

# Method for Predicting Photocatalytic Oxidation Rates of Organic Compounds

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## ABSTRACT

In designing a photocatalytic oxidation (PCO) system for a given air pollution source, destruction rates for volatile organic compounds (VOCs) are required. The objective of this research was to develop a systematic method of predicting PCO rate constants by correlating rate constants with physical-chemical characteristics of compounds. Accordingly, reaction rate constants were determined for destruction of volatile organics over a titanium dioxide ( $\text{TiO}_2$ ) catalyst in a continuous mixed-batch reactor. It was found that PCO rate constants for alkanes and alkenes vary linearly with gas-phase ionization potential (IP) and with gas-phase hydroxyl radical reaction rate constant. The correlations allow rates of destruction of compounds not tested in this research to be predicted based on physical-chemical characteristics.

## INTRODUCTION

The 1990 Clean Air Act Amendments require more stringent control of smaller sources of hazardous air pollutants (HAPs) and volatile organic compounds (VOCs) that are precursors to tropospheric  $\text{O}_3$  formation. In addition, with the recent promulgation of an 8-hr standard for  $\text{O}_3$ , new areas in the United States will be designated

### IMPLICATIONS

The 1990 Clean Air Act Amendments require more stringent control of smaller sources of hazardous air pollutants (HAPs) and VOCs that are precursors to tropospheric  $\text{O}_3$  formation. In addition, with the recent promulgation of an 8-hr standard for  $\text{O}_3$ , new areas in the United States will be designated non-attainment and may need to control precursor VOC emissions from smaller sources. PCO, a relatively new technology, shows promise for economically controlling HAPs and VOCs from smaller sources. This research develops a method for predicting PCO rate constants, which will be useful in sizing and designing photocatalytic systems.

non-attainment and may need to control precursor VOC emissions from smaller as well as larger sources. Technologies like incineration and condensation that have traditionally been applied to larger sources of VOCs will in many cases not be cost-effective for smaller sources. An alternative technology that has been under development over the past two decades, photocatalytic oxidation (PCO) shows promise for economically controlling VOCs from smaller sources, such as wastewater treatment plants, dry-cleaning facilities, painting facilities, carbon regeneration plants, air-stripping towers, soil venting processes, hazardous waste incinerators, and municipal landfills.<sup>1-3</sup> Operating at ambient temperatures and pressures, PCO can also reduce concentrations of VOCs that are hazardous air pollutants (HAPs) and indoor air pollutants.<sup>4,5</sup> It has also shown promise for degrading various inorganic and metal ions and even biological pathogens such as bacteria and viruses.<sup>6,7</sup>

Rather than simply transferring contaminants from one medium to another, PCO systems can convert VOCs completely to  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , leaving no harmful byproducts (in the case of chlorinated compounds, HCl is produced as well). PCO systems can handle a large number of different VOCs simultaneously and can also handle humid gas streams. They can effectively destroy chlorinated compounds, although they may have difficulty with completely halogenated compounds.

Because of the strong dependence of PCO cost on VOC concentration and because other methods, such as condensation, are suitable for high-concentration waste streams, PCO is best suited to low-concentration (1000 ppm or less) waste streams.<sup>8</sup> In addition, PCO is best suited to low- to moderate-volume streams (<20,000 cfm) because its modular nature offers system flexibility, a key advantage when treating smaller-flow-rate streams.<sup>9</sup>

PCO converts organic compounds to  $\text{CO}_2$  and water through transmission of ultraviolet radiation to a solid catalyst. Of the various semiconductor catalysts that have

been tested, titanium dioxide (TiO<sub>2</sub>) has been found to be the most effective for destroying organic compounds.<sup>10,11</sup> UV light of wavelength 350–400 nm is used to promote an electron to the conduction band of TiO<sub>2</sub>. The promoted electron leaves a positively charged hole behind in the valence band. Although the exact mechanism is not completely understood, it is believed that in the presence of water vapor, the hole (an excellent oxidizing species) oxidizes OH<sup>-</sup> from water vapor to form a hydroxyl radical (OH°). The OH°, which is extremely reactive, acts as a nonselective oxidizer and repeatedly attacks most organics, converting them to CO<sub>2</sub> and water via free radical reactions. Although PCO can occur via other mechanisms in the absence of water vapor, catalytic activity has been found to decrease dramatically after only a few minutes of irradiation and eventually to become negligible.<sup>12,13</sup> Thus, this research focused only on PCO with water vapor present.

### RESEARCH OBJECTIVE

Reaction rates are important in reactor design because they determine the length of time the gas stream will need to reside in the reactor to achieve the desired level of destruction. If the gas flow rate is fixed, the required gas residence time determines the necessary reactor volume: for a slower reaction, a longer residence time and a larger reactor will be required. Thus, to size a photocatalytic reactor, destruction rates for HAPs and VOCs are needed.

So that destruction rates do not have to be experimentally determined for every candidate organic compound individually, a systematic method of PCO rates would be useful, especially given the large number of organics that would be candidates for PCO. However, little research information is currently available to develop a systematic way of predicting PCO rates. Typical studies measure destruction rates for a few compounds as isolated cases without generalizing the results. Reaction rates found in the literature for different compounds cannot easily be compared because of various empirical factors that cause reaction rates to vary from one experimental system to another, such as catalyst pretreatment. For factors that can be explicitly accounted for in rate expressions, such as light intensity and catalyst surface area, sufficient information usually is not available in the literature for rate constants from different studies to be compared. Therefore, this research aimed to develop a systematic method of predicting PCO rates for organic compounds in air. PCO rates were measured for volatile straight-chain alkanes, alkenes, and alcohols to determine whether PCO rate constants could be correlated with physical-chemical characteristics, such as ionization potential (IP) and OH° reaction rate constant.

IP is the energy required to remove an electron from an outer energy level of a molecule. The IP serves as an inverse measure of the tendency of a gaseous molecule to lose an electron and form a gaseous ion. The larger a compound's IP, the greater the energy required to form a gaseous ion and the lower the compound's reactivity. Thus, the larger a compound's IP, the lower the PCO rate constant would be anticipated to be.

Because PCO is thought to proceed primarily via OH° attack, it follows logically that a compound's PCO rate constant would correlate directly with the compound's measured atmospheric OH° reaction rate constant. In other words, the faster a compound reacts with OH°, the faster its destruction in the photoreactor would be expected to be.

If a compound's PCO reaction rate constant correlates with IP, it would be also be expected to correlate with the OH° reaction rate constant because gas-phase OH° reaction rate constants themselves have been shown to correlate with IP. Gaffney and Levine<sup>14</sup> developed structure-reactivity relationships to allow estimation of rate constants for reactions between organics and OH° based on physical properties of the organics. The correlation between OH° reaction rate constant and IP presented by Gaffney and Levine is<sup>14</sup>

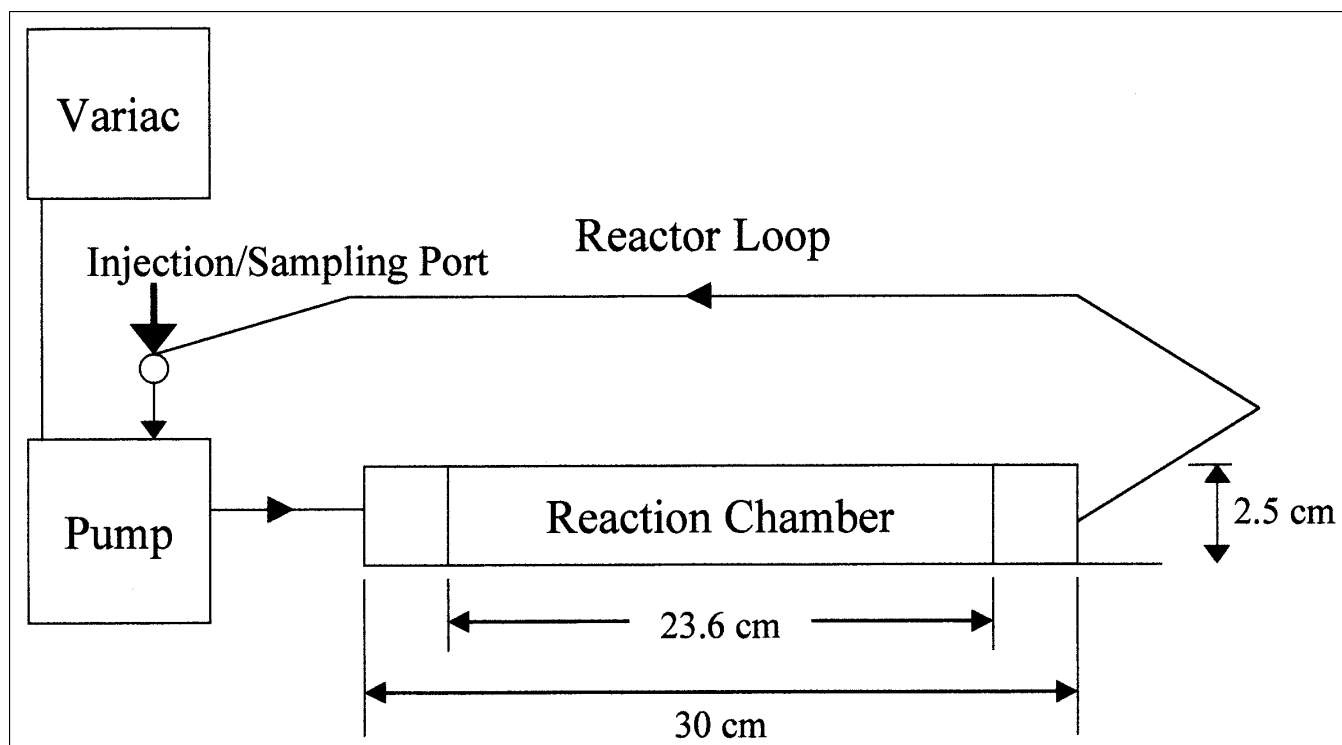
$$\log k_{\text{OH}} = -0.613 (\pm 0.039) \times \text{IP} - 4.68 (\pm 0.37) \quad (1)$$

Measurement of rate constants for photocatalytic oxidation of alkanes, alkenes, and alcohols is important because these classes of compounds play significant roles in O<sub>3</sub> smog formation. Alkenes, such as ethene and propene, are among the most important O<sub>3</sub> generators in urban air. In Los Angeles air, *i*-pentane and butane have been shown to be the most effective O<sub>3</sub>-forming alkanes, stemming from their concentration and reactivity. Ethanol, an alternative motor-vehicle fuel, oxidizes in the atmosphere to produce acetaldehyde, a precursor to PAN.<sup>15</sup>

### EXPERIMENTAL METHODS

Degussa's P-25 grade TiO<sub>2</sub>, which is widely used in photocatalysis research, was used as the photocatalyst. Adapting a procedure employed by McLintock and Ritchie,<sup>16</sup> TiO<sub>2</sub> was deposited onto a 2.5 × 30 cm glass plate by immersing the plates in a suspension of TiO<sub>2</sub> in distilled water and allowing the water to evaporate, leaving behind a TiO<sub>2</sub> coating on the plate surface. Using a Hitachi S-4500 field emission scanning electron microscope (SEM) to obtain SEM images of a cross-section of the TiO<sub>2</sub> layer, the coating was determined to be about 4 particles thick, or about 80 nm.

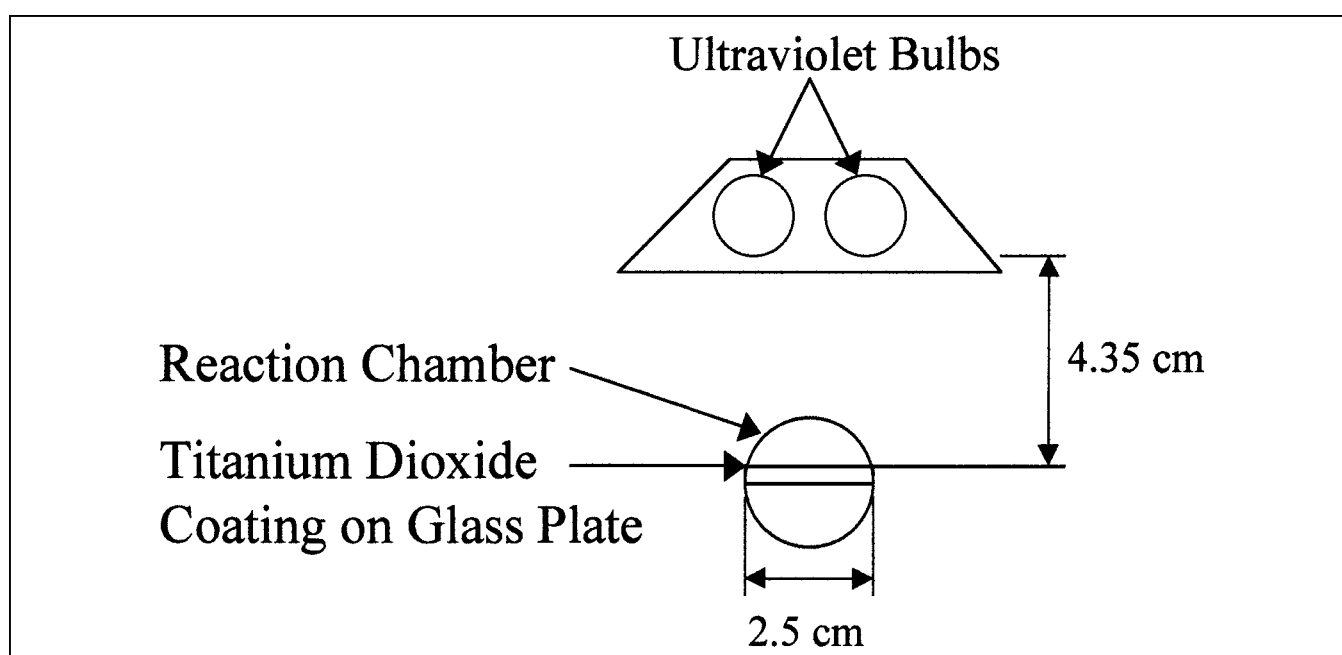
Figure 1 shows the closed loop batch reactor used to measure compound destruction rates. All materials



**Figure 1.** Experimental photocatalytic system—top view.

contacting the gas stream were either Teflon or glass to prevent reactions with organics. The loop itself consisted of 1/4-in. Teflon tubing. An empty liquid chromatography column, placed horizontally, served as the photocatalytic reaction vessel, as shown in Figure 2. The TiO<sub>2</sub>-coated glass plate, described previously, was placed in the

column. A lamp with two 15-W cylindrical bulbs (NIS F15 T8BLB 15W black light blue) provided illumination at a wavelength of 366 nm (light of a wavelength 376 nm or lower is required for the photons to have enough energy to promote an electron to the conduction band of TiO<sub>2</sub> to induce photocatalysis). A diaphragm pump (Cole-Parmer



**Figure 2.** End view of experimental photocatalytic reaction chamber.

Model No. L-79200-00) set at maximum pressure of 25 psi provided circulation through the loop.

Compounds to be tested were injected as pure liquids into an injection/sampling port. Except for alcohols, compound concentrations ranged from 10 to 1000 ppm, representative of industrial waste streams for which PCO should be cost-effective.<sup>17</sup> Before each experiment, a sufficient amount of water was injected into the port so that the reaction would not be water-vapor-limited (100% relative humidity). Because commercially available photocatalytic reactors are typically designed to operate at room temperature, the experiments were conducted at room temperature ( $25 \pm 2$  °C).

A Tracor 550 gas chromatograph with a flame ionization detector (FID) and 3-foot Porapak Q packed column, 1/4 in. in diameter, was used to measure compound concentration. He was used as the carrier gas. The inlet was set to a temperature of 200 °C and the detector was set to a temperature of 165 °C. All experiments were conducted with the chromatograph in isothermal mode. Injection volumes were constant for a given experiment but ranged from 200  $\mu$ L for some experiments to 500  $\mu$ L for other experiments.

## REACTOR DESIGN AND OPERATION VARIABLES AFFECTING REACTION RATE CONSTANTS

### Catalyst

A mixture of 60–80% anatase and 20–40% rutile TiO<sub>2</sub> has been found to have greater activity than either of the purer forms.<sup>18,19</sup> In addition to the anatase/rutile ratio, the catalyst preparation, such as doping or thermal pretreatment, can affect reaction rate constants. A standard TiO<sub>2</sub> photocatalyst should be used for research work to eliminate differences in results caused by composition and preparation of the catalyst.<sup>20</sup> Degussa's P-25 grade TiO<sub>2</sub>, which is widely used in photocatalysis research, was used as the photocatalyst for this research. P-25 contains a mixture of 70–80% anatase and 20–30% rutile.<sup>21</sup>

### Oxygen Concentration

Because the PCO occurred in air, the partial pressure or percentage of oxygen was 21%. It has been found in previous studies that oxygen is not a limiting species in gas-phase PCO if present, as is typical in air, in quantities of 20% by volume.<sup>22</sup> The oxygen concentration was thus high enough that oxygen was not a limiting reactant, and the reaction rates were independent of oxygen concentration.

### Water Vapor Concentration

Water vapor can increase destruction rates by replenishing adsorbed OH<sup>-</sup>, which is then converted to OH<sup>o</sup>.<sup>23,24</sup> A

20% relative humidity content has been found to delay deactivation of TiO<sub>2</sub> for compounds such as toluene that would tend to deactivate the photocatalyst.<sup>25</sup> However, previous studies have shown that if water-vapor concentrations are too high, water vapor may decrease destruction rates by competing with contaminant molecules for available surface sites.<sup>26–28</sup> In an actual field installation of a PCO reactor, a relative humidity of around 40% would probably be optimal (humidity greater than 50% can lower destruction rates).

For the experiments described here, water vapor was added to achieve 100% relative humidity so that the reactions would not be water-vapor-limited. Initial water-vapor concentrations were calculated to be approximately 26,000 ppm<sub>v</sub>, although water-vapor concentrations were not monitored during experiments. This humidity level was higher than optimum, however, for achieving maximum destruction rates. Because the goal of this research was to correlate destruction rates with compound properties, and not to maximize destruction rates, the high humidity would only have posed a problem if it interfered with measuring contaminant destruction rates. This may have been the case for alcohols, as explained in a later section.

### Irradiance

The irradiance was held constant for all experiments and averaged 0.028 W/cm<sup>2</sup>, as calculated from the bulb wattage and distance from the catalyst-coated glass plate. Because the irradiance was constant, it did not have to be accounted for explicitly in rate expressions. For cases where irradiance must be explicitly accounted for, it has been shown that for low intensities, the rate constant is directly proportional to the light intensity, but for high intensities, the rate constant is proportional to the square root of the light intensity, as explained in detail by Teichner and Formenti.<sup>29</sup>

### Reactor Configuration

Five processes must be considered in determining the overall rate of a reaction on a catalyst surface:

- (1) mass transfer of the molecule from the main gas stream flow to the catalyst surface by turbulent mixing to the boundary layer and diffusion to the surface;
- (2) adsorption of the molecule onto the catalyst surface;
- (3) reaction of the molecule on the surface to form products;
- (4) desorption of the products from the surface; and
- (5) mass transfer of the products back into the main gas stream flow by diffusion through the boundary layer and mixing into the well-mixed fluid.<sup>30</sup>

The reactor configuration potentially could affect steps 1 and 5 of this process. However, mass transfer calculations showed that mass transfer to and from the surface should not have been rate-limiting. Mass transfer through the bulk gas stream was assumed not to be rate-limiting. Mass transfer from the bulk phase to the catalyst surface was calculated using Fick's First Law of Diffusion according to film theory. To employ Fick's Law, diffusivities were calculated using a method outlined by Bird et al., and the gas film thickness for flow over a flat plate was calculated using an equation developed by Roberson and Crowe.<sup>31,32</sup> It was found that the mass transfer rate ranged from 19 to 110 times the rate of reaction on the surface. Thus, only steps 2–4 are accounted for in the reaction rate expression.

### Temperature

A number of previous PCO studies have found contaminant destruction rates to vary with temperature in a manner consistent that presented by Pichat and Herrmann.<sup>33</sup> At low temperatures, reaction rates increase with increasing temperature. In this region, adsorption dominates, and thus, desorption can be the rate-limiting step. Increasing the reaction temperature causes products to desorb faster and thus increases the reaction rate. For mid-range temperatures, the reaction rate is independent of temperature. For high temperatures, the reaction rate decreases with increasing temperature, most likely because adsorption is decreasing with temperature in this range. The temperature in the lab room was approximately  $25 \pm 2$  °C during all experiments. Because it was held constant, the temperature did not have to be accounted for explicitly in the rate expression.

### Catalyst Surface Area/Reactor Volume Ratio

The illuminated surface area on the photocatalytic plate was 59 cm<sup>2</sup> (geometric surface area on the glass plate), and the system volume was 275 cm<sup>3</sup>. The catalyst-surface-area-to-reactor-volume ratio was thus 0.215/cm. The rate constants determined in this research are only valid for this same surface-area-to-reactor-volume ratio, a criterion that could be satisfied in reactor design.

### Summary of Reactor Design and Operation Variables' Impact on PCO Rate Constant

The PCO rate varied between experiments in this research only as a function of compound concentration. All other factors were constant for all experiments and were absorbed into the rate constant. The rate constants developed in this research should thus be applicable to any

system that similarly uses Degussa P-25 TiO<sub>2</sub> to carry out photocatalysis in air at room temperature and 100% relative humidity and is not mass transfer limited. For a system with a different light intensity, standard relationships between rate constant and light intensity can be used to adjust the rate constant accordingly. When designing a reactor system based on the rate constants developed in this research, the catalyst-surface-area-to-reactor-volume ratio would need to be held constant at 0.215/cm, as discussed previously. The rate constants, although determined for a batch reactor system, could be applied to a plug flow system using appropriate mass balance equations.

## RESULTS

### Determination of Rate Constants

Rate constants were determined for the disappearance of straight-chain alkanes and alkenes. Figure 3, which shows destruction of ethylene, is presented as a representative curve for compound destruction. The photocatalytic reactor system was assumed to be well-mixed and was analyzed as a batch reactor.

Reaction rate constants were determined for first-order decay as shown

$$dC/dt = r = -kC \quad (2)$$

where  $r$  = reaction rate (moles/unit volume/unit time),  $k$  = reaction rate constant (time<sup>-1</sup>), and  $C$  = concentration of parent organic molecule in the gas stream (moles/volume). The integrated form of eq 2 is

$$C = C_0 \times \exp(-kt) \quad (3)$$

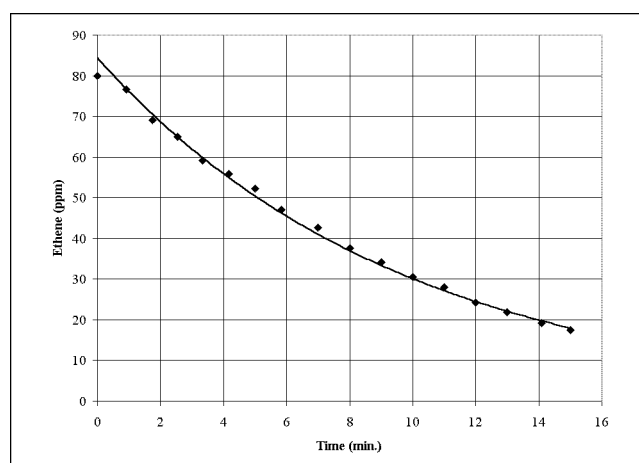
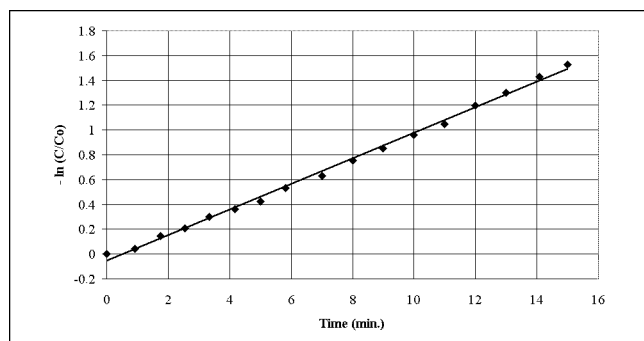


Figure 3. Sample compound destruction curve.



**Figure 4.** Sample determination of first-order PCO rate constant.

It follows then follows that

$$\ln(C/C_0) = -kt \quad (4)$$

The first-order rate constant  $k$  can then be found by plotting  $\ln(C/C_0)$  versus  $t$ , and determining  $k$  using linear regression. A sample plot of  $-\ln(C/C_0)$  versus  $t$ , corresponding to the destruction of ethylene shown in Figure 3, is shown in Figure 4. For this trial,  $k = 0.10 \text{ min}^{-1}$  with  $R^2 = 0.997$ .

A Langmuir-Hinshelwood rate expression was also fit to the data, but the first-order expression provided better curve fits. A study of ethylene degradation over  $\text{TiO}_2$  conducted by a different research group also rejected a

**Table 1.** First-order photocatalytic oxidation rate constants for alkanes.

Compound	Trial	CO (ppm)	Number of Data Points Collected	$R^2$	$k$ Value ( $\text{min}^{-1}$ )
Butane	1	873	26	.994	0.0231
	2	291	21	.999	0.0328
	3	182	21	.996	0.0430
	4	182	21	.995	0.0306
	5	109	17	.987	0.0492
Average					0.0357
Pentane	1	232	18	0.990	0.0643
	2	309	18	0.997	0.0691
	3	386	22	0.994	0.0558
Average					0.0631
n-Hexane	1	204	19	0.997	0.1097
	2	204	17	0.995	0.0983
	3	204	20	0.997	0.1084
Average					0.1055
Heptane	1	303	16	0.992	0.1110
	2	425	18	0.989	0.1049
	3	303	15	0.975	0.1262
Average					0.1140

**Table 2.** First-order photocatalytic oxidation rate constants for alkenes.

Compound	Trial	CO (ppm)	Number of Data Points Collected	$R^2$	$k$ Value ( $\text{min}^{-1}$ )
Ethene	1	74.0	21	0.992	0.114
	2	73.4	27	0.995	0.133
	3	80.0	17	0.997	0.103
	Average				
Propylene	1	23.2	19	0.999	0.241
	2	18.3	14	0.997	0.280
	3	30.5	17	0.995	0.239
Average					0.253
1-Butene	1	49.9	15	0.995	0.238
	2	49.9	17	0.998	0.227
	Average				

Langmuir-Hinshelwood rate expression, in their case in favor of a half-order power law expression.<sup>34</sup> It has been reported that for most oxidation catalysts and VOC concentrations practically encountered, the rate dependence

**Table 3.** First-order photocatalytic oxidation rate constants for alcohols.

Compound	Trial	CO (ppm)	Number of Data Points Collected	$R^2$	$k$ Value ( $\text{min}^{-1}$ )
Ethanol	1	1523	13	0.997	0.488
	2	1219	14	0.983	0.431
	Average				
n-Propanol	1	5944	18	0.990	0.360
	2	5944	15	0.984	0.374
	3	5944	13	0.986	0.322
Average					0.352
Isopropanol	1	1162	5	0.974	0.293
	2	1162	13	0.984	0.206
	3	1162	16	0.991	0.300
	4	1162	12	0.983	0.273
Average					0.268
1-Butanol	1	1943	15	0.997	0.348
	2	1943	13	0.995	0.257
	3	971	10	0.979	0.339
	4	1943	13	0.983	0.254
Average					0.300
2-Butanol	1	668	13	0.986	0.246
	Average				
3-Pentanol	1	828	7	0.966	0.339
	2	1657	14	0.974	0.242
	3	1657	16	0.992	0.258
	4	1657	16	0.985	0.286
Average					0.281

**Table 4.** Ionization potential, hydroxyl radical reaction rate constant, and average photocatalytic oxidation rate constant values for alkanes.

Compound	IP (eV)	$k_{OH}$ ( $10^{12}$ cm <sup>3</sup> /molecule/sec)	Average kPCO Value (min <sup>-1</sup> )
Butane	10.53 <sup>a</sup>	2.43 <sup>b</sup>	0.0357
Pentane	10.35 <sup>a</sup>	4.1 <sup>c</sup>	0.0631
n-Hexane	10.13 <sup>a</sup>	5.9 <sup>b</sup>	0.1055
Heptane	9.92 <sup>a</sup>	7.2 <sup>d</sup>	0.1140

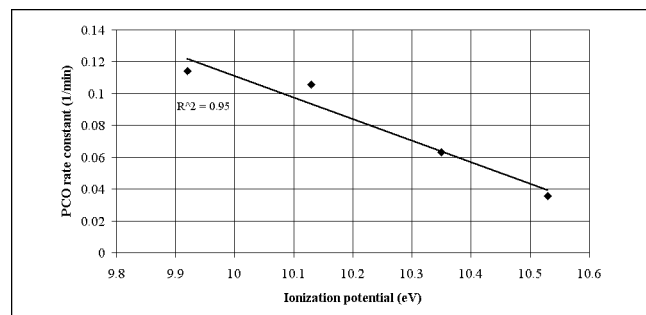
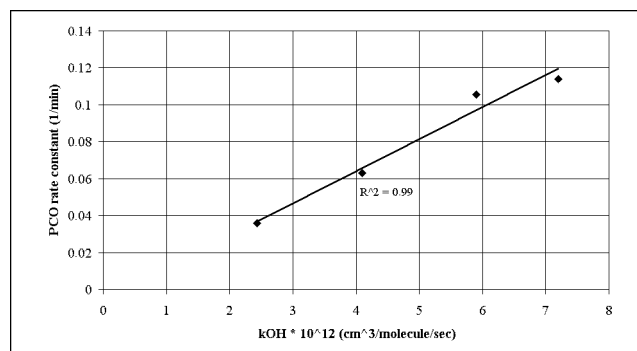
<sup>a</sup>Finlayson-Pitts, B.J.; Pitts, J.N. Jr. *Atmospheric Chemistry: Fundamentals and Experimental Techniques*; Wiley: New York, 1986; <sup>b</sup>Heicklen, J. The Correlation of Rate Coefficients for H-Atom Abstraction by HO Radicals with C-H Bond Dissociation Enthalpies; *Int. J. Chem. Kinet.* **1981**, *13*, 651–665; <sup>c</sup>Finlayson-Pitts, B.J.; Pitts, J.N. Jr. *Atmospheric Chemistry: Fundamentals and Experimental Techniques*; Wiley: New York, 1986; <sup>d</sup>Grosjean, D.; Seinfeld, J.H. Parameterization of the Formation Potential of Secondary Organic Aerosols; *Atmos. Environ.* **1990**, *23*, 1733.

on VOC concentration appears to follow a first-order kinetics.<sup>35</sup>

Tables 1–3 show the first-order rate constants obtained for PCO destruction of alkanes, alkenes, and alcohols, respectively. For each trial, the table shows the initial compound concentration  $C_0$  in ppm, the number of data points collected, the  $R^2$  value for the first-order decay curve fit to the data, and  $k$  value for the first-order decay curve. The first-order rate expressions fit the data well, with  $R^2$  values ranging from 0.96 to 0.99 for any given trial. Average  $k$  values for each compound are also shown.

#### Correlation of Rate Constant with Ionization Potential and Hydroxyl Radical Rate Constant

This research proposed that PCO rate constants could be correlated with compound structure. IP was chosen as a measure of compound structure likely to correlate with PCO rate constants because IP has been shown to correlate with gas-phase  $OH^\circ$  reaction rate constants ( $k_{OH}$ ), and PCO proceeds primarily via  $OH^\circ$  attack.<sup>36</sup>

**Figure 5.** Alkanes: first-order PCO rate constant vs. IP.**Figure 6.** Alkanes: first-order PCO rate constant vs.  $OH^\circ$  reaction rate constant.

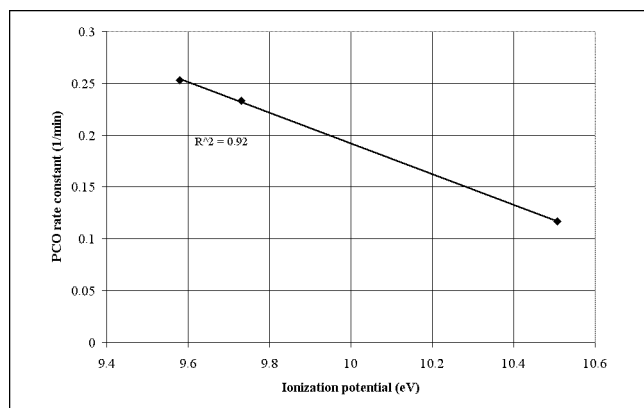
Alternatively, direct  $H^+$  attack on the VOC could remove an electron and ionize the sorbed VOC. In this case, ionization would initiate the destruction mechanism, and the PCO rate constant would be anticipated to correlate inversely with IP. The larger a compound's IP, the greater the energy required to ionize the sorbed VOC and the lower the PCO rate constant would be anticipated to be. Because the primary mechanism of compound destruction in humidified PCO systems is  $OH^\circ$  attack, the PCO rate constant for a given compound would be anticipated to correlate directly with  $k_{OH}$ . In other words, the faster a compound reacts with the  $OH^\circ$ , the faster its destruction in the photoreactor will be.

**Alkanes.** Table 4 shows IP,  $OH^\circ$  reaction rate constant ( $k_{OH}$ ), and average PCO rate constant values for alkanes tested (the average PCO rate constant values are repeated from Table 1). Figures 5 and 6 show the average PCO rate constants plotted versus the IP and  $k_{OH}$  values.  $R^2$  values for the correlations were 0.95 and 0.98, respectively. The PCO rate constants decrease with increasing IP, which is what would be expected, because a higher IP indicates that the compound is harder to

**Table 5.** Ionization potential, hydroxyl radical reaction rate constant, and average photocatalytic oxidation rate constant values for alkenes.

Compound	IP (eV)	$k_{OH}$ ( $10^{12}$ cm <sup>3</sup> /molecule/sec)	Average kPCO Value (min <sup>-1</sup> )
Ethylene	10.507 <sup>a</sup>	8.5 <sup>a</sup>	0.117
Propene	9.58 <sup>a</sup>	31 <sup>a</sup>	0.253
1-Butene	9.73 <sup>a</sup>	26 <sup>a</sup>	0.233

<sup>a</sup>Finlayson-Pitts, B.J.; Pitts, J.N. Jr. *Atmospheric Chemistry: Fundamentals and Experimental Techniques*; Wiley: New York, 1986.

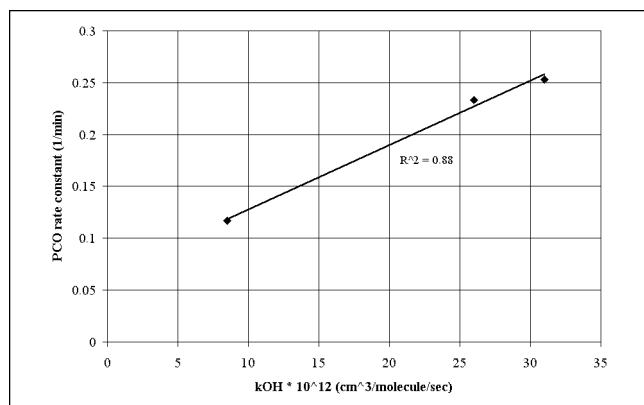


**Figure 7.** Alkenes: first-order PCO rate constant vs. IP.

ionize. The PCO rate constants increase with increasing  $k_{OH}$ , as would be expected because the primary mechanism of organic destruction in a humidified photocatalytic system is proposed to be  $OH^\circ$  attack.

**Alkenes.** Table 5 shows IP,  $OH^\circ$  reaction rate constant ( $k_{OH}$ ), and average PCO rate constant values for the alkenes tested (the average PCO rate constant values are repeated from Table 2). Figures 7 and 8 show the PCO rate constants plotted versus IP and  $k_{OH}$ .  $R^2$  values for the correlations were 0.92 and 0.88, respectively. As was the case with alkanes, the PCO rate constants decrease with increasing IP and increase with increasing  $k_{OH}$ , as would be expected.

**Alcohols.** Table 6 shows IP,  $OH^\circ$  reaction rate constant ( $k_{OH}$ ), and average PCO rate constant values for the alcohols tested (the average PCO rate constant values are repeated from Table 2). Figures 9 and 10 show the PCO rate constants plotted versus IP and  $k_{OH}$ .  $R^2$  values for the correlations were 0.76 and 0.72, respectively. The linear relationship holds for both primary and secondary alcohols.



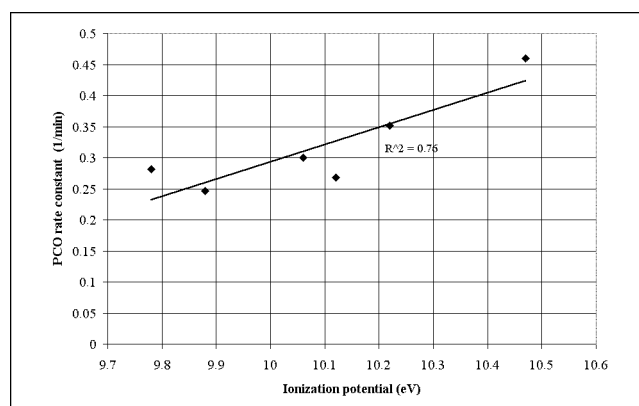
**Figure 8.** Alkenes: first-order PCO rate constant vs.  $OH^\circ$  reaction rate constant.

**Table 6.** Ionization potential, hydroxyl radical reaction rate constant, and average photocatalytic oxidation rate constant values for alcohols.

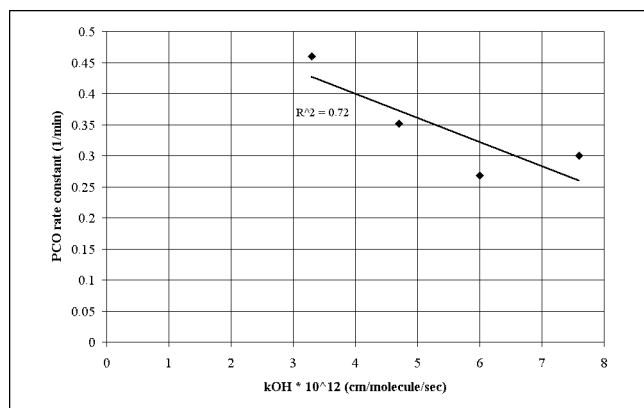
Compound	IP (eV)	$k_{OH}$ ( $10^{12}$ cm <sup>3</sup> /molecule/sec)	Average kPCO Value (min <sup>-1</sup> )
Ethanol	10.47 <sup>a</sup>	3.3 <sup>b</sup>	0.460
n-Propanol	10.22 <sup>a</sup>	4.7 <sup>b</sup>	0.352
Isopropanol	10.12 <sup>a</sup>	6.0 <sup>b</sup>	0.268
1-Butanol	10.06 <sup>a</sup>	7.6 <sup>b</sup>	0.300
2-Butanol	9.88 <sup>a</sup>	Not available	0.246
3-Pentanol	9.78 <sup>a</sup>	Not available	0.281

<sup>a</sup>Finlayson-Pitts, B.J.; Pitts, J.N. Jr. *Atmospheric Chemistry: Fundamentals and Experimental Techniques*; Wiley: New York, 1986; <sup>b</sup>Heicklen, J. The Correlation of Rate Coefficients for H-Atom Abstraction by  $HO$  Radicals with C-H Bond Dissociation Enthalpies; *Int. J. Chem. Kinet.* **1981**, *13*, 651–665.

The relationships for alcohols are, however, the opposite of what would be expected. Unlike alkanes and alkenes, the PCO rate constants increase with increasing IP and decrease with increasing  $k_{OH}$ . In general, the greater the number of carbons in the alcohol (the larger the R value), the slower the PCO rate. This trend can potentially be explained as follows. Henry's Law constants for alcohols tested are 3–4 orders of magnitude larger than those for alkanes and alkenes tested, which means that the alcohols have a greater tendency to partition into the liquid phase. Experiments were run at 100% relative humidity, which was not optimum. Alcohols likely competed with water for hydrophilic surfaces or were absorbed into a liquid film on the catalyst surface, and gas-phase removal thus correlated with Henry's Law constants. Surface tension may have held some liquid at the contact points of the  $TiO_2$  particles. Additional experiments should be run with alcohols using a lower humidity.



**Figure 9.** Alcohols: first-order PCO rate constant vs. IP.



**Figure 10.** Alcohols: first-order PCO rate constant vs. OH<sup>•</sup> reaction rate constant.

### Applicability of Correlations

The specific rate constants and correlations developed in this research should be applicable to any system that similarly uses Degussa P-25 TiO<sub>2</sub> to carry out photocatalysis in air at room temperature and 100% relative humidity, and is not mass transfer limited. Although a different system may have a different light intensity, the relationship between rate constant and light intensity has been established<sup>37</sup> and was described in the previous section "Reactor Design and Operation Variables." Although the rate constants were developed for a batch system, they could be applied to a CSTR or plug-flow system using the appropriate mass balance equations. When designing a reactor system based on the rate constants developed in this research, the geometric (flat plate) catalyst-surface-area-to-reactor-volume ratio would have to be held constant at 0.215/cm.

No stable intermediates were detected for alkanes and alkenes; hence, the correlations developed should be able to be used directly to design a system. For alcohols, however, stable intermediates were detected. If one of the intermediates degrades more slowly than the parent compound, which is usually the case, then the system must be designed based on the decay rate of the slowest-degrading intermediate.

### CONCLUSIONS

This research demonstrates a means of predicting regular trends in observed PCO rate constants. It was found that rate constants for PCO of straight-chain alkanes and alkenes vary linearly with IP and with OH<sup>•</sup> reaction rate constant for each class of compounds. IP and OH<sup>•</sup> reaction rate constant were equally valid parameters for correlating the PCO rate constant, according to correlation coefficient values, which is expected, because OH<sup>•</sup> reaction rate constant can itself be correlated with IP. Additional research should be conducted to determine whether the correlations hold for cyclic

and branched alkanes and alkenes. Further research also should be conducted to determine correlations for ketones, aldehydes, organic acids, and other classes of compounds.

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