**Homogeneous Catalysis**

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# Highly Efficient $NaNO_2$-Catalyzed Destruction of Trichlorophenol Using Molecular Oxygen**

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Polychlorinated phenols (PCPs) are a class of compounds once widely used as wood preservatives, pesticides, insecticides, and defoliants. Moreover, an alarming amount of these compounds are produced by the pulp industry as a result of lignin chlorination by chlorine-based bleaching processes. The remarkable resistance of these compounds toward degradation led to their substantial release into the environment, even in treated pulp waste streams.[1,2] Their numerous and abundant points of entry, inherent toxicity, persistence, and their presence in significant quantities in the environment have resulted in chlorophenols becoming one of the worst offenders in the environment, and are listed by the US Environmental Protection Agency as priority pollutants.[3]

Eradication of these persisting pollutants from the environment has attracted much attention from academia, industry, and governmental agencies. However, for a number of reasons, decades of efforts aimed at the treatment of PCPs have met with a limited degree of success with regard to efficiency, complexity, and industrial viability. While biological methods for the treatment of PCPs have been intensively investigated,[4–6] progress in this field to date has been hampered by the inherent toxicity of PCPs against the organisms used. Adding to the frustration is the finding of the tendency of some microorganism to convert some PCPs into even more toxic and more persistent pollutants such as polychlorinated dibenzo-*p*-dioxins.[7] As a result of these limitations on bioremediation, environmental chemists have turned their attention to chemical methods for destroying these pollutants. Catalytic reductive dechlorination (CRD) has been extensively investigated as a direct method to decrease the level of PCPs, and high efficiency has been achieved.[8,9] A major drawback to this method is its inability to reduce the overall chemical oxygen demand (COD) in the waste, thus necessitating a secondary treatment of the waste stream after reductive dechlorination. In addition, catalysts for CRD are usually noble metals, which could be deactivated by complex pollutants. On the other hand, advanced oxidation processes (AOPs), which are designed to destroy the environmental pollutants and reduced COD level, are emerging as a versatile strategy to achieve this goal.[10–12] A representative example of an AOP highlighted by Meunier and co-workers is the $H_2O_2$-based oxidative degradation method.[2,13] In this process a degradation of 99% of trichlorophenol (TCP) was obtained with release of 70% chlorine and 14% carbon mineralization by using iron phthalocyanines as a catalyst, 30% $H_2O_2$ (5 equiv) as an oxidant, and acetonitrile as a cosolvent in a buffered solution. Lenoir, Collins, et al. have further demonstrated the effectiveness of this homogeneous oxidation pathway for PCPs.[14] They have demonstrated a degradation of 99% TCP by using an iron complex of a tetraamidomacrocyclic ligand (Fe-taml) with 100-fold excess of $H_2O_2$ at 25°C. In that process, 35% carbon mineralization was achieved, together with 46.5% conversion to low-molecular-weight acids and 83% of the chlorine atoms being released as free chloride. In light of these ground-breaking results, we sought to discover and develop innovative and economically feasible technologies that would be intrinsically easy to industrialize. Specifically, we focused our efforts on finding a catalytic system that uses inexpensive and easily available oxidants/catalysts, and are operationally economical in an industrial setting. As such, one key criterion is the use of minimum quantities or total elimination of transition metals, organic solvents, and hazardous oxidants. Herein we reported our preliminary results toward achieving these goals.

Recently we reported a highly efficient catalytic aerobic oxidation system for alcohols that did not necessitate a transition-metal catalyst.[15,16] Key to the newly developed oxidation process is the ability of a nitrite salt to activate molecular oxygen as well as the suitability of the system towards an aqueous environment. It was intriguing to see if this $NaNO_2$/molecular oxygen method could be adopted for the destruction of the environmental pollutants such as PCPs. Thus, we started our research with TCP as the prototypical PCP substrate in high dilution (thus mimicking the environmental contaminant level) with $NaNO_2$ under pressurized oxygen. After systematic investigation and optimization of the reaction conditions (temperature, oxygen pressure, and amount of $NaNO_2$), we developed an efficient and simple oxidative degradation method for TCP.

Several features of this simple yet robust system are worth noting. First, the catalytic system results in fairly efficient removal of TCP at a moderate reaction temperature (Table 1 entries 1–4). As the reaction temperature increases, the rate of TCP destruction increased correspondingly and the color of the reaction mixture underwent the anticipated changes: from colorless to pink, then to yellow, and finally to colorless,

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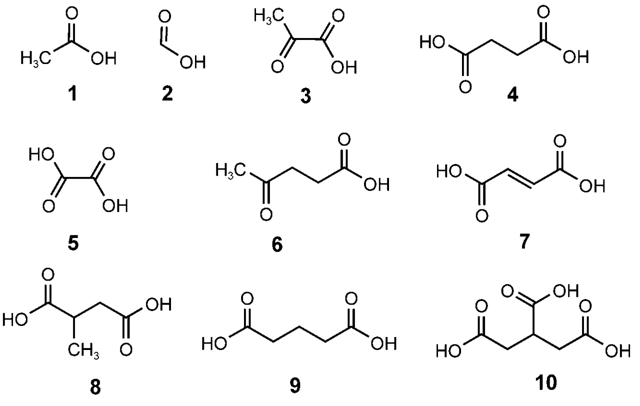
**Table 1:** Oxidation of TCP with $NaNO_2$ and oxygen under different reaction conditions.[a]

| Entry | T [°C] | P [MPa] | t [h] | $NaNO_2$ [mol%] | Removal of TCP [%] | Removal of COD [%] | Mineralization of Cl [%] | Removal of TOC [%] |
|---|---|---|---|---|---|---|---|---|
| 1 | 90 | 0.5 | 4 | 100 | 86 | 16 | 52 | – |
| 2 | 110 | 0.5 | 4 | 100 | 94 | 39 | 72 | – |
| 3 | 130 | 0.5 | 4 | 100 | 96 | 51 | 86 | – |
| 4 | 150 | 0.5 | 4 | 100 | 99 | 70 | 91 | 56 |
| 5 | 150 | 0.5 | 4 | 1 | 25 | 1 | 11 | – |
| 6 | 150 | 0.5 | 4 | 10 | 86 | 24 | 71 | – |
| 7 | 150 | 0.5 | 4 | 50 | 97 | 59 | 83 | – |
| 8 | 150 | 0.5 | 1 | 100 | 92 | 37 | 68 | – |
| 9 | 150 | 0.5 | 2 | 100 | 96 | 54 | 90 | – |
| 10 | 150 | 0.5 | 8 | 100 | 99 | 72 | 96 | 65 |
| 11 | 150 | 0.1 | 4 | 100 | 91 | 52 | 81 | – |
| 12 | 150 | 0.2 | 4 | 100 | 93 | 55 | 86 | – |
| 13 | 150 | 0.3 | 4 | 100 | 96 | 66 | 92 | – |
| 14 | 150 | 0.4 | 4 | 100 | 97 | 69 | 91 | – |
| 15[b] | 150 | 1.5 | 4 | 100 | 97 | 60 | 90 | – |
| 16[c] | 150 | 0.5 | 4 | 100 | 91 | 60 | 82 | 57 |
| 17[c] | 170 | 0.5 | 4 | 100 | 92 | 64 | 82 | 63 |
| 18[c,d] | 190 | 0.5 | 6 | 100 | 100 | 70 | 92 | 70 |
| 19[c] | 210 | 0.5 | 6 | 100 | 100 | 73 | 90 | 76 |
| 20[c] | 210 | 1.0 | 6 | 100 | 100 | 77 | 92 | 77 |

[a] Experimental conditions: TCP stock solution (20 mL) was treated with $NaNO_2$ and oxygen in the 50-mL teflon-lined autoclave. [b] Air was used as the oxidizing agent in the 50-mL teflon-lined autoclave. [c] The 100 times scale-up experiments were carried out in the 5-L Hastelloy autoclave. [d] The trace of dioxin in the TCP raw material was decreased by more than 80% under the above conditions. –: not determined. TCP: trichlorophenol; COD: chemical oxygen demand; TOC: total organic carbon.

as observed in previous research studies.[13,14] We were pleased to find that at a relatively mild reaction temperature (150 °C) with a stoichiometric amount of $NaNO_2$, 99 % TCP was removed and 91 % of the chlorine atoms of the TCP were released as innocuous inorganic chloride (entry 4). With a catalytic amount (1 mol%) of $NaNO_2$, 25 % TCP degradation and 11 % chlorine mineralization was observed (entry 5). This result clearly implicated the role of $NaNO_2$ as an active catalyst. Furthermore, a control experiment indicated that the oxidative destruction of TCP was totally ineffective in the absence of $NaNO_2$. This catalytic system also shows the degradation rate of TCP is rapid, for example, within only 1 hour, 92 % TCP was removed and 68 % chloride was released from the TCP (entry 8). Increasing the reaction time led to a slow increase in the removal of TCP, but a much greater extent of COD reduction. It is noteworthy that with 100 mol% $NaNO_2$, (which is within the feasible range given the relatively low environmental concentration of PCPs) under 0.5 MPa of $O_2$ and at 150 °C, more than 99 % TCP was destroyed with 96 % dechlorination and 72 % COD reduction after 8 h (entry 10). The oxygen pressure had no significant influence on the reaction efficiency of the current catalytic system (entries 11–14). When air was used in place of pure oxygen, no apparent difference was observed (entry 15 versus entry 13). Finally, to demonstrate the viability of this new aerobic TCP degradation method for potential industrial applications, a scale-up experiment was carried out in a 5-L Hastelloy autoclave (entry 16). We observed a slightly lower degradation at this larger scale compared with the reaction in the small autoclave (entry 16 versus entry 4), which can be attributed to better agitation efficiency in the smaller vessel and can be easily compensated by a modest increase in temperature (entries 17–20). Overall, when all the facets of this new oxidation system is considered, the use of inexpensive $NaNO_2$ and air as reagents rendered it very attractive for potential application at an industrial scale for the treatment of these persistant environmental pollutants.

The extent of mineralization is also one of the critical factors for the evaluation of a new oxidative degradation system. Toward this end, we determined both the inorganic chloride released and the residual total organic carbon (TOC). The amount of chloride ions generated was measured by ion chromatography. As shown in Table 1, chlorine mineralization is up to 96% after 8 h at 150 °C (entry 10). TOC measurements indicated that 77 % of the carbon in TCP was mineralized (entry 20). These analyses demonstrate that TCP was nearly completely destroyed and a considerable amount was mineralized; only a fraction of the TCP was converted into lower organic products (Scheme 1). The mass balance was determined by reduction of the TOC and some measurable reaction products such as acetic acid (**1**), formic acid (**2**), pyruvic acid (**3**), succinic acid (**4**), and oxalic acid (**5**) were identified and quantified with known standards by ion chromatography (Figure 1). The fate of 90 % of the carbon atoms is accounted for (Table 2, entry 19). Gas chromatography/mass spectrometry (GC-MS) was used to identify residual organic compounds in the reaction mixture (Table 1, entry 18) and the results show that the major product is succinic acid (**4**), a fairly innocuous compound with a short environmental half-life. Other detectable minor



**Scheme 1.** Products formed after TCP degradation by $NaNO_2$-catalyzed oxidation.

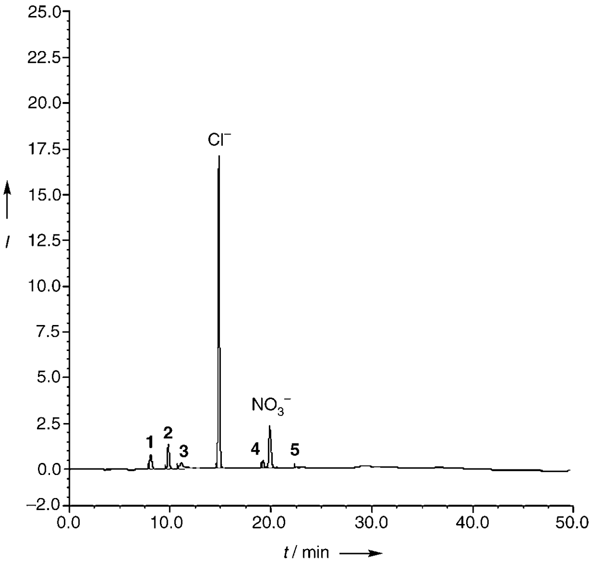


*Figure 1.* Products detected by ion chromatography after TCP degradation.

*Table 2:* Mass balance after the $NaNO_2$-catalyzed oxidation of TCP.

| Compound | Entry 18[a] | | Entry 19[a] | | Entry 20[a] | | Entry 10[a] | |
|---|---|---|---|---|---|---|---|---|
| | mM | % C | mM | % C | mM | % C | mM | % C |
| $C + CO_2$ | | 70.0 | | 75.6 | | 77.4 | | 65.0 |
| acetic acid | 0.15 | 4.9 | 0.16 | 5.3 | 0.16 | 5.4 | 0.19 | 6.3 |
| formic acid | 0.32 | 5.4 | 0.26 | 4.3 | 0.25 | 4.2 | 0.33 | 5.5 |
| pyruvic acid | n.d. | n.d. | 0.05 | 2.4 | n.d. | n.d. | 0.07 | 3.5 |
| succinic acid | 0.04 | 2.5 | 0.04 | 2.5 | 0.03 | 2.0 | 0.07 | 4.3 |
| total | | 82.8 | | 90.1 | | 89.0 | | 84.6 |

[a] From Table 1. n.d. = not detected.

components from the degraded mixture include levulinic acid (**6**), fumaric acid (**7**), 2-methylsuccinic acid (**8**), glutaric acid (**9**), and 3-carboxypentanedioic acid (**10**, Figure 2). Interestingly, the GC-MS results indicated that most detectable degradation products do not contain chlorine atoms, which is consistent with the extent of mineralization of the chlorine atoms. To the best of our knowledge, this is the first demonstration of $NaNO_2$, a simple, inexpensive and biodegradable inorganic compound, as a catalyst to activate molecular oxygen for the destruction of PCPs. Its remarkable effectiveness at attacking substances with low reduction potentials such as polychlorinated aromatic compounds has not been reported previously. However, several reports on biologically mediated systems[17–22] have provided useful insights for understanding the current oxidative degradation process. We postulate that peroxynitrite, which possesses activity similar to a hydroxyl radical, is most likely to be involved in the present catalytic system and acts as the veritable active oxidant for the degradation of TCP. Elucidation of the detailed mechanistic pathway will undoubtedly shed light on the pathway and allow further optimization of this aerobic oxidative degradation system.

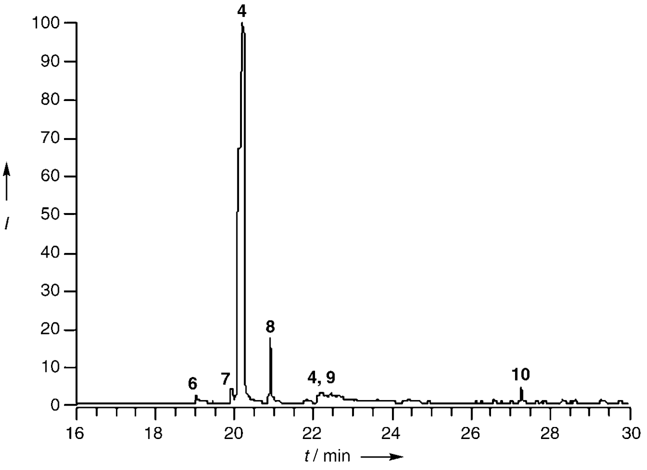


*Figure 2.* Products of TCP degradation detected by GC-MS after esterification.

The $NaNO_2/O_2$ system efficiently oxidizes the recalcitrant TCP into $CO_2$ and/or CO and a small fraction of biodegradable organic products with a high conversion rate. To the best of our knowledge, such a high extent of mineralization has not been reported previously without resorting to the extreme measure of high-temperature combustion. In addition, this system is intrinsically devoid of complications caused by other components found in industrial effluents, which tend to deactivate metal catalysts and render metal-based aerobic oxidation of pollutants ineffective. This non-transition-metal system is also free of the risk of secondary pollution during treatment as the catalyst, $NaNO_2$, was oxidized to $NaNO_3$. Therefore, this practical, inexpensive and efficient catalytic system represents a significant step forward in the fight against recalcitrant chlorinated organic pollutant and displays considerable promise for its practical application in an industrial setting.

## Experimental Section

The catalytic oxidation of trichlorophenol (TCP) was carried out in a 50-mL teflon-lined stainless-steel autoclave. The reaction temperature was measured using a thermocouple and controlled by a PID regulator. TCP solution (20 mL, 1 mM) and $NaNO_2$ (20 μL, 1M) were added to the autoclave with a magnetic stirrer, thus, the mole ratio of $TCP/NaNO_2$ was 1:1. The autoclave was then closed and charged with pure oxygen to 0.5 MPa and then heated to the desired temperature. The stirring speed was set at 500 rpm. After reaction (heating time included), the autoclave was cooled to room temperature with a water bath, carefully depressurized, and sampled to perform further analysis. For scale-up experiments, TCP (395 mg, 1 equiv) and $NaNO_2$ (27.6 mg, 1 equiv) were added to the 5-L Hastelloy autoclave containing pure water (2 L, Millipore). The stirrer speed was set at 600 rpm. The rest of the procedure was similar to that described for the small-scale reaction.

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