

## RESEARCH NOTE

Photocatalytic Selective Oxidation of Hydrocarbons  
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Received October 5, 1998; revised December 23, 1998; accepted December 26, 1998

The sustainable transformation of an inert alkane into its corresponding oxygenates has been the subject of intense chemical research. These oxygenates typically produced from processes using stringent conditions and materials offer disadvantages that include decreased selectivities to the partial oxygenates and by-product formation. As environmental concerns and regulations become more rigorous, the need for alternative catalytic oxidation processes that use mild or ambient conditions is increased. In this Note, the authors have investigated the use of photocatalysis as a low-temperature and "green" alternative for the direct and selective oxidation of alkanes with molecular oxygen.

**Key Words:** green chemistry; photocatalysis; hydrocarbon oxidation; selective oxidation; TiO<sub>2</sub>; aqueous.

## INTRODUCTION

The selective oxidation of alkanes and aromatics to their corresponding alcohols, ketones, aldehydes, and carboxylic acids offers an attractive synthesis of higher-value products from relatively inexpensive feedstocks. However, many of the current pathways to produce these products are environmentally hazardous, offer low single-pass conversions, and achieve product selectivities that are lower than desired.

Recent research has seen an increased effort in the investigation of the use of alternative oxidation technologies (AOTs) as catalytic processes for the oxidation of hydrocarbon substrates. One such alternative oxidation technology that can possibly avoid most of the above-mentioned pitfalls is photocatalysis. This light-induced catalytic reaction possesses unique reaction conditions that include ambient reaction temperatures and pressures, as well as the use of an inexpensive semiconductive material and nontoxic solvents. This material, TiO<sub>2</sub>, is biologically and chemically in-

ert, adding to the environmental friendliness of this process. On irradiation with ultraviolet light below a wavelength of ~390 nm, the inert anatase TiO<sub>2</sub> generates electron holes which are believed to have an oxidation potential of 3.2 V (1). The high-degree of oxidation potential of this material has been demonstrated by the photocatalytic activation of halogenated hydrocarbons, aromatics, and phenols for the complete destruction, i.e., mineralization, of these environmental pollutants (2–5).

Previous attempts to use photocatalysis for the production of oxygenates from saturated hydrocarbons have been reported (6–10); however, many of these studies were performed as a proof-of concept and the experimental conditions were or may not have been fully optimized. Our research efforts have been directed toward demonstrating the feasibility and gaining an understanding of using photocatalysis as a synthesis tool. In doing so, the high oxidation potential of TiO<sub>2</sub> must be controlled to prevent overoxidation of the primary oxygenates. This aqueous-based oxidation process is performed as a screening tool as well as providing experimental information on the conditions necessary for the activation of hydrocarbons. This experimental information was then used in the design, construction, and implementation of a gas-phase photocatalytic reactor system (11, 12). It is anticipated the continuous-flow gas-phase reactor, which eliminates a solvent stream, offers a more controlled and characterized substrate : water : oxidant feed stream, and the need for separation steps will increase the feasibility of using a light-induced process for the oxidation of alkanes.

In this Note, the authors have investigated the use of photocatalysis as a low-temperature "green" alternative for the direct and selective oxidation of saturated hydrocarbons with molecular oxygen in an aqueous environment. Research has been directed toward the use of a heterogeneous liquid-phase reactor for the partial oxidation of cyclohexane, toluene, methylcyclohexane, ethylbenzene, and cumene to their corresponding oxygenates.

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## METHODS

**Photoreactor.** Oxidation experiments were performed in an Ace Glass Micro Photochemical reactor assembly. This apparatus consists of a 20-ml quartz batch annular reactor. The TiO<sub>2</sub> slurry was stirred mechanically using a magnetic stirrer and additional agitation was provided by bubbling air through the reactor. Air also served as an additional oxidant in this process. Illumination was provided by 5.5-W quartz Pen-Ray, low-pressure, cold cathode mercury lamp. Maximum emission for this lamp occurs at a wavelength of 365 nm. The lamp was placed in an 11-mm-i.d. jacketed immersion well. Water was allowed to flow through the jacket to remove any heat produced by the lamp. The entire reactor assembly was wrapped with aluminum foil to prevent light from entering the apparatus.

**Reagents.** Finely divided titanium dioxide (TiO<sub>2</sub>) P25 was used as received from Degussa. This catalyst is mostly anatase phase and has a BET surface area and average particle size of  $50 \pm 10 \text{ m}^2 \text{ g}^{-1}$  and 30 nm, respectively. Toluene, cyclohexane, methylcyclohexane, cumene, ethylbenzene, and *o*-dichlorobenzene were purchased from Aldrich. All chemicals were used as received, without any further purification.

**Oxidation procedure.** A specified quantity of TiO<sub>2</sub> was added to 13 ml of deionized water, and the mixture was stirred for 10 min while being purged with oxygen. The substrate (2.0 ml) was introduced into the reaction mixture by pipett and the lamp assembly added. If additional oxidant was needed, air was bubbled into the reactor during the specified reaction time.

**Analysis.** All samples were centrifuged for 10 min to facilitate separation of the TiO<sub>2</sub> particles from the solution and then filtered. The filtrate was then collected for GC/MS analysis. The supernate was rinsed with ethanol to remove any additional products and then centrifuged and filtered. On separation the filtrate fraction was collected for GC/MS analysis.

The reaction products were analyzed using a Hewlett-Packard 6890 gas chromatograph outfitted with a low-bleed HP-5MS (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ) column and a split/splitless injector. The carrier gas used was helium. A Hewlett-Packard 5973 mass selective detector equipped with a quadrupole mass filter was used as the detector. Each sample had 0.05 ml of *o*-dichlorobenzene added as an internal standard. Samples were then analyzed in duplicate with an injection volume of 1.0  $\mu\text{l}$ . Quantification of the oxygenated products was obtained using a multipoint calibration curve for each product.

Analysis for CO and CO<sub>2</sub> was performed on a Hewlett-Packard 5890 gas chromatograph equipped with a J.W. Scientific GS-GasPro capillary column (30 m  $\times$  0.32 mm) and a thermal conductivity detector. Infrared spectroscopy analy-

sis was performed on a Perkin-Elmer Spectrum 2000 FT-IR spectrometer equipped with a tungsten halogen source and a DTGS detector. The sample was prepared as a KBr pellet.

## RESULTS AND DISCUSSION

Prior to performing the oxidation reactions, a number of blank experiments were performed. These experiments would demonstrate if the desired oxidation reactions were proceeding via a photocatalyzed pathway. Conditions for the blank runs constituted reactions performed in the absence of catalyst and "dark" reactions, in the absence of UV light. Each blank experiment exhibited no measurable amount of oxidation products for each substrate, thereby demonstrating the oxidation reaction was proceeding via a photocatalyzed mechanism.

The substrates were chosen for their unique properties. Toluene, ethylbenzene, and cumene, each being an aromatic and possessing benzylic carbons, are expected to be quite reactive toward a free radical oxidation. Cumene, with a tertiary benzylic carbon, offering a more stable free radical, should be the most responsive toward oxidation. Cyclohexane and methylcyclohexane, both saturated hydrocarbons, were chosen to demonstrate the feasibility of using this oxidation reaction for the activation of alkanes. Methylcyclohexane, with its pendant methyl group, allowed us to observe the regioselectivity of this free radical oxidation reaction. In most cases, the overoxidation of the primary oxygenates to aldehydes and ketones can also be observed.

Oxidation experiments performed with toluene (See Table 1) exhibited a direct selectivity to benzaldehyde (90.9%), the result of overoxidation of benzyl alcohol (9.1% selectivity). Detection for the formation of benzoic acid by derivatization of the aqueous and solid fractions with BF<sub>3</sub>/MeOH was attempted. Results from this test determined no benzoic acid had been produced. IR analysis of the spent catalyst also confirmed no benzoic acid had been generated. An overall conversion of 11.61%, based on products, was obtained for this oxidation reaction.

Experiments for the oxidation of cumene (Table 1) were not as successful. It was anticipated cumene would be more reactive toward oxygenation under the current conditions. However, no oxidation products were observed. Attempts to increase the oxidizing power of the reaction, by adding of 30% H<sub>2</sub>O<sub>2</sub> (3.0 ml), adding larger quantities of catalyst (twofold), bubbling air (10 ml min<sup>-1</sup>) through the reaction slurry, and increasing reaction time (8 h), also demonstrated lack of oxidized products. Navio and co-workers (13) and Nizova and Shul'pin (14) reported that the oxidation of cumene proceeds via formation of a cumylhydroperoxide intermediate. This intermediate then forms acetophenone and methanol via a C-C bond cleavage mechanism. The methanol is subsequently overoxidized to form CO<sub>2</sub>. The decreased activity in our process is possibly due to an

**TABLE 1**  
**Results for Liquid-Phase Photocatalyzed Oxidation**  
**of Hydrocarbons<sup>a</sup>**

Substrate	Products	Selectivity <sup>c</sup> (%)	Conversion <sup>d</sup> (%)
Toluene	Benzyl alcohol	9.1	11.61
	Benzaldehyde	90.9	
Methylcyclohexane	1-Methylcyclohexanol	15.52	8.18
	2-Methylcyclohexanol	7.63	
	3-Methylcyclohexanol	15.89	
	4-Methylcyclohexanol	4.94	
	2-Methylcyclohexanone	15.18	
	3-Methylcyclohexanone	24.20	
	4-Methylcyclohexanone	10.86	
1-Methanolcyclohexane	5.77		
Cyclohexane <sup>b</sup>	Cyclohexanol	30.08	4.24
	Cyclohexanone	44.03	
	2-Cyclohexeneone	5.10	
	1,1'-Bicyclohexane	20.79	
Ethylbenzene	Acetophenone	100	6.71
Cumene	None	None	0.00

<sup>a</sup> Reaction conditions, 1.0 g TiO<sub>2</sub> (Degussa P25), 13 ml deionized H<sub>2</sub>O, 2 ml substrate, 5-W UV-vis Pen Ray lamp, reaction time 2 h.

<sup>b</sup> 3.0 ml 30% H<sub>2</sub>O<sub>2</sub> added.

<sup>c</sup> Selectivity is calculated as moles of specified product/total moles of oxygenates expressed as a percentage.

<sup>d</sup> Conversion is calculated as total moles of oxygenates/moles of substrate (initial) expressed as a percentage.

insufficient concentration of cumylhydroperoxide. The inability to form a large quantity of the alkylhydroperoxide may be due to the low lamp power, an insufficient quantity of oxidant, or solvent incompatibility. Further demonstrating the lack of reactivity of cumene is the inability to produce phenol or acetone. This result is attributed to the lack of oxidation potential necessary for the cleavage of the benzylic and tertiary carbon bond. Additional investigation is needed to determine the exact cause and how to improve on the current results.

To further investigate the inability to activate cumene, oxidation experiments were performed on ethylbenzene. This molecule, which possesses a secondary benzylic carbon, should afford acetophenone as the sole product. Table 1 exhibits the results obtained for this oxidation after 2 h of reaction. The sole reaction product, acetophenone (100% selectivity), was obtained with an overall conversion of 6.71%. No additional products were obtained, including CO or CO<sub>2</sub>. It is interesting that only one product was obtained, in addition to the lack of cleavage products. It is apparent the oxidation of ethylbenzene is proceeding in a manner identical to that for toluene, benzylic carbon attack and subsequent oxidation.

Results obtained for the oxygenation of the saturated alkanes were also encouraging (see Table 1). Oxidation ex-

periments with methylcyclohexane yielded products with oxidation at a number of positions about the ring. Of these products the most prevalent were the four isomers for methylcyclohexanol and the three isomers for methylcyclohexanone. Higher selectivities were exhibited for the products with oxidation at the 2- and 3-positions. Also observed was the direct oxidation of the primary methyl position to produce 1-methanolcyclohexane (5.77% selectivity). Although oxidation at this position is difficult, as indicated by the low selectivity, this process at least allows for this oxidation to occur. Oxidation at the tertiary carbon accounts for 15.52% of the oxygenates, while oxidation at the secondary carbons accounts for 78.7% of the oxidized products. An overall conversion of 8.18% was obtained for methylcyclohexane.

The oxidation of cyclohexane also results in the production of the corresponding oxygenates. Attempts to oxidize cyclohexane in the absence of hydrogen peroxide did not afford any oxygenates. On addition of hydrogen peroxide (3.0 ml), cyclohexanol and cyclohexanone were obtained. It is speculated that the addition of hydrogen peroxide provides the reaction with a greater concentration of OH<sup>•</sup> species necessary for activation of the inert saturated hydrocarbon. Oxidation products obtained were cyclohexanol (30.08% selectivity) and cyclohexanone (44.03% selectivity), along with small quantities of 2-cyclohexeneone (5.1% selectivity) and trace quantities of cyclohexylhydroperoxide. The coupling reaction of two cyclohexane radical species to produce 1,1'-bicyclohexane (20.79% selectivity) also occurred. It is anticipated that on increasing the oxidant concentration in the reaction slurry, the undesired termination reaction can be inhibited and replaced with oxygenation of the radical species. Blank runs performed for the oxidation of cyclohexane with hydrogen peroxide and UV light in the absence of TiO<sub>2</sub> did produce trace quantities of cyclohexanol and cyclohexanone. However, the amounts produced were considerably less than those generated in the presence of TiO<sub>2</sub>, demonstrating the decomposition of hydrogen peroxide into OH<sup>•</sup> radicals in the presence of light is not solely responsible for the oxygenation of cyclohexane.

Increasing the oxygen concentration in the reaction slurry, by bubbling air or molecular oxygen, did not result in an increase in conversion. Since the reactor is not a closed system, bubbling gas increases the loss or escape of the volatile substrates and oxygenates from the solution. The design of the current reactor apparatus did not allow for the system to be pressurized. This will be corrected in the future to allow additional oxidant to be supplied to the reaction slurry.

Although a batch reactor was used, a high degree of selectivity toward the partial oxygenates was achieved. Further oxidation of the alcohols to ketones and aldehydes was obtained in the case of ethylbenzene, cyclohexane, and

methylcyclohexane. However, subsequent overoxidation and ring opening did not occur, exhibiting the selective nature of this oxidation process. As with all batch processes decreasing reaction time results in higher selectivities with an overall decrease in conversion. Increasing reaction times results in an opposite effect for selectivity and conversion. Therefore, a medium must be obtained; in this case it was 2 h. Experiments performed with increased reaction times (4 and 6 h) did lead to increased conversions, but not much improved over those represented in Table 1. Selectivities toward the alcohols did decrease along with subsequent increase in aldehyde and ketone formation, but degradation of the oxygenates did not result. This may be attributed to the low lamp power (5 W) used and the limited quantities of oxygen within the reactor.

### CONCLUSIONS

The direct activation and selective oxidation of saturated hydrocarbons to their corresponding oxygenates via a "green" process offer an attractive pathway for the production of commercial oxygenates. A catalytic oxidation reaction that proceeds in water with molecular oxygen at room temperatures offers many of the desired components for an oxidation process. The results for the photocatalyzed oxidation of toluene, ethylbenzene, cyclohexane, and methylcyclohexane demonstrate the feasibility of using this alternative oxidation technology as a synthesis tool. Further research must be performed to increase the efficiency and kinetics of the described reactions. Although this study is in the early stages, the current results demonstrate the ability to activate and selectively produce oxygenated products, without extensive overoxidation and degradation of the desired oxygenates, leading to consideration of this tech-

nology as a potential candidate for replacement of current oxidation processes.

### ACKNOWLEDGMENTS

This research was supported in part by an appointment to the Postgraduate Research Program at the U.S. Environmental Protection Agency (USEPA), Office of Research and Development, at the National Risk Management Research Laboratory administered by the Oak Ridge Institute for Science and Education through an interagency agreement between the U.S. Department of Energy and the USEPA.

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