



Ozonation of anilines: Kinetics, stoichiometry, product identification and elucidation of pathways



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ABSTRACT

Anilines as archetypes for aromatic amines, which play an important role in the production of, e.g., dyestuffs, plastics, pesticides or pharmaceuticals were investigated in their reaction with ozone. Due to their high reactivity towards ozone (1.2×10^5 – $2.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) the investigated aniline bearing different substituents are readily degraded in ozonation. However, around 4 to 5 molecules of ozone are needed to yield a successful transformation of aniline, most likely due to a chain reaction that decomposes ozone without compound degradation. This is inferred from OH radical scavenging experiments, in which compound transformation per ozone consumed is increased. Mechanistic considerations based on product formation indicate that addition to the aromatic ring is the preferential reaction in the case of aniline, *p*-chloroaniline and *p*-nitroaniline (high amounts of *o*-hydroxyaniline, *p*-hydroxyaniline, chloride, nitrite and nitrate, respectively were found). For aniline an addition to the nitrogen happens but to a small extent, since nitroso- and nitrobenzene were observed as well. In the case of *N*-methylaniline and *N,N*-dimethylaniline, an electron transfer reaction from nitrogen to ozone was proven due to the formation of formaldehyde. In contrast, for *p*-methylaniline and *p*-methoxyaniline the formation of formaldehyde may result from an electron transfer reaction at the aromatic ring. Additional oxidation pathways for all of the anilines under study are reactions of hydroxyl radicals formed in the electron transfer of ozone with the anilines (OH radical yields = 34–59%). These reactions may form aminyl radicals which in the case of aniline can terminate in bimolecular reactions with other compounds such as the determined *o*-hydroxyaniline by yielding the detected 2-amino-5-anilino-benzochinon-anil.

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1. Introduction

Investigations of the ozonation of anilines in aqueous solution can help to elucidate the mechanisms involved in the oxidation of

many micropollutants by ozone. Compounds belonging to the class of anilines are often present as micropollutants in water since some of them are widely used as pesticides or pharmaceuticals. According to their manifold utilisations, anilines can reach the environment through several input paths, e.g., from municipal wastewater effluents (Huber et al., 2005; Gabet-Giraud et al., 2010). However, anilines are also found in groundwater and leachate water (Schmidt et al., 1998). Micropollutants in turn are of major concern in surface and ground water that are used as source for

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drinking water supply (Nöthe et al., 2007; Ternes et al., 2002). Even at low concentrations in surface water, they can be harmful to aquatic life (Huggett et al., 2002; Küster et al., 2010). Therefore, advanced wastewater treatment with ozone or powered activated carbon is frequently discussed as means to abate micropollutant emissions (Snyder et al., 2006; Schwarzenbach et al., 2006; Hollender et al., 2009; Benitez et al., 2011). Reaction rate constants of micropollutants with ozone are an important tool for a first assessment of their degradability in ozonation of waste- and drinking water (Lee and von Gunten, 2010). To assess the importance of OH radical ($\cdot\text{OH}$) reactions the determination of $\cdot\text{OH}$ yield is crucial (von Sonntag and von Gunten, 2012). In addition, the amount of ozone needed for full compound degradation is of fundamental importance (Nöthe et al., 2009). Furthermore, the knowledge of possible reaction pathways and quantitative formation of transformation products during ozonation, especially with regard to ecotoxicological concerns, will allow assessing the treatment (Shang and Yu, 2002; Schmidt and Brauch, 2008; Boxall et al., 2014).

The purpose of this study is to elucidate the rate constants of the following aromatic amines bearing different substituents: aniline, *p*-methylaniline, *p*-chloroaniline, *p*-nitroaniline, *p*-methoxyaniline, *p*-hydroxyaniline, *o*-hydroxyaniline, *p*-phenylenediamine, *p*-aminobenzoic acid, *N*-methylaniline and *N,N*-dimethylaniline in their reaction with ozone in aqueous solution. The investigated amines should be archetypes for assessing kinetic data in the degradation of micropollutants (e.g., diclofenac as an anti-inflammatory drug, the decongestant and bronchodilator clenbuterol, the chemotherapy agent cytarabine or the antibiotic sulfamethoxazole used for urinary tract infections (Sein et al., 2008; Ternes and Joss, 2006)). A considerable number of papers deal with the ozone chemistry of anilines (Gilbert and Zinecker, 1980; Doré et al., 1980; Elmghari-Tabib et al., 1982; Caprio and Insola, 1985; Pierpoint et al., 2003; Turhan and Uzman, 2007, 2008; Galstyan et al., 2008; Machulek et al., 2009). Thus, for ozone reactions with anilines some basic principles are well-known. Since ozone is a strong electrophile the ozone-reactive sites of aromatic amines are the electron-rich aromatic ring and/or the lone electron pair at nitrogen. In case the amines are deprotonated (pK_a in general around 5) the free electron pair can either conjugate into the aromatic ring system (activation) or be attacked by ozone at the nitrogen moiety. Hence, the ozone reactivity of aromatic amines depends on pH (von Sonntag and von Gunten, 2012). Besides, ozone is a highly selective reactant and ozone rate constants with aromatic compounds (Neta et al., 1988) and nitrogen-containing compounds (von Sonntag and von Gunten, 2012) vary strongly with the nature of substituents by up to ten orders of magnitude.

Mechanistic information on ozonation products formed through the investigated anilines is of high interest since it could be transferred subsequently to more complex micropollutants. Literature information allow us to consider addition of ozone and electron transfer as conceivable for the ozone-amine-reactions in aqueous solution (Doré et al., 1980; Muñoz and von Sonntag, 2000b; Muñoz et al., 2001; Mvula and von Sonntag, 2003, 2009; von Sonntag, 2008; Ramseier and von Gunten, 2009; von Gunten et al., 2010; von Sonntag and von Gunten, 2012; Tekle-Röttering et al., 2016). Ozone addition is often exergonic and may yield oxidized nitrogen moieties or hydroxylation of the benzene moiety by oxygen transfer as well as by forming an ozonide in a Criegee type reaction (von Sonntag and von Gunten, 2012). Outer and inner sphere electron transfer as well as H-abstraction is also possible. A mechanistic discussion and a mechanistic demonstration are presented in the theoretical background in Schemes 1 and 2, reactions (1)–(26).

Even though there is quite a lot of qualitative information about

oxidation products and possible reaction pathways in the oxidation of anilines, complementary knowledge about the quantitative contribution of the different transformation pathways, when ozone and $\cdot\text{OH}$ are present as oxidants, is still missing. Furthermore, with the current literature at hand it is still unknown if ozone prefers attack at the nitrogen or the aromatic moiety in its reaction with aniline. Thus, in the present paper the kinetics, stoichiometry and product formation including most abundant primary and advanced oxidation pathways in the reaction of anilines bearing different substituents with ozone were investigated. The substituents on the aromatic ring should influence the reaction behaviour significantly by activating or deactivating the aromatic ring. The information on the quantitative generation of transformation products (TPs) during ozonation will allow the assessment or prediction of TPs of micropollutants with similar structural elements and functional groups.

2. Theoretical background

The following primary processes are conceivable for the ozone-amine-reactions in aqueous solution. The examples in Scheme 1 and Scheme 2 are for aniline, but all reactions are effectual for the investigated compounds as well.

The initial step of the ozone addition at nitrogen (Scheme 1, reaction (1), pathway 1) is well-established for aliphatic amines (Muñoz and von Sonntag, 2000b; Muñoz et al., 2001). The first step of ozone addition to the aromatic ring (Scheme 2, reaction (13), pathway 5) is well-known for the electron-rich benzene derivative, phenol, which also can lead to the formation of an ozone adduct (Mvula and von Sonntag, 2003; Ramseier and von Gunten, 2009). In the breakdown of the ozone adduct singlet oxygen, $^1\text{O}_2$, is released (Scheme 1, reaction (2) and Scheme 2, reaction (14)). This is followed by a proton shift by forming hydroxylated products (Scheme 2, reaction (15)) for ozone addition at the aromatic ring. For phenols and some other aromatic compounds singlet oxygen yields in ozone reactions were measured (Muñoz et al., 2001). In the case of *N,N*-dimethylaniline a yield of 7% singlet oxygen was obtained (Muñoz et al., 2001). For further details on singlet oxygen see Supporting Information Text S1.

In competition, the ozone adduct may dissociate by forming different radicals through reactions like electron transfer or H-abstraction (von Sonntag and von Gunten, 2012). In principle these radical processes could also proceed directly via an outer sphere electron transfer without adduct as intermediate (von Sonntag and von Gunten, 2012). However, in experiments the direct pathway and the adduct pathway cannot be distinguished. The electron transfer leads to a radical cation (Scheme 1, reaction (3), pathway 2 and Scheme 2, reaction (16), pathway 6) and ozonide radical anion, $\text{O}_3^{\cdot-}$ (adduct of the hydrated electron to ozone (Elliot and McCracken, 1989; reaction see there)). The amine radical cation, formed after electron transfer at nitrogen is in equilibrium with an aminyl radical (reaction (4)). The pK_a value for the acidic dissociation of the amine radical cation is 7.05 (Qin et al., 1985) so that in neutral solution based on equilibrium 50% of each amine radical cation and aminyl radical are present. From the H-abstraction process an aminyl radical and hydrotrioxyl radical, HO_3^{\cdot} (Scheme 1, reaction (6), pathway 3) are generated. The above mentioned ozonide radical anion, $\text{O}_3^{\cdot-}$ reacts with water (Scheme 1, reaction (5) and Scheme 2, reaction (17)) giving rise to $\cdot\text{OH}$ whereas HO_3^{\cdot} decomposes to $\cdot\text{OH}$ and oxygen (reaction (7), Bühler et al., 1984).

Furthermore, ozone attack can lead to an insertion via ozone addition concomitant with proton transfer (Scheme 1, reaction (8), pathway 4 and Scheme 2, reaction (20), pathway 8). The insertion process on nitrogen can lead to a nitroxyl radical (Scheme 1, reaction (9)) or oxyl radical at the aromatic ring (Scheme 2, reaction

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