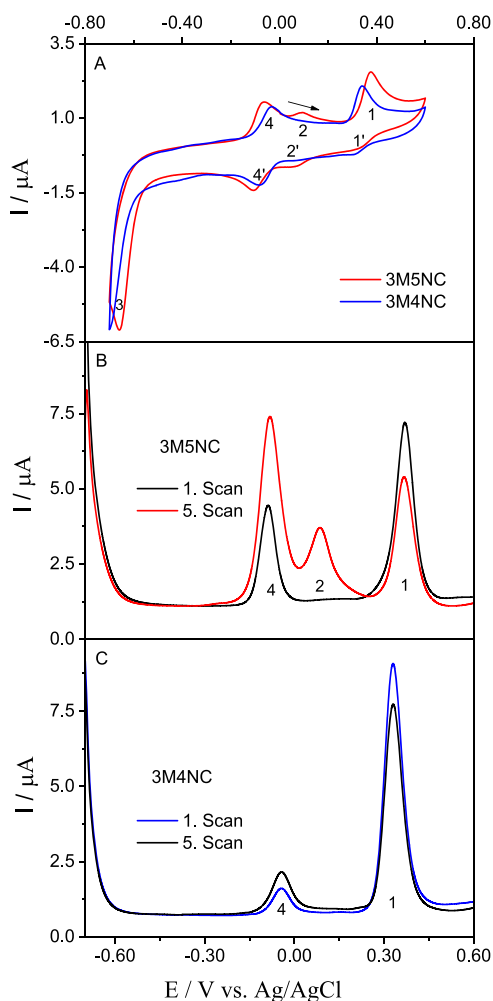


**Figure 1.**  $m/z$  123 extracted ion chromatograms (XIC) of (A) the synthesis mixture and (B) the reaction mixture; in the intercepts are the  $m/z$  123 fragmentation patterns of the chromatographic peaks at 3.1 min corresponding to (A) syn-3MoQ and (B) 3MoQ.

An effort was further made to quantify the unstable intermediate species in the reaction mixture (0.1 mM 3MC, 0.2 mM  $\text{NaNO}_2$ , pH = 3.1; see SI Section 2 for details). The determined concentrations at different reaction times were compared to the modeled concentrations in our previous study (the same reaction conditions at pH = 3.1) and are in good correlation ( $r = 0.87$ ,  $p = 0.01$ ); a slight overestimation of the modeled concentrations can be noted; however, the concentration range is the same (Figure S4).

**Electrochemical Platform Development.** Once the existence of a quinone species in the experimental mixture had been confirmed, the idea was to skip the initial reaction steps by forming 3MoQ electrochemically (heterogeneous reaction at the electrode surface) and to determine whether it reacts homogeneously (i.e., in the water bulk) with  $\text{NO}_2^-$  to the same nitrated products as in the solely homogeneous aqueous-phase reaction in the presence of  $\text{HNO}_2/\text{NO}_2^-$ . To detect the products (3M5NC and 3M4NC), a novel electroanalytical method was developed for the selective determination of positional isomers. For details, see also SI Sections 3–8.

Cyclic voltammograms of 3M5NC and 3M4NC standards are shown in Figure 2A (the fifth voltammetric scan, GC disk electrode) and are in agreement with the existing literature on substituted catecholic compounds.<sup>31–36</sup> The corresponding square wave (SW) voltammograms in Figure 2B,C are in line with the gathered cyclic voltammograms. The main difference between the two analogues is that in the case of 3M5NC, repetitive voltammograms show alteration in the number of



**Figure 2.** (A) Cyclic voltammograms of both standard compounds (the fifth voltammetric scans are shown; scan range and scan rate were  $-0.7$ – $0.6$  V and  $120 \text{ mV s}^{-1}$ ), and the first and fifth scans of the SW voltammograms of (B) 0.1 mM 3M5NC and (C) 0.1 mM 3M4NC standard in 0.1 M phosphate buffer (pH 6.5) scanned from  $-0.7$  to  $0.6$  V.

peaks with the scan number, which is not so in the case of 3M4NC. Specifically, 3M5NC gives a new peak at the potential of around 0.1 V in consecutive scans (peak 2 in Figure 2B), while the appearance of this peak is concomitant with the decrease of peak 1.

According to the experimental results and the literature,<sup>31–33,35</sup> a specific electrode reaction can be ascribed to each peak in the voltammogram, which is summarized in Table 1. A short description of each peak is given below. See SI Section 4 for further details.

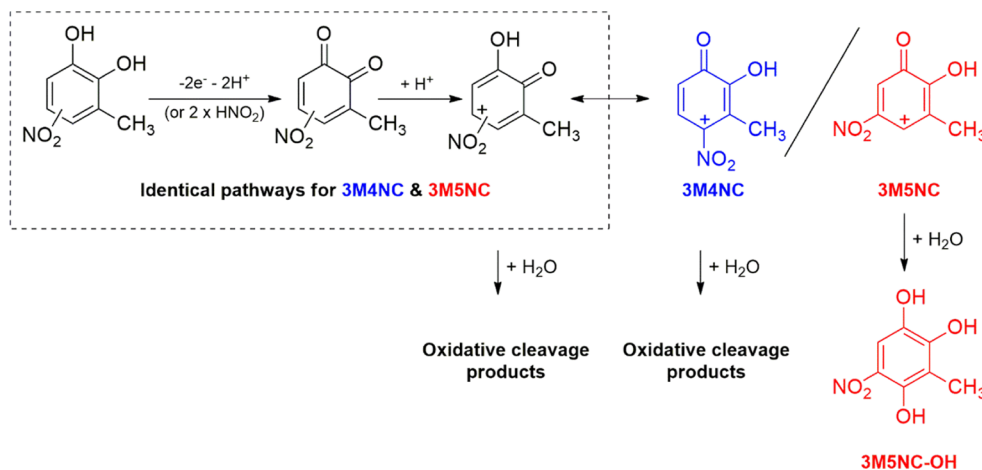
**Electrochemical Behavior of 3M5NC. Redox Couple 1/1'.** Initial oxidation of 3M5NC at the potential of around 0.4 V (peak 1 in Figure 2) leads to the formation of 3-methyl-5-nitro-*o*-quinone (3M5NoQ) in a two electron-transfer step. In the cathodic part, however, only a small reduction peak is observed (1'), corresponding to the reversible reduction of remaining 3M5NoQ that has not reacted with water (see further discussion).

**Redox Couple 2/2'.** The nucleophilic attack of water on 3M5NoQ leads to the formation of 3-methyl-5-nitrobenzene-1,2,4-triol (hydroxylated 3M5NC or 3M5NC-OH), whose redox feature is observed as a 2/2' pair in Figure 2A. At the

**Table 1.** List of Identified Electrode Reactions; 3-Methylcatechol (3MC), 3-Methylnitrocatechol (3MNC), 3-Methyl-5-nitrocatechol (3M5NC), 3-Methylaminocatechol (3MAC), the Corresponding Oxidized *o*-Quinone (*o*Q) Analogues, and Hydroxylated 3-Methyl-5-nitrocatechol (3M5NC-OH)

| peak no. | peak potential (V) | electrode reaction                                    | selectivity |
|----------|--------------------|---|-------------|
| 0        | 0.24               | $3MC \rightleftharpoons 3MoQ + 2H^+ + 2e^-$           | ✓           |
| 1/1'     | 0.38               | $3MNC \rightleftharpoons 3MNoQ + 2H^+ + 2e^-$         | ×           |
| 2/2'     | 0.08               | $3M5NC-OH \rightleftharpoons 3M5NoQ-OH + 2H^+ + 2e^-$ | ✓           |
| 3        | -0.64              | $3MNC + 6H^+ + 6e^- \rightarrow 3MAC$                 | #           |
| 4/4'     | -0.09              | $3MAC \rightleftharpoons 3MAoQ + 2H^+ + 2e^-$         | ×           |

**Scheme 2.** Observed EC Mechanisms for 3-Methyl-4-nitrocatechol (3M4NC; Blue) and 3-Methyl-5-nitrocatechol (3M5NC; Red)



potential of around 0.1 V (peak 2), 3M5NC-OH gets oxidized to the hydroxylated *o*-quinone analogue (3M5NoQ-OH), in a two electron-transfer step.

**Redox Process 3.** The reduction of nitroaromatic compounds is well known to produce anilines.<sup>37</sup> This is observed at the potential of around -0.7 V in our case (peak 3 in Figure 2A), corresponding to the reduction of the nitro group ( $-NO_2$ ) and the formation of 3-methyl-5-aminocatechol (3M5AC).

**Redox Couple 4/4'.** Once 3M5AC has been formed and the potential is scanned back in the anodic direction, peak 4 appears at the potential of around -0.1 V (Figure 2). This corresponds to the oxidation of 3M5AC to its quinone analogue (3-methyl-5-amino-*o*-quinone, 3M5AoQ). Note that peak 4' corresponds to the reduction of 3M5AoQ and appears only from the second electrochemical scan on, after  $-NO_2$  has been reduced in the former cycle.

**Electrochemical Behavior of 3M4NC.** As it has already been mentioned, 3M4NC behaves similarly to 3M5NC, except for the redox feature 2/2'. Only shortly, in the anodic direction (from 0 to 0.6 V), 3M4NC first oxidizes to corresponding 3-methyl-4-nitro-*o*-quinone (3M4NoQ; peak 1 in Figure 2). Partial irreversibility of 1/1' is still present but cannot be attributed to the formation of a ring-retaining product this time. Same as for 3M5NC, peak 3 corresponds to the irreversible reduction of  $-NO_2$  forming 3-methyl-4-aminocatechol (3M4AC), which is further oxidized to corresponding 3-methyl-4-amino-*o*-quinone (3M4AoQ; peak 4).

The SW voltammogram of 3M5NC in Figure 2B suggests an unconventional, nonradical pathway of nitrocatechol hydroxylation that is also applicable to the atmospheric waters. In the first scan (black lines), only the peaks that correspond to the oxidation of standard compounds (peak 1) and their reduced

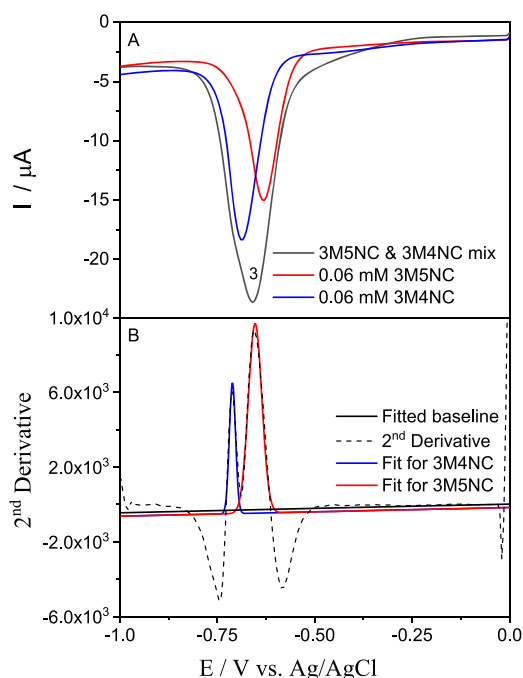
amino analogues (peak 4) are detected. In the consecutive scans (red lines), however, peak 2 appears in the case of 3M5NC (Figure 2B), which has been attributed to the oxidation of its hydroxylated form (3M5NC-OH). It is believed that after 3M5NC has been oxidized to 3-methyl-5-nitro-*o*-quinone (3M5NoQ), it further chemically reacts with water, forming 3M5NC-OH. In contrast to 3M5NoQ, 3-methyl-4-nitro-*o*-quinone (3M4NoQ) presumably undergoes an oxidative cleavage rather than forming the stable hydroxylated product, which explains the absence of the corresponding electrochemical peak in Figure 2C. Similar behavior has already been observed for 4-nitrocatechol.<sup>35</sup> The mechanisms of both reactions are shown in Scheme 2. In general, the difference in the electrochemical behavior of 3M4NC and 3M5NC can be ascribed to the altered position of the nitro group; see SI Section 4 for further discussion on this process.

Moreover, peak potentials of isomeric molecules are typically very similar, same as in the case of the nonselective redox pairs 1/1' and 4/4'.<sup>38</sup> Note that SW voltammetry was used for the determination of peak potentials gathered in Table 1, as cyclic voltammetry in Figure 2A is less sensitive and thus not reliable in the determination of peak potentials. Nonetheless, the electrochemical behavior of the two studied analogues is different and was exploited for their distinction.

**Optimization of the Electrochemical Procedure for Low-Concentration Quantification of 3M5NC in Real Time.** Electrochemical characterization implies that the two isomers can be selectively detected with the GC electrode if appropriate electrochemical conditions are applied. Specifically, redox feature 2/2' is characteristic of 3M5NC and does not appear in the case of 3M4NC, regardless of the number of scans. To optimize the method in terms of its performance and

the sensitivity, a 3MSNC-specific hydroxylated analogue was pregenerated at the GC disk electrode at the constant potential of 0.34 V (60 s accumulation time), followed by an SW voltammetry (see SI Section 5 for parameter optimization). In this case, the GC disk electrode simultaneously served as a preparative and analytical electrode. After some optimization, the 3MSNC-OH peak 2 was well separated from the other characteristic peaks (cf. Figure S17).

**Numerical Treatment of the Signal for 3M4NC Quantification.** Because of the minimal overlapping of the voltammograms of 3MSNC and 3M4NC, cathodic peak 3 (black line in Figure 3A; corresponding to the reduction to



**Figure 3.** (A) Individual SW voltammograms of 0.06 mM 3MSNC (red line), 0.06 mM 3M4NC (blue line), and their equimolar mixture (black line) scanned from 0 to  $-1$  V (peak 3) and (B) the second derivative of the electrochemical signal together with the fitted Gaussian distributions corresponding to the superpositioned analytes.

amino analogues) was recognized to have the best potential for the selective determination of 3M4NC and was further investigated. To quantify 3M4NC in a mixture of both isomers, numerical treatment has to be applied to deconvolve the single redox peak into two peaks (one for each isomer).<sup>39–41</sup> The deconvolution was performed by differentiation of the signal (for details, see SI Section 6), which has already turned out to be of great use in signal processing in conventional analytical chemistry.<sup>38,42,43</sup> The smoothed second derivative of the SW signal in Figure 3A is shown in Figure 3B, together with two Gaussian functions that were successfully fitted to the two maxima and allowed the quantification of both analytes on the basis of their intensities. All of this significantly improved the accuracy, precision, and detection limit of the method. Calibration curves and method validation (i.e., comparison with the reference offline HPLC-UV/VIS analysis) are in SI Sections 7 and 8.

**Confirmation of the Nitration Mechanism by Electrochemically Assisted Nitration of 3-Methylcatechol (EC Mechanism).** To study the nitration of 3MC with the electrochemical EC mechanism, it was important that the

oxidation by nitrous acid ( $\text{HNO}_2$ ) be prevented in the electrochemical cell. Namely,  $\text{HNO}_2$  could homogeneously oxidize 3MC to 3MoQ (or another reactive intermediate), additionally to the electrochemically produced quinone. To avoid this, two conditions must have been met: (i)  $\text{NO}_2^-$  was in great excess over  $\text{HNO}_2$ ; the pH of the reaction mixture should have been at least two units above the  $\text{p}K_a$  of  $\text{HNO}_2$  ( $\text{p}K_{a(\text{HNO}_2)} = 3.3$ )<sup>44</sup> and (ii) the two reactants ( $\text{NO}_2^-$  and 3MC) were mixed at sufficiently low concentrations that the kinetics of the homogeneous reaction was slow enough to not influence the electrode-assisted mechanism (EC mechanism). Optimal conditions were determined to be 0.1 mM 3MC and 1 mM sodium nitrite ( $\text{NaNO}_2$ ) in 0.1 M phosphate buffer (pH 6.5); for details, refer to SI Section 3. Under such conditions, only 5% of the initial 3MC was consumed in 7 h of the solely homogenous reaction (Figure S5).

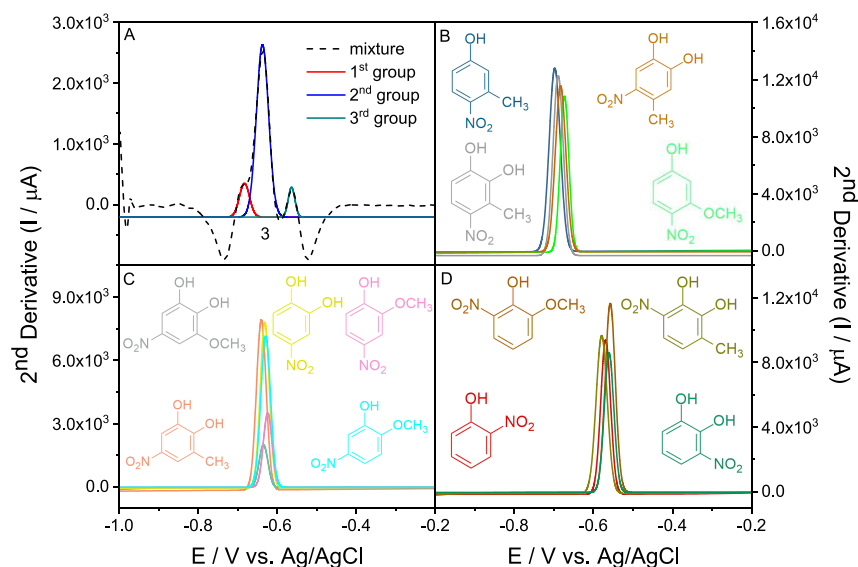
To meet the sufficient rate of the chemical reaction between the electrochemically generated 3MoQ and bulk  $\text{NO}_2^-$  and to allow for the timely detection of the products, a high concentration of 3MoQ was required. For this purpose, a GC rod electrode (more than 100 times larger electrode surface than that of the GC disk electrode) was utilized for the accumulation of 3MoQ in the solution (at the constant potential of 0.55 V; see SI Sections 1 and 3 for more information) and the GC disk electrode was again used for the electroanalytical quantification of the formed methylnitrocatechol products (MNC). Note, in this case, the GC rod electrode was a preparative electrode, and the GC disk electrode was an analytical electrode.

Once the reaction conditions had been optimized and the quantification of both 3MSNC and 3M4NC had been made possible in a solution, the electrochemically assisted nitration of 3MC was carried out. Anodic and cathodic SW voltammograms of 3MC (black line) and the reaction mixture containing 3MC,  $\text{NO}_2^-$ , and the formed products measured at different times of electrolysis (colored lines) are shown in Figure S8. 3MC produces one anodic peak (0) at the potential around 0.2 V, which corresponds to the formation of 3MoQ (see Table 1).<sup>45,46</sup> After 10 min of electrolysis, new anodic peaks appear, which correspond to the oxidation of the formed MNC (cf. Figure 2 and Table 1; the reduction peaks not shown). With increasing the time of electrolysis, peak 0 is decreasing (due to the consumption of 3MoQ in a chemical reaction with  $\text{NO}_2^-$ ), whereas the other peaks should be simultaneously increasing (MNC production). However, as the products are being consumed in other irreversible bulk reactions (vide infra), the height of their signal results from the competition between their formation and degradation pathways.

As described before, the mathematical treatment was applied to determine the concentrations and the product ratio of both nitrated products of the EC mechanism. The obtained concentrations are in good agreement with the reference values measured by HPLC-UV/VIS (Figure S25). Furthermore, the derived mean product ratio of  $11 \pm 1$  (refer here to Table S1) agrees very well with the obtained product ratio in our recent study determined experimentally and with modeling ( $3\text{MSNC}/3\text{M4NC} = 10$ ).<sup>17</sup>

## ENVIRONMENTAL RELEVANCE

The atmosphere is one of the largest natural reactors and most challenging reaction environments to investigate. Its significant scientific complexity has recently been recognized by leading



**Figure 4.** Deconvolved voltammograms (peak 3) of (A) a mixture of 13 standard compounds,  $0.08 \mu\text{mol L}^{-1}$  each (2-nitrophenol, 3-methyl-4-nitrophenol, 3-methoxy-4-nitrophenol, 4-, 5-, and 6-nitroguaiacol, 3- and 4-nitrocatechol, 3-methyl-4-, 3-methyl-5-, and 3-methyl-6-nitrocatechol, 4-methyl-5-nitrocatechol, 3-methoxy-5-nitrocatechol) and (B–D) contributing components to each of the deconvolved peaks, grouped according to their matching redox properties.

scientists in the field, advocating the need to embrace interdisciplinary and collaborative research that will advance the understanding of the oxidation mechanisms of organic molecules and the related importance of multiphase chemistry in the atmosphere.<sup>47</sup>

In the first place, the present study introduces a novel experimental platform building upon electrochemistry for studying the mechanisms of complex condensed-phase reactions involving redox processes. Utilizing its versatile means in the sense of electrosynthesis and electroanalysis, electrochemistry can be efficiently used in line with complementary analytical techniques, providing a powerful platform with great potential for innovative research in the field of atmospheric chemistry and wider. In this work, we demonstrate how the advantage of heterogeneous electrode reactions in the generation of reactive intermediates can be of great help in the mechanistic investigation of complex reaction systems. Beyond the applications presented in this paper is applying particular oxidation/reduction potentials to the artificial aerosol or cloud water, mimicking different environmental oxidants/reducing agents and allowing for the separate investigation of their redox influences on distinct target species in a simplified reaction environment. In this way, electrochemistry assures controlled high-throughput screening and helps identify potentially relevant atmospheric processes, which are to be further explored.

**Confirmation of the New Mechanism of Aromatic Nitration in the Dark.** Using this multidisciplinary approach, we have completely resolved the proposed reaction mechanism of dark catechol nitration under mild aqueous-phase conditions, which has been shown relevant for the nighttime nitroaromatic formation in the atmosphere.<sup>17</sup> With the identification of the same intermediate, the same products, and the same product ratio, we provide convincing evidence for the involvement of a common reaction mechanism in the two experimental setups (dark 3MC nitration under acidic conditions and EC mechanism at neutral pH where 3MC nitration only in bulk is prevented). To the best of our

knowledge, direct experimental evidence of the intermediate role of *o*-quinone in catechol nitration under environmentally relevant conditions has never been provided before. Supporting the two-step reaction mechanism (i.e., oxidation by  $\text{HNO}_2$  and conjugated addition by  $\text{NO}_2^-$ ), one can expect that initial oxidation to quinone intermediate be also possible by other naturally present oxidative species that react pH-independently (e.g.,  $\text{H}_2\text{O}_2$ ). Considering this, the relevant pH range of this reaction pathway expands toward higher pH values and becomes relevant also to less acidic in-cloud conditions with presumably higher nitrite concentrations. Furthermore, the formed nitrated products absorb visible light and are potentially toxic to living organisms.<sup>17,48</sup> Therefore, the confirmed nonradical multiphase chemistry toward aqSOA and BrC formation in the dark can have direct and indirect implications to human health and climate forcing. We believe that after its inclusion in the atmospheric models, the predictive capabilities, especially in terms of toxicity and radiative balance, can be significantly improved.

**New Mechanism of Nitrocatechol Hydroxylation in the Atmospheric Aqueous Phase.** Moreover, the study presents a novel route of nitroaromatic hydroxylation in the dark that has never been considered in atmospheric chemistry before. However, the described hydroxylation by water molecule acting as a nucleophile is rather controversial. Typically, daytime and nighttime oxidants, such as  $\text{OH}^\bullet/\text{O}_2$ ,  $\text{NO}_3^\bullet/\text{O}_2$ , and  $\text{O}_3$ , are considered in the atmospheric hydroxylation of aromatic compounds.<sup>49</sup> Hydroxylation by water following the initial attack of sulfate radical to the aromatic ring has also been reported;<sup>50</sup> however, in our case, a completely nonradical mechanism is proposed. Therefore, we were motivated to also detect the electrochemically generated product, 3MSNC-OH, in the reaction mixture under the oxidative conditions of the atmosphere (i.e., aerated solution of  $\text{HNO}_2$ ).

The reaction system from Vidović et al.<sup>17</sup> was repeated, chromatographic conditions were optimized with the addition of an ion-pair reagent, and the same product compound was

detected in the homogeneous reaction mixture as in the electrochemically assisted nitration (see also Figures S26 and S27 and SI Section 9 for details). Again, in the case of 3M4NC, hydroxylation did not occur; we detected oxidative ring-cleavage products (presumably carboxylic acids) when subjecting the reaction mixture to the new chromatographic conditions.

To the best of our knowledge, hydroxylation by oxidation and the nucleophilic attack of water has neither been included in global atmospheric models nor been considered possible to date. This untargeted discovery can be of even-greater importance for the atmospheric chemistry community than the targeted nitration reaction, especially because of the prolonged light absorption of 3MSNC-OH far in the visible light range (Figure S26). The formed product could significantly contribute to the atmospheric light absorption by BrC influencing the radiative balance of the Earth.

**Real Sample Measurements—Proof of Concept.** The investigation also implies that the ability of electrochemistry to distinguish between aromatic isomers could be efficiently employed in the assessment of the burden of (nitro)aromatic pollutants in the atmosphere. The developed methodology allows for the determination of groups of emerging nitroaromatic pollutants in atmospheric samples. To demonstrate its possible application, the described electroanalytical technique was applied to a mixture of 13 nitroaromatic compounds known to be present in ambient aerosols.<sup>51–53</sup>

From the obtained SW voltammograms (Figures 4 and S28), which were systematically compared to the voltammograms of the individual standards, six groups of nitrated aromatic pollutants could be determined in a real sample: cumulative nitrocatechols and 5-nitrocatechols (in the anodic part; Figure S28), and cumulative nitrophenols and differently substituted nitrophenols (in the cathodic part of the voltammogram; Figure 4). For more details, see SI Section 10.

In contrast to the commonly applied LC-MS, which is known to often fail in the quantification of a group of compounds by use of a surrogate standard, the electrochemical signal can be fairly well quantified by the standard addition method with the use of a single surrogate molecule.<sup>54</sup> The represented analytical technique thus promises a better quantitative method for the determination of total nitroaromatics in real atmospheric samples (aerosol particles, fog and cloud water, or precipitation). The anticipated limit of detection is in the nanomolar range, which is sufficient and comparable to the LC-MS. It should be emphasized that until now estimates have been provided in this regard.<sup>55,56</sup> Nevertheless, we recognize that the fingerprint of the obtained signal needs to be further investigated for the possible chemical speciation of the underlying nitroaromatic components. However, this is out of the scope of this study and remains a challenge for the future.

Ultimately, because of its dual character in terms of preparation and detection, the experimental platform is ideal for the studies of atmospheric aqueous-phase processes and samples and also in many other related fields.

## ■ ASSOCIATED CONTENT

### 🔗 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b02456.

Reagents, electroanalytical and chromatographic measurements, quinone identification, EC mechanism, new product identification, and proxy of real sample measurements (PDF)

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### Author Contributions

K.V. performed electrochemical measurements, conducted the research, and helped writing the manuscript. A.K. conducted the research and wrote the manuscript. M.Š. performed product identification by LC-MS/MS. P.J. and I.G. contributed to scientific discussions.

### Notes

The authors declare no competing financial interest.

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