



Isomer-specific oxidation of nonylphenol by potassium permanganate



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HIGHLIGHTS

- This is the first report on isomeric selectivity in the advanced oxidation of nonylphenol.
- The oxidation of nonylphenol isomers by KMnO_4 is efficient and isomer-specific.
- Nonylphenol isomers with α -dimethyl substituents have higher reactivity.
- Nonylphenol isomers with α -dimethyl substituents have higher pH dependence.
- This isomer-specificity may influence on water safety, human health and its risk assessment.

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ABSTRACT

Nonylphenol (NP), the metabolite of non-ionic surfactant nonylphenol ethoxylates, is a well-known environmental endocrine disruptor. Nonylphenol is frequently detected in treated wastewater effluent, impacted surface water and even in drinking water due to its heavy use. Nonylphenol has been treated as a single compound in most studies to date, but in reality it is a mixture of numerous isomers. Recent studies showed that different NP isomers displayed different estrogenicity and biodegradability in the environment. In this study, we examined, for the first time, the potential isomeric selectivity in the oxidation of NP. The reaction kinetics of 19 NP isomers, including 6 diastereoisomers, with potassium permanganate was measured at pH 5, 7 and 9. At pH 7 with 10 mg L^{-1} of KMnO_4 and $50 \mu\text{g L}^{-1}$ technical mixture of NP, the half-lives of 19 isomers varied from 4.8 to 6.3 min. In general, the reaction followed the order: α -dimethyl > α -ethylmethyl \approx α -methylpropyl \approx α -iso-propylmethyl. The oxidation rate of NP isomers with KMnO_4 increased with increasing pH and a greater dependence on pH was observed for isomers with α -dimethyl substituents. This study suggested that α -substituents may be the dominant factor regulating the reactivity and persistence of NP isomers during advanced oxidation processes.

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1. Introduction

Nonylphenol (NP) is the metabolite of the heavily used nonylphenol ethoxylate surfactants [1,2]. Due to the wide use of nonylphenol ethoxylates in agricultural, industrial and domestic products, NP is frequently detected in surface water, effluents of wastewater treatment plants and even in drinking water [2,3]. For example, levels up to $48 \mu\text{g L}^{-1}$ have been reported in water from Hudson River Estuary, New York [4]. In a recent study, NP was found in 55 samples out of 62 drinking water samples from 31 major cities across China with a median concentration of 27 ng L^{-1} , whereas and in all 62 source water samples with a median concentration of 123 ng L^{-1} [3]. Nonylphenol is known as a potent endocrine disruptor and the potency of NP relative to 17β -estradiol ranges from 0.001 to 0.05 with arithmetic mean of 0.023 in *in vivo* bioassays [1].

Nonylphenol is commonly treated as a single compound in the evaluation of its environmental occurrence, fate and transport, treatment removal and toxicity [1,2,5]. However, technical nonylphenol (tNP) is in fact a mixture of more than 100 isomers [6,7]. A few recent studies showed that NP isomers have different estrogenicity or biodegradability in the environment [6,8–10]. For example, Gabriel et al. [8] reported that if the average estrogenicity of tNP in the yeast estrogen assays was set to be 1, the value for NP_{93} was 1.87 while the value for NP_{112} was only 0.60. Biodegradation of NP by *Sphingobium xenophagum* Bayram was also isomer specific, with 99.7% of NP_{128} degraded after 9 d while only 31% of NP_{193} dissipated under the same conditions [8]. The isomer-specific biodegradation was expected to result in the selective enrichment of recalcitrant and possibly highly estrogenic NP isomers in the environment [8]. This prediction was corroborated by the profile of NP isomers found in river water and sea water [9,11]. Such isomer selectivity arises from differences in physicochemical properties due to changes in spatial hindrance and electron distribution among the isomers [8], and is thus an intrinsic property of NP that has not been adequately understood.

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Advanced oxidation with potassium permanganate is a promising process for removing NP [5,12] and also other micropollutants [13]. A recent study showed that KMnO_4 was more effective at removing endocrine disrupting chemicals, including 4-n-NP (i.e., NP_1), than ozone, ferrate or chlorine in wastewater [5]. At pH 7, 80% of NP (1.0 mg L^{-1}) was degraded in 120 min by 3.2 mg L^{-1} KMnO_4 [12]. When KMnO_4 concentration was increased to 16 or 32 mg L^{-1} , 100% NP removal was achieved in 100 min. In another study, with 9.48 mg L^{-1} of KMnO_4 at pH 7, the half-life of 4-n-NP ($33 \text{ } \mu\text{g L}^{-1}$) was only 3.0 min [5]. However, to date no study has considered the isomer specificity in the chemical oxidation of NP with permanganate or any other oxidants [14,15].

The objectives of this study were to investigate the oxidation of tNP by KMnO_4 , to obtain isomer-specific oxidation rates and to understand the influence of side chain length and α -substituents. The oxidation kinetics of each isomer was measured under different KMnO_4 concentrations and pH conditions. Statistics were used to analyze the relationship between the reaction rate and structural properties including the side chain length and types of α -substituents.

2. Materials and methods

2.1. Chemicals

Technical NP (tNP), a mixture of NP isomers with branched side chains (CAS No. 84852-15-3) was purchased from TCI America (Portland, OR). Isomers NP_{36} , NP_{37} , NP_{119} , NP_{128} and NP_{194} (10 mg g^{-1} in hexane; >95% purity) were obtained from ChemCollect GmbH (Remscheid, Germany). Isomers NP_{38} (48.2 mg g^{-1}), NP_{65} (59.5 mg g^{-1}), NP_{111} (49.5 mg g^{-1}) and NP_{112} (48.52 mg g^{-1}) in methanol were kindly provided by Prof. Rong Ji at Nanjing University, China. Potassium permanganate (KMnO_4 , 99+%), 4-tert-octylphenol (>97%), sodium phosphate dibasic (Na_2HPO_4 , 99+%), sodium tetraborate decahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, >99.5%) and L-ascorbic acid (>99.0%) were from Sigma-Aldrich (St. Louis, MO). Sodium acetate trihydrate (99.0–101.0%) and gas chromatography (GC) grade hexane were from Fisher Scientific (Fair Lawn, NJ). Reagent water ($18.3 \text{ M}\Omega\text{-cm}$ resistivity) was prepared using a Barnstead Nanopure water system (Barnstead, Dubuque, IA). The stock solution of 100 mg L^{-1} tNP in methanol was stored at $-20 \text{ }^\circ\text{C}$ before use. The stock solution of 1000 mg L^{-1} KMnO_4 was prepared with boiled reagent water and stored at $4 \text{ }^\circ\text{C}$. The KMnO_4 stock solution was used within a month after preparation and before each use, its concentration was determined on a UV-Vis spectrometer at 525 nm after dilution to 20 mg L^{-1} . The results showed there was no change in KMnO_4 under these conditions.

2.2. Reaction setup with reagent water

Batch experiments were conducted in 125-mL wide-mouth amber borosilicate glass bottles with Teflon-faced caps at room temperature ($22 \pm 0.5 \text{ }^\circ\text{C}$). Reaction solutions prepared with reagent water were maintained at the desired pH using 0.01 mol L^{-1} of the following pH buffers: pH 5, sodium acetate; pH 7, sodium phosphate dibasic; pH 9, sodium tetraborate decahydrate. The

reaction solution (50 mL) with $50 \text{ } \mu\text{g L}^{-1}$ tNP was constantly stirred at 480 rpm. The reaction was initiated by adding KMnO_4 to arrive at the initial concentration of 1, 2 or 10 mg L^{-1} . At selected time intervals (0, 2, 4, 6, 8, 10, 15, 20, 30, 40 min), 0.5 mL of 200 g L^{-1} L-ascorbic acid was added to quench the reaction. A control group was included with $50 \text{ } \mu\text{g L}^{-1}$ tNP at pH7 but without KMnO_4 . All reactions were carried out in 4 replicates. Additional groups at pH 5, 7 and 9 with $50 \text{ } \mu\text{g L}^{-1}$ tNP and 10 mg L^{-1} or 1 mg L^{-1} KMnO_4 were used to monitor the change in temperature, pH or KMnO_4 concentration during the reaction. During the 40 min of reaction, there was no detectable change in pH or KMnO_4 concentration, while the temperature increased by $2.0 \text{ }^\circ\text{C}$, likely due to the constant stirring.

2.3. Experiments with reclaimed water

Reclaimed water (COD 21 mg L , $\text{NO}_3^- \text{-N}$ 3 mg L , $\text{NH}_3\text{-N}$ 0.062 mg L , o-phosphate-P 0.06 mg L) was collected from Michelson Water Reclamation Plant, Irvine, CA and filtered with $0.7 \text{ } \mu\text{m}$ glass fiber membranes. The reaction was initiated by adding 0.5 mL of 1000 mg L^{-1} KMnO_4 to 50 mL filtered reclaimed water containing $50 \text{ } \mu\text{g L}^{-1}$ tNP maintained at pH 7 using 0.01 mol L^{-1} of phosphate buffer. The other conditions were the same as above. The detailed reaction conditions of the batch experiments with reagent and reclaimed water are listed in Table 1.

2.4. Chemical analysis

The quenched reaction solutions were extracted twice with hexane (15 and 10 mL, respectively) by liquid-liquid extraction. The combined extracts were condensed to about 1 mL under a gentle nitrogen stream and then $10 \text{ } \mu\text{L}$ of 100 mg L^{-1} 4-tert octylphenol was added as the internal standard. The samples were analyzed on an Agilent 6890 GC coupled with 5973 mass spectrometer (Agilent Technologies, Santa Clara, CA). Samples ($2 \text{ } \mu\text{L}$) were introduced into the inlet at $250 \text{ }^\circ\text{C}$ and the separation was achieved on a DB-5MS Ultra Inert capillary column ($60 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ } \mu\text{m}$, Agilent, Wilmington, DE). The carrier gas was helium (99.999%) and the flow rate was set at 1.0 mL min^{-1} . The column temperature was programmed initially at $80 \text{ }^\circ\text{C}$ for 0 min, then ramped to $160 \text{ }^\circ\text{C}$ at $10 \text{ }^\circ\text{C min}^{-1}$ and held for 42 min, and further ramped to $300 \text{ }^\circ\text{C}$ at $30 \text{ }^\circ\text{C min}^{-1}$ and held for 3 min. The mass spectrometer was operated in the electron ionization – selective ion monitoring (SIM) mode at 70 eV. The ion with m/z 135 was used for the quantification of the internal standard and ions with m/z 121, 135, 149, 163, 177 and 191 were used for the quantification of different NP isomers. For the identification of NP isomers, both a full scan mode (m/z 40 to m/z 800) and the SIM mode (m/z 107, 121, 135, 149, 163, 177, 191 and 220) were applied. The recovery of NP isomers was $97 \pm 3\%$.

2.5. Data analysis

All statistical analyses, including linear regression, one-way ANOVA and two-way ANOVA, were carried out using SigmaPlot 11 (San Jose, CA) at the significant level of 0.05. The Holm-Sidak

Table 1
Matrix, pH, KMnO_4 and nonylphenol concentrations in the batch experiments.

Reaction conditions	A	B	C	D	E
Matrix	Reagent water	Reagent water	Reagent water	Reagent water	Reclaimed water
pH	5	7	7	9	7
KMnO_4 concentration (mg L^{-1})	10	10	2	1	10
tNP concentration ($\mu\text{g L}^{-1}$)	50	50	50	50	50

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