

Heterogeneous photocatalytic degradation of ethylene glycol and propylene glycol

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Abstract—The photocatalytic decomposition of ethylene glycol and propylene glycol was investigated by using UV-illuminated TiO₂ and metal-loaded TiO₂ catalysts. The effects of pH, initial concentration, and wavelength of light on the decomposition rate of the glycols were explored. Platinum- and palladium-loaded TiO₂ catalysts enhanced the rates of photodecomposition compared to unloaded TiO₂. The glycols were oxidized primarily to carbon dioxide and water. Formaldehyde was found to be an important reaction intermediate. A detailed chemical reaction mechanism for the destruction of ethylene glycol and propylene glycol in water via free radical pathway and trapped hole reactions at the particle surface is proposed.

Key words: Ethylene Glycol, Metal Loaded Photocatalyst, Oxidation, Photocatalysis, Photocatalytic Activity, Propylene Glycol, TiO₂

INTRODUCTION

Photocatalysis applied to the oxidation of organic pollutants in aqueous solution has been studied extensively. The mechanisms of semiconductor photocatalysis are known to involve hydroxyl radicals, trapped electrons, and trapped holes at the particle surface [1-7]. Many organic compounds have been shown to be completely oxidized to carbon dioxide, water and other inorganic constituents by this process.

Ethylene glycol and propylene glycol are widely used in commercial processes, because they have relatively high boiling points and freeze well below 0 °C [8]. In addition, they possess excellent solvent properties for synthetic resins. However, ethylene glycol is highly toxic when administered orally. Propylene glycol is often used as an automotive antifreeze as a substitute for ethylene glycol. Although the recovery of glycols from aqueous solutions is possible, it is difficult to recover them from low volatility chemical mixtures and dilute aqueous solutions because of their strongly hydrophilic character [9].

The primary objective of this study was to demonstrate the feasibility of degradation of glycols in aqueous solution by photocatalysis with TiO₂. The photodegradation of ethylene glycol and propylene glycol was investigated as a function of pH, substrate concentration, and the addition of a metal dopant to TiO₂. The secondary objective of this study was to examine the mechanistic aspects of the photooxidative degradation of the glycols with an eye on improvement of photocatalytic activity.

METHODS

1. Materials

Highly purified ethylene glycol, propylene glycol and formaldehyde were purchased from Junsei Chemicals in Japan and were used without further purification. Two different titanium dioxide photo-

catalysts were involved in these experiments: P-25 (Anatase+Rutile) was purchased from Degussa in Germany and Hombikat UV 100 (Anatase) was obtained from Sachtleben Chemie GmbH in Germany. Purified water used in all experiments was prepared by initial passage through an AQUAPURI (13.2 µs, Young-In Co.) system followed by treatment with a Milli-Q plus (higher than 18.2 MΩcm resistivity, Millipore S. A.).

2. Catalysts

The loading of noble metals onto TiO₂ was performed via the photodeposition method [10]. Five grams of TiO₂ and 3.3 g methanol were added to an aqueous solution of tetrachloroplatinic acid (H₂PtCl₆ 6H₂O, Aldrich) or palladium(II) chloride (PdCl₂, Aldrich). The resulting suspensions were irradiated in a quartz reactor with a 20 W fluorescent bulb for one hour. The resultant slurry was filtered and then dried overnight at room temperature.

3. Photocatalytic Experiments

Photocatalytic reactions were carried out in an annular quartz

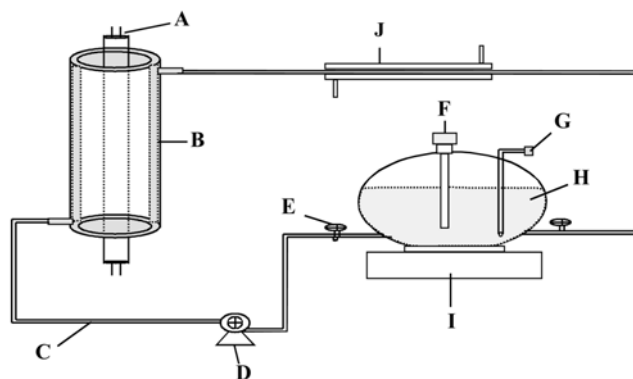


Fig. 1. Schematic diagram of annular photoreactor system

- | | |
|---------------------------|---------------------|
| A. 20 W UV Lamp | F. pH electrode |
| B. Quartz annular reactor | G. Oxygen inlet |
| C. Teflon tubing | H. Sampling vessel |
| D. Peristaltic pump | I. Magnetic stirrer |
| E. Sampling port | J. Water cooling. |

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reactor system which consists of a motor-driven peristaltic pump (Cole-Parmer Instr. Co.), Teflon tubing, and Pyrex sampling vessel as shown in Fig. 1. A 0.1 wt% aqueous slurry of titanium dioxide was recirculated by the peristaltic pump at a rate of 400 cm³/min. The total volume of the reactor system was 1,260 cm³ with the annular reactor volume of 200 cm³, the sampling vessel volume of 1,030 cm³, and the tubing volume of 30 cm³. The reactant solution was prepared by adding ethylene glycol (or propylene glycol) into the laboratory-grade water with mechanical mixing for 30 minutes. After mixing, the catalyst was suspended into the solution, then the slurry was bubbled with oxygen for 30 minutes. The contents of the reactor were recirculated and stirred for 20 minutes to obtain a uniform suspension. The pH was adjusted with 0.1 N NaOH (or dilute HNO₃) solution to obtain the desired value. A 20 W commercial fluorescent bulb (253.7 nm, Sankyo Denki GL20) was used as a light source in these experiments. The reaction with fluorescent bulb for photolysis showed no activity in a blank run without a catalyst. The fluorescent bulb was placed at the center of the quartz annular reactor.

4. Analytical Procedures

10 ml samples were regularly taken from the reservoir and filtered through a 0.2 µm PVDF syringe filter (Whatman), and then analyzed with a Shimadzu 5000A total organic carbon analyzer. In addition, the same sample was analyzed by gas chromatography (Hewlett-Packard Model 5890 II) equipped with split injection (1 : 100), FID detector and a VOCOL capillary column (60 m×0.53 mm ×3.0 µm film thickness, Supelco). The presence of carbon dioxide in the gas phase was also detected by GC using a TCD detector and a Porapak-Q column (80/100 mesh size, 1.83 m×3.2 mm). Mass balance calculations for carbon on based GC and TOC analyses were in agreement within 7%.

Formaldehyde was measured spectrophotometrically during reaction by using the Nash method [11,12], which involves the coupling of formaldehyde with 2,4-pentanedione (acetylacetone) and ammonium acetate to form 3,5-diacetyl-1,4-dihydrolutidine which is quantified by its absorption at 415 nm.

RESULTS AND DISCUSSION

The decomposition reactions of ethylene glycol and propylene glycol were carried out in the presence of the various photocatalysts and levels of UV illumination. Under most conditions, the main organic decomposition products were CO₂ and H₂O with formaldehyde observed as an intermediate in the oxidation of both glycols. Only small amounts of several other unknown byproducts were produced depending on the specific catalysts and the given process conditions. The overall stoichiometric reactions for the glycols are written as follows:

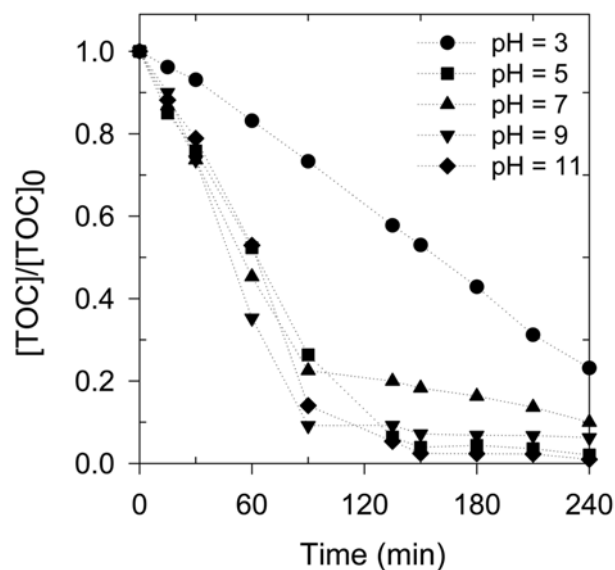
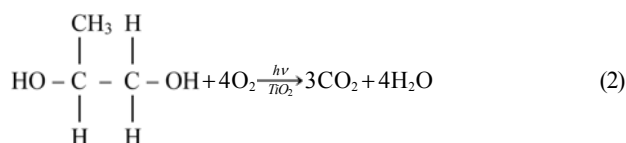
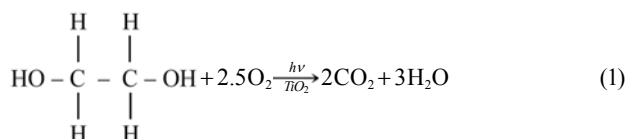
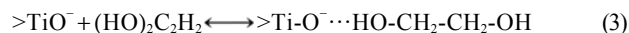


Fig. 2. Effect of initial pH on removal of ethylene glycol over P-25 catalyst.

1. Photodecomposition of Ethylene Glycol

1-1. pH Effects

The pH dependence of the photodecomposition of ethylene glycol on P-25 TiO₂ was investigated over the pH range 3 to 11 as shown in Fig. 2. The rate of decomposition was high at pH's ≥ 5; a slightly slower rate was observed at pH 3. The rate of decomposition at pH 9 was found to be slightly higher. At low (e.g., pH 3) pHs the catalytic surface is highly protonated (pH_{zpc}=6.6) while at pH > 6 the surface is dominated by negatively charged sites (>TiO⁻). The pH dependence is consistent with a higher level of sorption of ethylene glycol to the TiO₂ surface at high pH.



Typical pH changes observed during the decomposition of ethylene

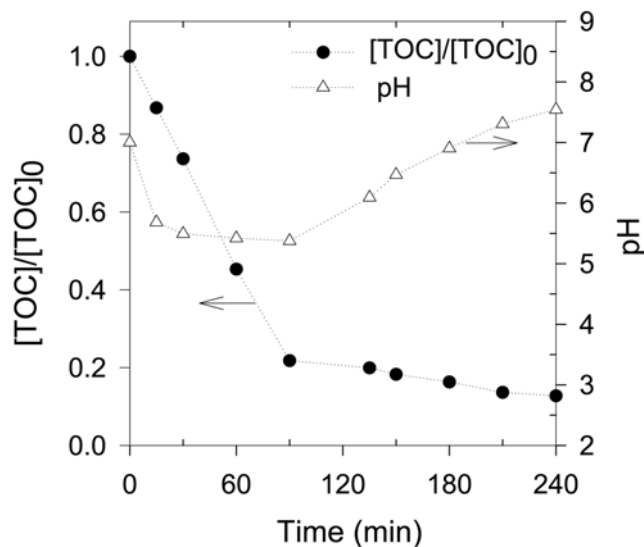


Fig. 3. The pH change on the decomposition of ethylene glycol.

glycol are shown in Fig. 3. The initial pH of 7 decreased to about 5 as the decomposition proceeded and then rose slowly to near its initial pH value toward the end of the reaction. Although not shown, the changes in pH for other initial conditions such as pH 9 and 11 followed the same trend as observed for pH 7, whereas those at the initial pH 3 and 5 did not vary over the entire course of the reaction. For the reactions initiated at high pH, acidification is due primarily to the formation of CO_2 and formic acid, HCOOH . Formaldehyde has been observed previously as an intermediate of the photooxidation of the glycols. The plot of formaldehyde generated from the destruction of ethylene glycol is shown in Fig. 4 as a function of reaction time. In a 1 mM ethylene glycol solution, the formaldehyde reached its highest concentration of 0.28 mM after 60 min and then completely degraded after 180 min. The kinetic data of Fig. 4 is

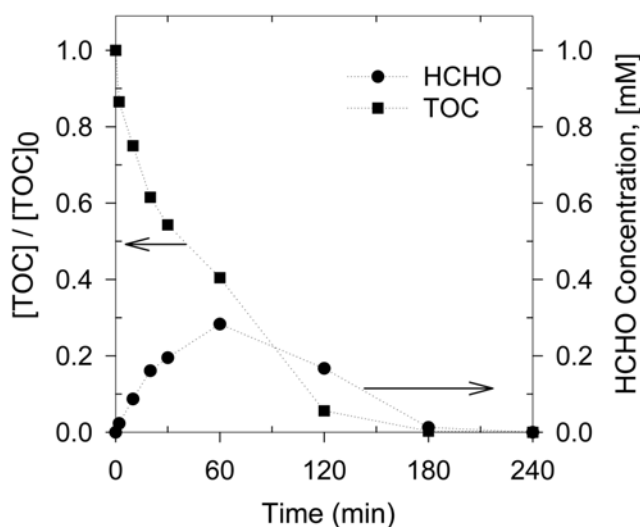


Fig. 4. Plot of concentration of formaldehyde vs. reaction time during degradation of ethylene glycol.

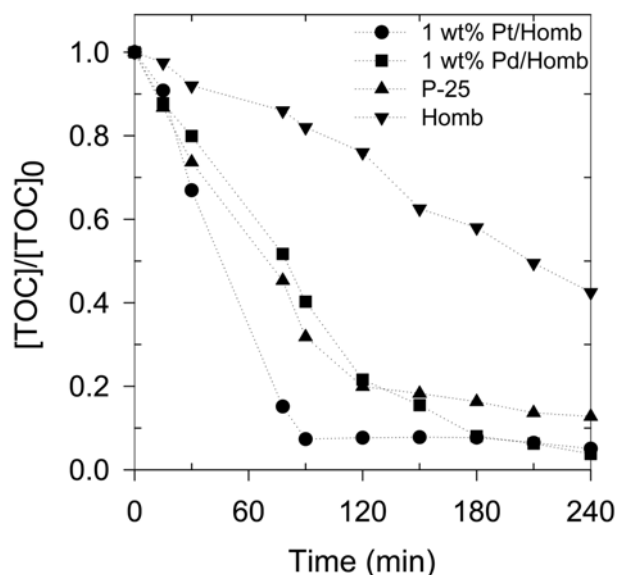


Fig. 5. Effect of metal loaded TiO_2 on decomposition of ethylene glycol at pH=7.

consistent with the following reaction sequence of transformation:



Although formic acid was not detected in these experiments, it is assumed that the formic acid is an intermediate in the oxidation of formaldehyde to carbon dioxide [13]. This is consistent with our results that show a rapid change in pH during the reaction.

1-2. Effect of Metal Loading on TiO_2

The photocatalytic activity of the metal loaded TiO_2 was investigated as a function of illumination time as shown in Fig. 5. The noble metals (Pt and Pd) deposited onto Hombikat TiO_2 (Homb) enhanced the rates of decomposition of ethylene glycol when compared with the unloaded Hombikat TiO_2 catalyst. The role of the metal islands is to serve as effective electron sinks, which in turn retards electron-hole recombination rate and thereby improves the efficiency of photocatalytic oxidation. The catalytic activity of Pt loaded Hombikat was higher than that of Pd loaded Hombikat as shown in Fig. 5.

1-3. Effect of Initial Substrate Concentration

The decomposition rate of ethylene glycol was significantly influenced by the initial concentration of substrate as demonstrated in Fig. 6. The observed rate of decomposition decreased as the initial reactant concentration increased. These results indicate that ethylene glycol is competitively adsorbed on the surface of catalyst. This suggests that the reaction rate is a complicated function of the extent of adsorption, the transfer of trapped electrons and holes to oxygen and ethylene glycol, respectively, the concentration of $\bullet\text{OH}$ radicals produced during illumination, and the competition of the decomposition products for surface sites.

2. Photodecomposition of Propylene Glycol

2-1. pH Effects

Fig. 7 shows the photodecomposition of propylene glycol on P-25 TiO_2 over the pH range of 3-11. The decomposition rate of propylene glycol was very similar to that of ethylene glycol except for some pH conditions. The rates of decomposition at pH 7 and 9 were higher than those at pH 3 and 11.

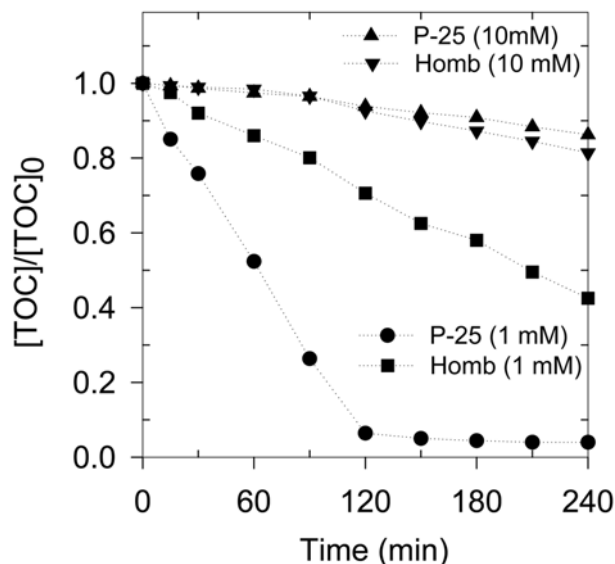


Fig. 6. Effect of initial concentration of ethylene glycol on removal of TOC.

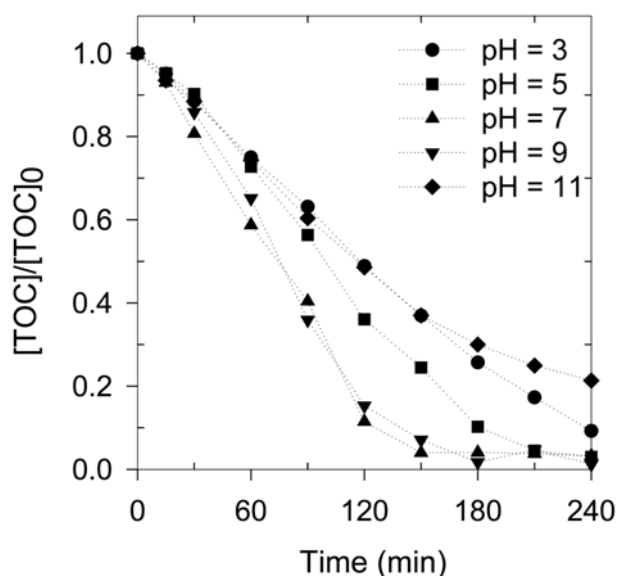


Fig. 7. Effect of initial pH on removal of propylene glycol over P-25 catalyst.

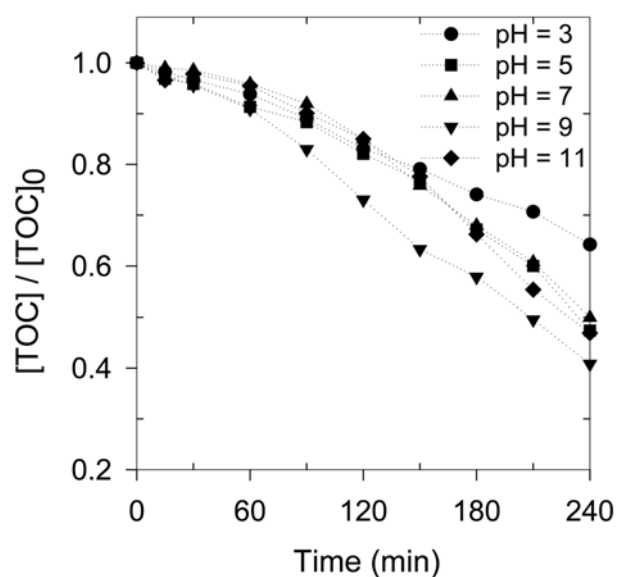


Fig. 8. Effect of initial pH on removal of propylene glycol over Hombikat catalyst.

In an effort to investigate the pH effect on the different catalysts, the photodecomposition of propylene glycol over the Hombikat catalyst was carried out over the same pH range of 3–11 (Fig. 8). The decomposition rate was relatively high at pH 9, when compared to other pH conditions. At higher pH conditions ($>\text{pH } 7$), the TiO_2 surface is dominated by $>\text{TiO}$ -sites. However, the activity of the Hombikat TiO_2 was lower than that of the P-25 TiO_2 , even though the Hombikat catalyst has four times the net reactive surface area of the P-25 catalyst.

Fig. 9 shows the extent of conversion of both glycols as a function of pH with after 1 hour of irradiation. The extent of removal of ethylene glycol was greater than that of propylene glycol except at pH 3. The highest TOC reduction rate for ethylene glycol was

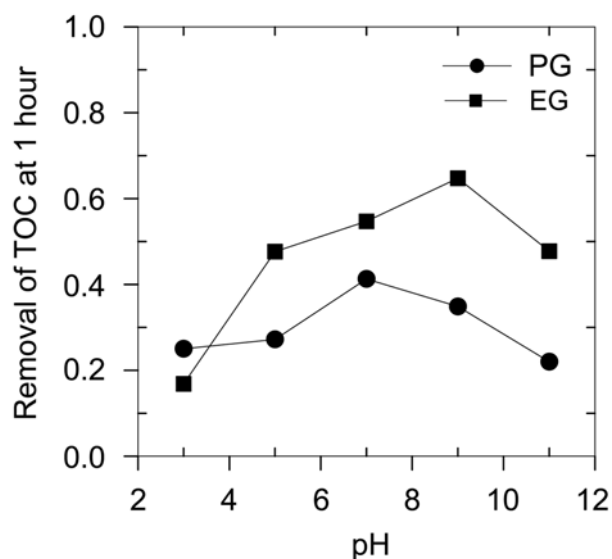


Fig. 9. Effect of glycol on removal of TOC as a function of pH.

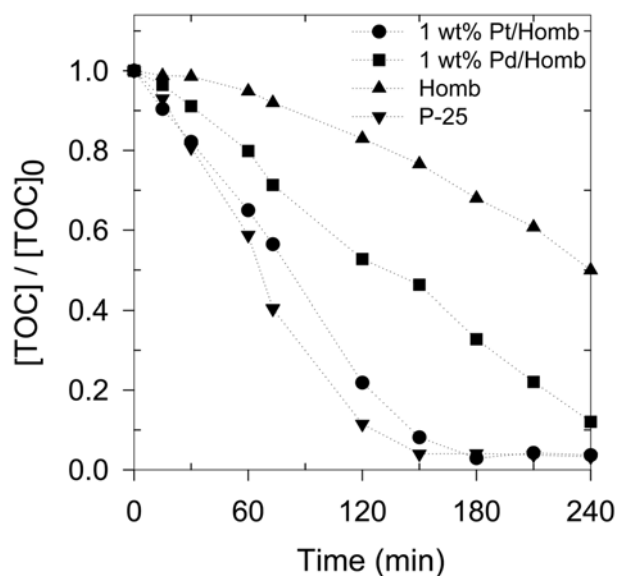


Fig. 10. Effect of metal loaded TiO_2 on decomposition of propylene glycol at $\text{pH}=7$.

obtained at pH 9, whereas for propylene glycol the highest TOC reduction rate was obtained at pH 7. Ethylene glycol with two methylene groups degraded faster than propylene glycol with three methylene.

2-2. Effects of Metal Loading on TiO_2

The catalytic activity of the metal-loaded TiO_2 was also investigated with propylene glycol as shown in Fig. 10. As expected, the Pt-loaded TiO_2 showed higher decomposition rates than pure TiO_2 . However, the decomposition rate obtained with the Pt-loaded TiO_2 was similar to that of the P-25 catalyst. This result can be explained in terms of trapping of photogenerated electrons on the Pt islands of the particle. Again, the role of the Pt islands is to provide a site for more efficient trapping of the photogenerated electrons and to reduce the extent of electron-hole recombination.

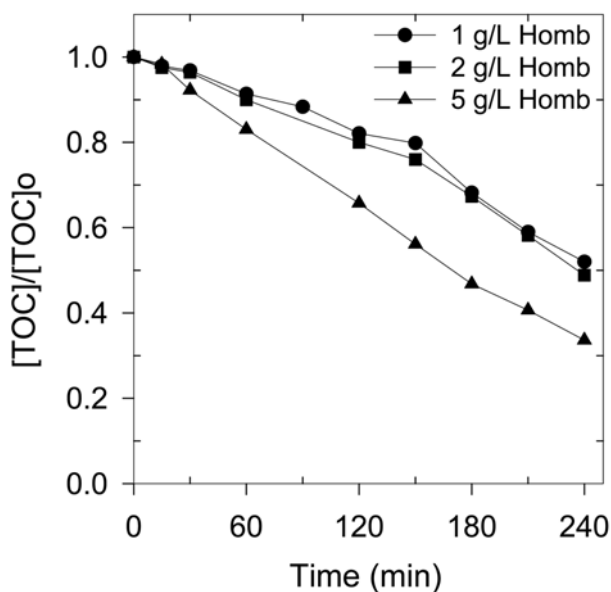


Fig. 11. Effect of Hombikat catalyst concentration on decomposition of propylene glycol.

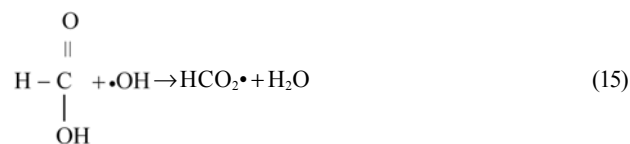
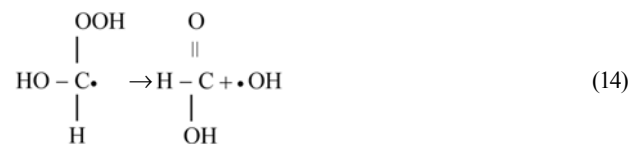
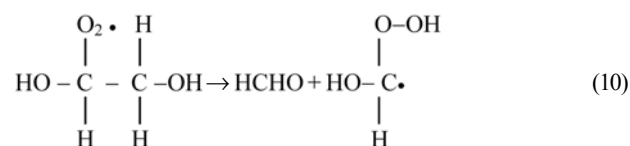
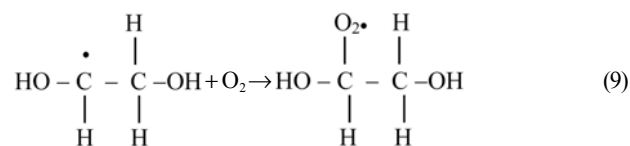
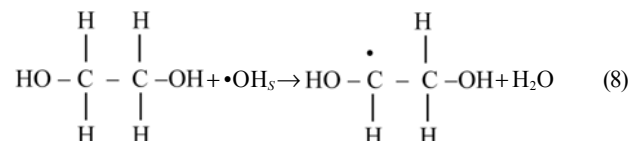
2-3. Effects of Catalyst Concentration

Fig. 11 shows the decomposition rate of propylene glycol at different catalyst concentrations. The rates of degradation increased with increasing catalyst loading. In these experiments, the rate of reaction with Hombikat at 5 g/L is 1.5 times faster than that with at 1 g/L of Hombikat. These results indicate that there is an optimum catalyst loading to obtain the maximum possible rate of glycol degradation. At present, however, it is difficult to explain the dependence of the decomposition rate on the catalyst concentration since the photocatalytic activity depends upon a wide range of effects such as photonic efficiency, extent of adsorption of organic molecules, light absorption rate, pH, electron acceptor concentration and temperature.

3. Mechanistic Implications

The decomposition products of simple aliphatic alcohols are carbon dioxide and water [1,14-19]. On the basis of our current experimental results, the photocatalytic decomposition of glycols can be explained in terms of a standard H-atom abstraction mechanism involving surface-bound hydroxyl radical generated after photoexcitation. The subsequent carbon-centered radical quickly adds CO_2 as shown in the sequence of equations.

Thus the aldehyde is proposed here as an intermediate because the pH of the solution was slightly decreased by the intermediate during the reaction and then gradually increased to the near its initial pH condition when the reaction was completed. As this intermediate is then further oxidized to CO_2 and H_2O , the pH begins to rise. However, we do not account for the other products of acid, such as formic acid, since the formic acid was not able to be detected in our products. Thus, our detailed mechanism of the degradation of ethylene glycol and propylene glycol is suggested in terms of the formaldehyde as the intermediate and the final products of carbon dioxide and water.



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