

The Photooxidative Degradation of *N*-Methylpyrrolidinone in the Presence of $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ and TiO_2 Colloid Photocatalysts

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The mechanisms of the heterogeneous photocatalytic behavior of TiO_2 and $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ for the oxidative destruction of *N*-methylpyrrolidinone (NMP) in water are discussed. Both photocatalysts generate *N*-methylsuccinimide (NMS) and succinimide as the main intermediates from oxidation at the α -carbon and methyl positions. 2-Pyrrolidinone (2P) and 5-hydroxy-*N*-methylpyrrolidinone (5-HNMP) have also been identified as primary intermediates. These intermediates are all broken down under further photooxidation. However, differences in product distribution indicate the possibility of several mechanistic pathways. Hydroxyl radical-like attack predominates for TiO_2 -photocatalyzed degradation, whereas the polyoxotungstate appears to oxidatively destroy NMP by both OH radical attack and direct oxidation. For TiO_2 , the relative quantum yields for NMP oxidation ($0.5 \text{ g L}^{-1} \text{ TiO}_2$, pH 3, 254 nm, $7 \times 10^{-6} \text{ ein sec}^{-1}$) increase from <0.01 at 10 ppm NMP to near 0.03 at 60–100 ppm. For $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ under the same conditions, the apparent quantum yield is nearly invariant (0.005–0.009) over the concentration range 10–1000 ppm.

Introduction

In recent years, TiO_2 photocatalysis has become a widely studied option in the advanced oxidative treatment of organic pollutants in wastewater due to its ability to destroy a wide range of contaminants using solar or UV irradiation (1–6). The ultimate product of the photooxidative process can be CO_2 and H_2O (and relevant inorganic ions such as nitrate or chloride). However, in certain cases (e.g., atrazine, ref 7), facile mineralization to CO_2 does not occur due to the formation of a stable intermediate that is recalcitrant to TiO_2 photooxidation. These findings suggest that the development of other photocatalytic materials, which can access other mechanistic pathways, is important. We present herein initial studies on a comparison of a heterogeneous polyoxotungstate photocatalyst ($\text{Cs}_3\text{PW}_{12}\text{O}_{40}$) with TiO_2 for the destruction of a nonaromatic contaminant (*N*-methylpyrrolidinone) in water.

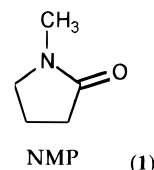
Titanium dioxide (TiO_2) is a UV-absorbing semiconductor material. Absorption of near-UV light results in the promotion

of an electron from the valence band to the conduction band of TiO_2 , resulting in the generation of a hole-electron pair. This pair can recombine within a few nanoseconds; however, the positive vacancy (h^+) in the valence band is a very strong oxidant and can undergo charge transfer with adsorbed species on the photocatalyst surface on a picosecond time scale (2, 8–10). For example, water on the surface of the TiO_2 particle can be oxidized, resulting in an adsorbed hydroxyl radical (11). These radicals attack the aqueous organic contaminant, generating a series of oxidized intermediates and ultimately resulting in total degradation of the contaminant to CO_2 . There can also be contributions from direct oxidation of adsorbed organics.

Recently, there has been an interest in molecular-based materials that perform similar functions. Some of the most promising are polyoxometalates, tungsten–oxygen clusters, such as $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (12–23). UV irradiation of this species results in the formation of a ligand-to-metal charge transfer (LMCT) excited state (lifetime approximately 100–200 ps in water) (24, 25) with considerable oxidizing capacity (2.63 V vs NHE, the normal hydrogen electrode) (26). This complex has recently been shown to photodegrade organic contaminants, such as chlorophenols to CO_2 and HCl (27–31). However, a major drawback to the practical use of this system is its high water solubility, which impedes ready recovery and reuse of the photocatalyst (and, therefore, its cost-effectiveness).

Cesium salts of polyoxometalates, such as $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$, are considered to be insoluble and are well-known for their thermal catalytic properties for reactions in both gas and liquid phases (32–41). We have recently found that $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ is also an effective heterogeneous photocatalyst for the photooxidation of 2-propanol to acetone (42). The present work is a further examination of this substance for the photocatalytic degradation of model contaminants in water. Specifically, two issues are addressed: (1) what are the degradation intermediates, and (2) what is the efficiency of contaminant degradation for $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$? These questions are examined in the context of a standard TiO_2 material (Degussa P25) and are important for evaluating the practicality of this material in schemes for contaminant degradation.

N-Methylpyrrolidinone (NMP), **1**, is a cyclic, nonaromatic amide commonly used as an industrial solvent and a component of cleaning solutions. It has been detected in textile mill effluents in Canada and in landfill leachates in Japan (43, 44). The present study evaluates the efficacy of TiO_2 and $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ for the photocatalytic destruction of NMP. Notably, its simple structure serves as an ideal model for the general comparison of photooxidative destruction of nonaromatic contaminants by TiO_2 and $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$. Furthermore, since NMP has minimal light absorption at 254 nm, complicating effects from direct photolysis can be minimized.



Experimental Section

TiO_2 (P25 grade) was obtained from Degussa Corp. $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was synthesized according to literature methods (45). *N*-

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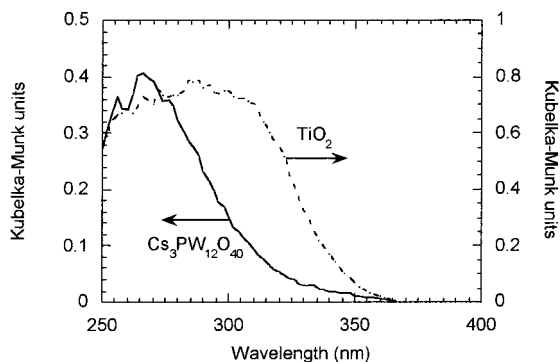


FIGURE 1. Diffuse reflectance spectrum of powdered $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ and TiO_2 in silica gel (8 mg/g silica gel) with pure silica gel as a background reference.

Methylpyrrolidinone was obtained from Aldrich. $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ was synthesized by the metathesis of concentrated solutions of CsCl and $\text{H}_3\text{PW}_{12}\text{O}_{40}$. Diffuse reflectance spectra were obtained using an Ocean Optics S1000 optical fiber spectrometer with a reflectance probe accessory.

The arrangement for photocatalysis consisted of an annular quartz cell (volume 150 mL) that surrounded a 15 W lamp (Philips TUV low-pressure Hg lamp for near monochromatic output at 254 nm). Suspensions of the photocatalyst and aqueous contaminant solutions were kept aerated and stirred by a steady stream of air. Irradiation periods were kept short (less than 10 min) in order to minimize the effects of heating. Incident light intensities were measured using ferrioxalate actinometry (46, 47). The light intensity from this setup as measured by actinometry was determined to be $7.2 \pm 0.2 \times 10^{-6}$ ein sec^{-1} . Photocatalytic degradations were monitored using HPLC–UV (Waters 600E controller and 484 UV absorbance detector). The degradation of NMP and formation of intermediates was monitored with isocratic elution (3–10% acetonitrile/90–97% water, 1 mL min^{-1}) on a reversed-phase C_{18} NovaPak column. The detection wavelength was 212 nm. The identity of intermediates was determined against authentic standards (Aldrich). TOC analysis was performed with a Technicon Autoanalyzer.

Electrospray-MS analysis was performed with an Autospec Q mass spectrometer (Micromass, UK) with an electrospray interface in the positive ion mode. Instrumentation settings have been given previously (48). For electrospray-MS/MS, the magnet was parked at m/z 115 or 85 (the molecular weights of the unknown intermediates), and the quadrupole was scanned from m/z 40–150.

Results

Characterization of Photocatalyst Material. The physical properties of cesium–polyoxotungstate materials, such as $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$, are well-known from thermal catalysis studies. The surface area for BET (Brunauer–Emmett–Teller) adsorption ($126 \text{ m}^2 \text{ g}^{-1}$) is in agreement with previous values and indicates a mesoporous material (32, 37). In comparison, TiO_2 (Degussa P25) has a specific surface area of $55 \text{ m}^2 \text{ g}^{-1}$. The particle size, as measured by light scattering in DMSO and in H_2O , is approximately 300 nm. Previous studies have indicated that $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ and $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ are made up of small crystallites of 10–12 nm diameter that can form larger aggregates (32, 37, 49). These aggregates are likely candidates for the suspended particles in liquid phase observed in the present study. At pH 7 or below, the white colloid remained insoluble and suspended in aqueous media. However, at high pH values (pH > 9) the colloidal polyoxometalate salt dissolved quickly and displayed a loss in the UV absorption spectrum above 230 nm, indicating a breakdown of the $\text{PW}_{12}\text{O}_{40}^{3-}$ unit due to basic conditions (29, 50, 51).

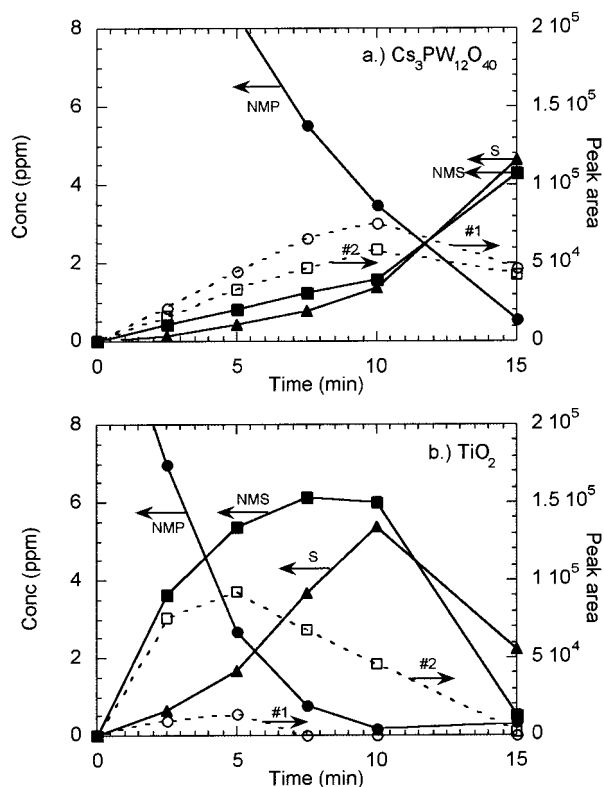


FIGURE 2. Concentration of intermediates (for known intermediates *N*-methylsuccinimide NMS and succinimide S) and peak areas (for intermediate 1 at 1.58 min elution and intermediate 2 at 2.00 min elution) arising from the irradiation (254 nm) of 12.2 ppm NMP and (a) 0.5 g L^{-1} $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ and (b) 0.5 g L^{-1} TiO_2 .

A diffuse reflectance spectrum for $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ powder diluted with silica gel (vs a pure silica gel reference) is shown in Figure 1. The spectrum shows an absorbance maximum between 265 and 270 nm, in agreement with the solution absorption spectrum for $\text{PW}_{12}\text{O}_{40}^{3-}$ (12, 29, 52). In contrast, light absorption for TiO_2 becomes significant between 300 and 350 nm. Both materials are significant absorbers at 254 nm, the irradiation wavelength used in this study.

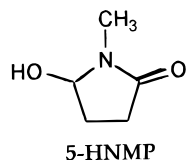
Photodegradation of *N*-Methylpyrrolidinone. *N*-Methylpyrrolidinone (1) is rapidly degraded upon 254 nm irradiation of aqueous slurries of TiO_2 or $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$. For example, at a lamp intensity of 7×10^{-6} ein sec^{-1} and a photocatalyst loading of 0.5 g L^{-1} , the apparent first-order rate constants for the disappearance of $1.2 \times 10^{-4} \text{ M}$ NMP are 0.34 min^{-1} for TiO_2 (P25) and 0.14 min^{-1} for $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$. In contrast, direct irradiation of NMP solutions in the absence of either photocatalyst leads to negligible photochemistry. The molar absorptivity of NMP was measured to be less than $1 \text{ M}^{-1} \text{ cm}^{-1}$ at 254 nm; thus, the contaminant does not act as a direct absorber or inner filter for the concentrations used in these experiments.

It is well-known that TiO_2 -photocatalyzed degradation of organics proceeds through the stepwise formation of intermediates, usually forming CO_2 as the ultimate oxidation product (1–6). For both TiO_2 and $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$, major intermediates formed by oxidation that were detected and quantified by HPLC–UV were *N*-methylsuccinimide (NMS) and succinimide (S). Two additional intermediates were detected that eluted at 1.6 min (intermediate #1) and 2.0 min (intermediate #2) with 5:95 acetonitrile/water under the LC conditions described in the Experimental Section. Extended photolysis led to the formation of more extensively oxidized products and led to mineralization of NMP by both photocatalysts as observed by TOC analysis. For example, a

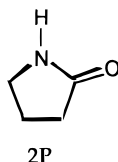
solution of 0.2 mM NMP was mineralized in 1.5 h by 0.5 g L⁻¹ TiO₂ and 3.5 h by 0.5 g L⁻¹ Cs₃PW₁₂O₄₀.



Figure 2 shows the time development (as measured by HPLC-UV) of NMP degradation and formation of the intermediates. The growth and decay of intermediates 1 and 2 occur early in the photolysis, and the concentration of NMS and succinimide continues to increase as the concentration of these intermediates decreases, which suggests that these may be precursors to NMS and succinimide formation. Intermediate 1 is almost absent for TiO₂ compared to Cs₃PW₁₂O₄₀. Electrospray positive-ion MS/MS of photocatalytically treated solutions of NMP detected significant amounts of an intermediate with mass 115 (*m/z* of M-H⁺ = 116), which was at much higher concentration for Cs₃PW₁₂O₄₀ than for TiO₂, a first indication of mechanistic differences. Collision-induced dissociation of this ion resulted in a peak at (M-H⁺ minus 18), which would be consistent with the loss of water and thus with the presence of a hydroxy group on the intermediate. From these results, we assign intermediate 1 as 5-hydroxy-*N*-methylpyrrolidinone (5-HNMP), shown below. This species has also been shown to be formed concurrently with NMS upon electrochemical oxidation of NMP in aqueous acetonitrile (53).



Appreciable formation of intermediate 2 was observed for both photocatalysts. Similarly, an intermediate of mass 85 (*m/z* M-H⁺ = 86) was detected using both GC-MS and electrospray-MS/MS for solutions treated by either photocatalyst. As suggested by the results in Figure 2b, intermediate 2 may be a precursor to succinimide formation and it is, therefore, assigned to 2-pyrrolidinone (2P). The time development of 2-pyrrolidinone and succinimide are similar for both photocatalysts. Figure 2b also shows that succinimide formation is accelerated as the rate of NMS formation decreases, strongly suggesting that the formation of succinimide can also result from oxidative attack at the *N*-methyl position of NMS.



The total concentration of NMP, NMS, and succinimide was monitored during the reactions represented in Figure 2. For TiO₂, the total amount represented by these three compounds was 91 (2.5 min), 77 (5 min), 83 (7.5 min), 92 (10 min), and 26% (15 min), based on the initial concentration of NMP. The high percentage at 10 min irradiation (where NMP has essentially disappeared) indicates efficient reaction of primary intermediates to form NMS and succinimide and a low degree of product adsorption. Further reaction results

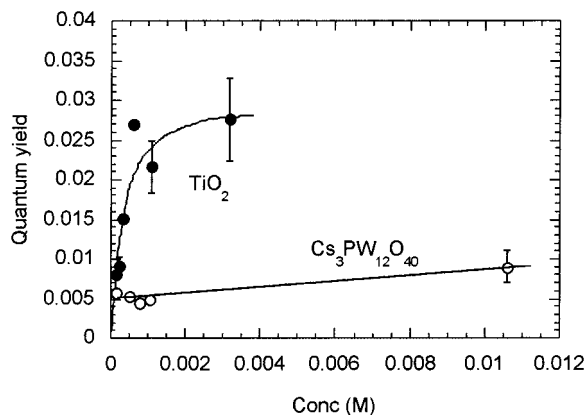


FIGURE 3. Relative quantum yield ϕ versus NMP concentration at pH 3 for TiO₂ and Cs₃PW₁₂O₄₀ slurries (0.5 g L⁻¹, 254 nm irradiation).

in degradation of the intermediates, until mineralization is achieved. The same trend is observed for Cs₃PW₁₂O₄₀, where the amount of NMP, NMS, and succinimide accounted for 81 (2.5 min), 71 (5 min), 56 (7.5 min), 47 (10 min), and 68% (15 min) of the initial concentration of NMP. The low percentages at 7.5 and 10 min are at the maximum concentrations of the primary intermediates 1 and 2 identified above, although overlapping peaks from minor amounts of other intermediates may also contribute. These react further to give NMS and succinimide, resulting in the higher percentage at 15 min. There may also be some contribution of overlapping peaks from secondary and tertiary intermediates that lower the measured concentration of succinimide.

Relative quantum yields ϕ for TiO₂- and Cs₃PW₁₂O₄₀-photocatalyzed degradation of NMP were determined in an annular cell configuration (with the slurry completely surrounding the lamp) at a wavelength of high absorbance (254 nm) for both photocatalysts. Initial experiments were performed to determine the reaction yield as a function of catalyst loading in the slurry. The yields did not increase above a loading level of 0.5 g L⁻¹ of TiO₂ or Cs₃PW₁₂O₄₀, indicating maximum photon absorption for the experimental setup (54). This loading level was used for the quantum yield determinations. The extent of reaction was kept below 15–20% conversion to limit the effects of lowered substrate concentration. It was found that for TiO₂ the quantum yields (based on ferrioxalate actinometry) varied from 0.008 at 1 × 10⁻⁴ M NMP to 0.022–0.027 above 6 × 10⁻⁴ M NMP (Figure 3). Over a range of 10⁻⁴–10⁻² M NMP, the quantum yields for Cs₃PW₁₂O₄₀ were nearly invariant at 0.005–0.009 (Figure 3). The origin of the differing behaviors with respect to contaminant concentration is still under investigation; however, in practical terms, it appears that TiO₂ is the more efficient photocatalyst for NMP degradation.

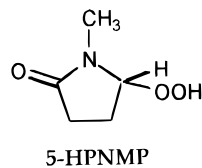
Discussion

Despite the contrast drawn between PW₁₂O₄₀³⁻ as a “molecular-based” material and TiO₂ as a semiconductor material, their redox characteristics are surprisingly similar. The ground-state redox potential for PW₁₂O₄₀^{4-/3-} is at -0.37 V vs NHE. The energy gap between the ground state and the excited LMCT state is 2.99 eV, which results in an excited-state potential vs NHE of +2.63 V (26). In comparison, the corresponding “ground-state” redox potential for TiO₂ at pH 3 is -0.2 V (55). With a band gap of 3.2 eV, the potential for reduction of the photogenerated valence-band hole is +2.9 V. The reduction potential for hydroxyl radical-hydroxide ion in homogeneous phase is +2.62 V vs NHE (56). Therefore, excitation of TiO₂ in water by UV light generates OH radicals at the surface that may be the primary oxidant in photo-

catalytic degradations (57). It appears from the above data that it may also be thermodynamically possible for the excited-state tungstate to generate OH radicals although the driving force is not as large as for TiO₂. Because of the small overvoltage, however, a rapid reaction with water is unlikely, whereas picosecond spectra (24) indicate initial oxidation of propanol in <20 ps. Efficient water oxidation on the surface of the tungstate colloid would depend on the surface environment making oxidation somewhat more favorable than in solution. Yamase has reported the detection of OH radicals by ESR spin trapping upon irradiation of related polyoxotungstates (58). However, polyoxotungstate species also possess an ability to undergo reversible multielectron reduction (59). In comparison, the $E_{1/2}$ value for oxidation of NMP from cyclic voltammetry is +2.1 V vs NHE (60). Thus, for both catalysts the potential exists for oxidation by both direct electron transfer and OH radical attack.

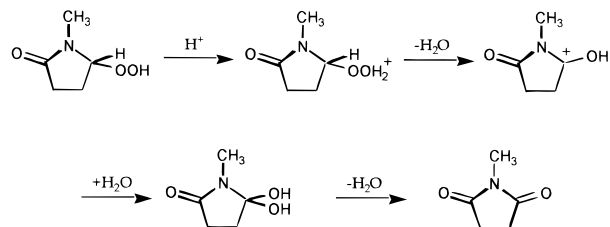
Chemical and electrochemical oxidation of NMP results in the substitution of carbonyl or hydroxyl groups at the α -carbon position, and it is well-known that the α -carbon of lactams such as NMP and 2-pyrrolidinone, is susceptible to H-atom abstraction (53, 60–63). Both OH radicals and excited-state polyoxotungstates are potent hydrogen atom abstractors (26, 64, 65). Thus, it is not surprising that for both photocatalysts, there is a substantial yield of NMS as a primary intermediate. An early study involving TiO₂ photocatalysis of NMP at relatively high concentrations (0.1 M NMP in water) showed nearly quantitative conversion to NMS under aerated conditions (66). However, no reaction was observed under deoxygenated conditions, and use of a metal-ion electron acceptor (Cu(II)) in the absence of oxygen led to the formation of an alkene elimination product rather than the carbonyl species. These findings underline the critical role of O₂ (or O₂-derived species) in the overall photocatalytic process.

It is generally accepted that O₂ promotes TiO₂ photocatalytic oxidation by acting as an electron acceptor, removing excess electrons from the surface of the semiconductor material and forming superoxide radical anions (which can subsequently protonate to form HO₂ radicals). The present results strongly suggest that O₂ or the derived superoxide also plays a reactive role in the TiO₂-based degradation of NMP. Masui et al. have shown that in oxygenated nonaqueous (acetonitrile) solution, the presence of a chemical H-atom abstractor (phthalimide *N*-oxyl) leads to NMS formation in high yield, most likely through a peroxide intermediate derived from O₂ substitution at the α -carbon (60). Recently, Drago et al. have synthesized and characterized 5-hydroperoxy-NMP (5-HPNMP) (61, 62). This species easily undergoes further reaction to form NMS.



An oxidation mechanism can be proposed that is consistent with these results. Photooxidation of NMP by TiO₂ is initiated via H-atom abstraction by a hydroxyl radical generated upon band gap excitation of the semiconductor. The attack occurs preferentially (but not exclusively, vide infra) at the α -carbon, resulting in a radical based at that position. Further attack by OH would be expected to yield 5-hydroxy-NMP (5-HNMP) by addition; however, attack by superoxide generated in the reductive photocatalytic step would yield the hydroperoxide intermediate. Upon protonation, 1° and 2° alkyl hydroperoxides can undergo a rearrangement to form carbonyls and alcohols or water (67,

68); in the case of NMP, this would lead directly to the formation of NMS:

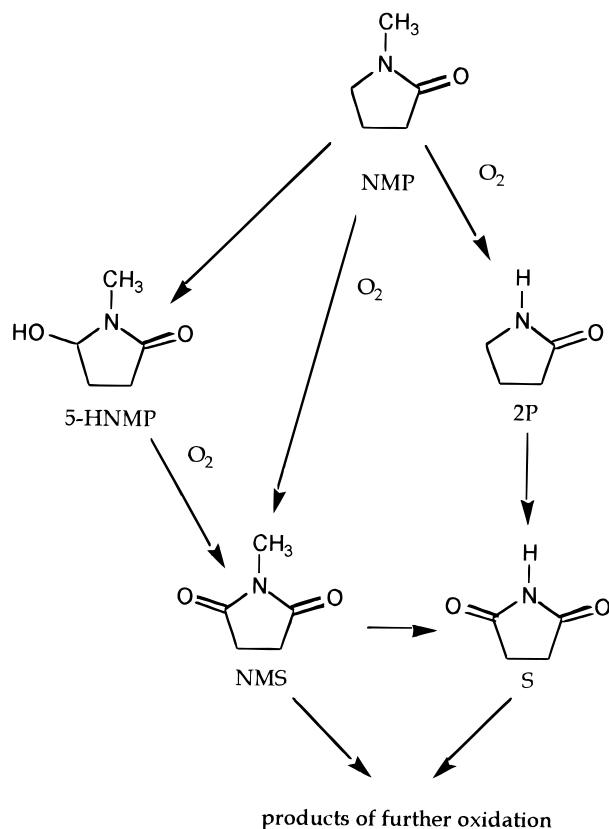


This is consistent with the high yield of NMS initially produced by TiO₂ photooxidation relative to NMP degradation (approximately 75% conversion at 2.5 min), and the low yield of 5-HNMP in Figure 2b, even at short irradiation times.

The similarity in intermediates makes it tempting to conclude that NMP degradation follows a mechanistic pathway derived from hydroxyl radical attack for Cs₃PW₁₂O₄₀ as well. However, in the case of Cs₃PW₁₂O₄₀, the primary product distributions (Figure 2) indicate that there are added complexities. After 2.5 min irradiation (Figure 2a), the yield of NMS from NMP was approximately 14%, with the significant presence of 5-HNMP. These results are similar to those found in the direct anodic oxidation of NMP in aqueous acetonitrile at a platinum electrode where the product ratio of 5-HNMP to NMS was 55:12% (yield based on conversion from NMP) (53). This is an indication that the hydroxy species could be preferentially formed in a direct oxidation process, such as on the surface of a platinum electrode. The low initial NMS yield for Cs₃PW₁₂O₄₀ photocatalysis would then indicate that direct oxidation of NMP on the surface of the excited polyoxometalate colloid is an important mechanistic pathway. Support for this possibility comes from the work of Hill et al. on the comparative photooxidation of tetrahydrothiophene by solution polyoxometalate and particulate TiO₂ (59). Anaerobic conditions led to the loss of reactivity of TiO₂; however, the polyoxometalate continued to function as a photooxidant, in part because of its ability to undergo reversible multielectron reduction. In the present case, two-electron oxidation of NMP by the polyoxometalate could lead to the formation of the alcohol by H-abstraction followed by electron transfer and water substitution of the resulting carbocation. Further oxidation of the hydroxy group leads to subsequent formation of the carbonyl group (i.e., NMS) as is well-known for the polyoxometalate photooxidation of alcohols and would account for the increased rate of formation of NMS after 10 min in Figure 2a.

A novel aspect of the present work is the early formation of succinimide by both TiO₂ and Cs₃PW₁₂O₄₀. In contrast to the formation of NMS, the yield of succinimide per amount of NMP degraded is very similar for both photocatalysts. Previous studies of NMP oxidation by photochemical and electrochemical means did not note the formation of succinimide by attack at the *N*-methyl group, although related seven-member ring lactams with *N*-methyl substituents showed demethylation upon direct anodic oxidation indicating that the *N*-methyl position is also potentially reactive toward oxidation (53, 60). *N*-Methylene groups with methyl or phenyl substituents also showed conversion to corresponding carbonyl forms upon chemically mediated H-atom abstraction in acetonitrile (60). In the case of photocatalyzed oxidation, abstraction of the methyl hydrogen followed by O₂ or HO₂ attack would lead to the formation of a reactive aldehyde substituent that would undergo further reaction to form 2-pyrrolidinone and formaldehyde or carbon dioxide. Subsequent oxidation at the α -carbon position as discussed above yields succinimide.

The following scheme summarizes the possible degradation pathways for TiO₂ and Cs₃PW₁₂O₄₀:



The oxidation proceeds through a combination of pathways to varying degrees for both photocatalysts. Direct oxidation of the contaminant as well as OH radical attack appears to be an important contributor to the degradation by the polyoxometalate. Further oxidation of succinimide in the presence of UV-light and TiO_2 leads to ring opening and mineralization to NH_4^+ and NO_3^- (69). Thus, photocatalyzed degradation appears to be an effective method for oxidative destruction of NMP contaminants (and in general, nonaromatic organic substances) in wastewater, with TiO_2 being the more efficient photocatalyst as also illustrated by our previous work with 2-propanol (42). However, the utilization of an additional significant degradation mechanism (i.e., direct oxidation) by the tungstate may make it an attractive alternative treatment in cases where TiO_2 photocatalysis cannot provide full mineralization. The most significant point may prove to be the reduced dependence on O_2 as the initial electron acceptor.

Acknowledgments

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