Corona-induced photoxidation of alcohols and hydrocarbons over TiO_2 in the absence of a UV light source – A novel and environmentally friendly method for oxidation†

Unnikrishnan R. Pillai‡ and Endalkachew Sahle-Demessie*

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Corona-induced photooxidation is a novel oxidation methodology for the efficient oxidation of alcohols and hydrocarbons utilizing the advantage of both the high oxidizing power of ozone formed in the reactor as well as the photooxidation capability of the UV light generated during the corona discharge.

Corona is a low energy (10–20 eV) electrical discharge around a conductor in a gas that occurs when the electric field around the conductor exceeds the value required to ionize the gas, but is insufficient to cause a spark. The corona discharge also produces a low power UV light of the order of $\sim$2.0 W in comparison to the high power UV light obtained from a UV source (1000 kW). Corona induced non-thermal plasma can be produced by using pulsed streamer corona or by dielectric barrier discharge.[1,2] The corona reactors have been primarily used for the purification of air and water as well as in the exhaust gas treatment for the decomposition of VOCs and removal of SO_2 and NO_x.[3–8] However, this potential technology has not been explored for other applications such as the oxidation of alcohols and hydrocarbons, which are of immense importance industrially.[9–11] This could be highly efficient and economical due to the powerful oxidizing property of ozone combined with its low energy utilization. The process is also environmentally friendly, as it does not involve the use of any harmful materials or precursors. Herein we report the application of a corona discharge reactor for the oxidation of alcohols and hydrocarbons to useful intermediates over a TiO_2 catalyst that can act as a photocatalyst in the presence of UV light generated during the corona discharge.

The corona discharger system includes a power supply with a variable voltage controller, a high-voltage transformer, and the treater station through which the material to be reacted passes (see ESI†). The treater station consists of a cylindrical ceramic tube of 30 cm length and 6 cm i.d containing a series of electrodes on its inside wall with a 0.5–1.0 cm gap on either side. The electrodes emit high-voltage corona discharge into the gap, ionizing the gas (oxygen and the feed vapor) inside. The ceramic tube containing the electrodes is placed in a plastic jacket, which is cooled by flowing water during its operation. The corona reactor assembly used in this study consists of a cylindrical glass tube of 28 cm length and 4 cm i.d closed at lower end and inserted inside the outer ceramic tube described above with proper bolted sealing at both the ends closing the corona compartment. A TiO_2 coated pad prepared by dip-coating method on a pre-shrunk silica quartz fiber mat of dimension 7.6 × 35 cm^2 is wrapped on a 26 cm long glass tube of 2 cm i. d and inserted inside the outer glass tube.[12] The ceramic and glass tube reactors were connected in such a manner that the ozone generated inside the ceramic corona discharger is carried into the glass tube along with the vapors of the substrate to be oxidized. The products come out through the vent and are condensed in a collector that is pre-cooled using a liquid N_2–isopropanol bath (−40 °C) and analyzed by GC-MS. The temperature inside the reactor near the catalyst surface is measured using a thermocouple placed inside the reactor just above the TiO_2 pad and measured to be around 80 °C throughout the reaction. It is found that approximately 5% ozone is generated in the corona reactor at the maximum operating power of 254 Watts (2.1 A) and an oxygen flow of 0.50 L min^{-1}. The amount of ozone generated increases from approximately 4% to 5% as the oxygen flow rate increases from 0.10 to 0.50 liter per minute.

The results of corona-induced photooxidation of alcohols in the presence of TiO_2 photocatalyst are shown in Table 1. It is apparent that the corona oxidation method is exceptionally useful in the selective oxidation of alcohols. Both activated and non-activated alcohols are converted to the corresponding carbonyls efficiently. The selectivity to the corresponding carbonyl product is almost complete for secondary and cyclic alcohols. Primary alcohols, on the other hand, are converted mainly to their formic esters. The initial high reaction rate declines after a pass time of 2 h and then more or less stabilizes. One interesting aspect of TiO_2 containing corona reactor is in the oxidation of primary alcohols, which form the corresponding formate ester as the main product unlike the acid product that is usually observed in the conventional photooxidation or oxidation using other traditional methods. The selectivity of primary alcohol to its corresponding aldehyde may be improved by varying the corona power, amount of ozone generated (O_2 flow through the reactor) or the flow rate (space velocity) of the alcohol in the reactor (Fig. 1). Primary aldehyde selectivity increases with decrease in corona power (Fig. 1a) and ozone amount generated (Fig. 1b) or by increasing the feed flow rate (Fig. 1c).

The relevance of this oxidation technology is further verified by extending the protocol to the oxidation of hydrocarbons especially the cycloalkanes such as cyclohexane, cycloheptane and cyclooctane (Table 2). Alkane oxidation is usually very difficult to achieve

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† Electronic supplementary information (ESI) available: experimental details and pictures of the corona reactor assembly, power supply and inside view of the corona generator. See http://www.rsc.org/suppdata/cc/b4/b418812h/

‡ Present address: New technology Research, Philip Morris USA, Richmond, VA 23234.

*Sahle-Demessie.Endalkachew@epa.gov

Table 1 Corona-induced photooxidation of alcohols in the presence of TiO_2[a]

					Selectivity (%)			
Entry No.	Substrate	Products	Time(h)	Conversion (%)	A	B	C	D
1	1-Pentanol	Pentanal- A	1	52	—	81	19	—
		Pentyl formate-B	2	42	—	54	16	30
		Pentyl acetate-C	3	37	—	34	15	51
		Pentanoic acid-D	4	38	—	35	16	49
2	2-Pentanol	2-Pentanone-A	1	72	100	—	—	—
			2	60	100	—	—	—
			3	46	100	—	—	—
			4	45	100	—	—	—
3	Cyclopentanol	Cyclopentanone-A	1	82	100	—	—	—
			2	71	100	—	—	—
			3	55	100	—	—	—
			4	55	100	—	—	—
4	1-Hexanol	Hexanal-A	1	62	12	86	2	—
		Hexyl formate-B	2	54	8	45	47	—
		Hexanoic acid-C	3	52	7	49	44	—
			4	52	7	48	45	—
5	2-Hexanol	2-Hexanone-A	1	88	100	—	—	—
		Formic acid sec-butyl ester-B	2	72	100	—	—	—
			3	60	91	9	—	—
			4	60	89	11	—	—
6	Cyclohexanol	Cyclohexanone-A	1	98	78	14	8	—
		Cyclohexyl formate-B	2	89	83	11	6	—
		Cyclohexyl acetate-C	3	79	75	15	10	—
			4	75	80	13	7	—
7	Cycloheptanol	Cycloheptanone-A	1	100	100	—	—	—
			2	90	100	—	—	—
			3	88	100	—	—	—
			4	85	100	—	—	—
8	1-Octanol	Octanal-A	1	94	—	100	—	—
		Octyl formate-B	2	80	10	39	5	46
		Octyl acetate-C	3	80	8	34	5	52
		Octanoic acid-D	4	78	10	33	6	51
9	2-Octanol	2-Octanone-A	1	91	100	—	—	—
		Formic acid 1-methyl-heptyl ester-B	2	89	93	7	—	—
		Heptanoic acid-C	3	88	87	7	6	—
		Hexanoic acid-D	4	88	88	7	6	—
10	Benzyl alcohol	Benzaldehyde-A	1	36	75	—	25	
		Benzyl formate-B	2	27	95	—	5	
		Benzoic acid-C	3	20	100	—	—	
			4	19	100	—	—	
11	1-Phenyl ethanol	Acetophenone-A	1	95	78	—	11	11
		Formic acid benzyl ester-B	2	95	81	—	13	6
		Benzyl phenyl ether-C	3	95	79	2	15	4
		Toluene-D	4	95	81	3	16	—
12	2-Phenyl ethanol	Phenyl acetaldehyde-A	1	96	—	100	—	—
		Formic acid phenethyl ester-B	2	95	—	90	10	—
		Acetic acid phenethyl ester-C	3	96	—	92	8	—
			4	95	—	90	10	—

[a] Reaction conditions: Substrate flow = 9 mL h^{-1}, O_2 flow = 0.50 L min^{-1}, temperature = 80 °C, Corona power = 254.1 Watts

due to the very inert nature of the C–H bond.[11,13,14] The corona oxidation is also found to be highly useful for the hydrocarbon oxidation where relatively high conversions in the range 20–35% could be achieved (Table 2). The initial higher reaction rate is not diminished even after 5 h of reaction pass time, unlike in the case of alcohol oxidation where the initial high rate declines after 2 h (Table 1).

These results reveal that the corona oxidation is an efficient oxidation technology for the oxidation of alcohols and hydrocarbons wherein no expensive or environmentally undesirable materials are employed. The unreacted reactants can easily be fed back to the reactor and recycled. A comparison of the power utilization (Fig. 2) shows a two fold increase in the conversion and a ten fold decrease in power consumption for the corona oxidation as compared to that in the case of the conventional photocatalytic oxidation using a powerful UV light (250 *vs* 2500 Watt per pass).

A control experiment carried out using cyclopentanol in the absence of a photocatalyst (no TiO_2) shows a much lower conversion (50%) when compared to the reaction in the presence of TiO_2 catalyst (82%). No reaction is observed in the case of a reaction using a corona discharger connected in series with another glass reactor wherein the ozone generated in the former is brought in contact with the vapors of cyclopentanol in the glass reactor kept at the same temperature as that in the original experiment (80 °C). These results highlight the important role of corona in causing the oxidation reaction and also suggest that oxidation using corona reactor is not merely due to the formation of ozone. The presence of TiO_2 improves the alcohol conversion and also

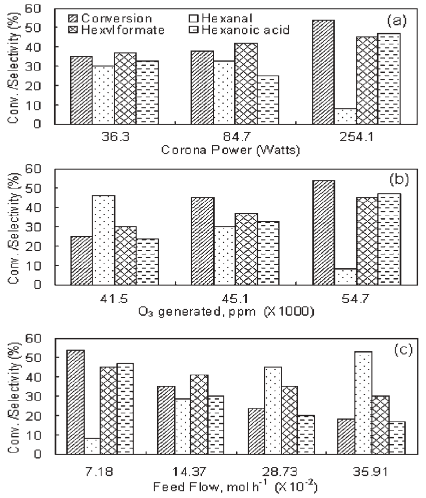

Fig. 1 Effect of (a) corona power (b) amount of O_3 and (c) feed flow rate on the conversion and selectivity of corona-induced photooxidation of 1-hexanol.

Table 2 Corona-induced photooxidation of hydrocarbons in the presence of TiO_2[a]

Entry No.	Substrate	Products	Time (h)	Conversion (%)	Selectivity (%) A	B	C
1	Cyclohexane	Cyclohexanol-A	1	18	—	100	—
		Cyclohexanone-B	2	20	10	90	—
		Cyclohexyl formate-C	3	31	12	83	5
			4	38	24	71	5
			5	38	24	71	5
2	Cycloheptane	Cycloheptanone-B	1	5	—	100	—
			2	11	—	100	—
			3	17	—	100	—
			4	18	—	100	—
			5	19	—	100	—
3	Cyclooctane	Cyclooctanone-B	1	7	—	100	—
			2	11	—	100	—
			3	22	—	100	—
			4	22	—	100	—
			5	22	—	100	—

[a] Reaction conditions: Substrate flow = 9 mL h^{-1}, O_2 flow = 0.50 L min^{-1}, temperature = 80 °C, Corona power = 254.1 Watts

affects the product selectivity, especially in the case of primary alcohols. Generally, corona treating is a very effective way to increase the surface tension of virtually any material. For example, the result after corona treatment on a surface is a surface that is unchanged to the naked eye, but is much more receptive to inks, coatings, and adhesives. In a similar fashion, the substrate material may also be getting activated upon exposure to corona. Corona discharge process also produces chemical free radicals and ions.[2,3] In addition, the generation of UV light could produce electron-hole pairs[15] that is believed to have an oxidation potential of *ca.* 3.0 V, and has, therefore, considerable oxidizing capability. Therefore, the combined effects of ozone and UV light generation result in the oxidative chemical transformation. Although ozone in the gaseous form is both toxic and corrosive, it presents no safety or handling problems in properly designed operating systems. Unlike most other oxidants that are stored on-site in bulk form, ozone is produced on-site in low concentrations and immediately consumed. Consequently, any accidental leakage can be easily controlled, as evidenced by ozone's long safety history in many applications.

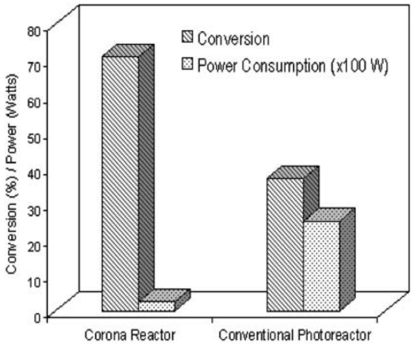

Fig. 2 Comparison of conversion and the power utilization for the corona reactor and a conventional photoreactor for the oxidation of cyclopentanol to cyclopentanone at a feed flow rate of 6.0 mL min^{-1} and a reaction pass time of 2 h.

In summary, a novel oxidation methodology is reported for the efficient oxidation of alcohols and hydrocarbons using a corona reactor. This oxidation protocol utilizes the advantage of both the high oxidizing power of ozone formed in the reactor as well as the photooxidation capability of the UV light generated during the ozone formation.

Unnikrishnan R. Pillai‡ and Endalkachew Sahle-Demessie*
National Risk Management Research Laboratory, Sustainable Technology Division, MS 443, United States Environmental Protection Agency, Cincinnati, Ohio-, 45268, USA.
E-mail: Sahle-Demessie.Endalkachew@epa.gov; Fax: 011-513-569-7677

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