Photocatalytic degradation of oxalic acid over TiO$_2$ power

Miroslav M. Kosanić

Institute of Chemistry, Faculty of Sciences, University of Novi Sad, Trg Dositeja Obradovića 3, 21000 Novi Sad, Yugoslavia

Abstract

The photocatalytic degradation of oxalic acid in aqueous suspensions of TiO$_2$ was investigated by following the formation of CO$_2$. Based on the data obtained the reaction mechanism was proposed. The oxidation of oxalic acid follows first-order kinetics in the studied range (0.3–4.0 µmol H$_2$C$_2$O$_4$). Initial rate of disappearance fits a Langmuir–Hinshelwood kinetic model. As a result, reaction rate constant and adsorption equilibrium constant were found to be 3.20 µmol min^{-1} and 0.22 µmol^{-1}, respectively. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Photocatalysis; TiO$_2$ catalyst; Oxalic acid; Degradation mechanism

1. Introduction

Titanium(IV) oxide suspended in oxygenated water has proven to be as a most active photocatalyst. The absorption of light with an energy greater than that of the band gap ($\lambda < 380$ nm) generates electron–hole pairs and subsequent oxidation reduction processes. Extensive work has shown that a wide range of organic compounds, in aqueous solutions containing near UV-illuminated suspensions of TiO$_2$, are oxidized completely to CO$_2$ [1,2]. The formation of OH radicals and the reduction of oxygen are thermodynamically favorable processes in the catalyzed oxidative degradation of organics in oxygenated aqueous solutions:

$$TiO_2(e^- + h^+) \overset{O_2, H_2O, OH^-}{\rightarrow} \ \cdot O_2^- + ^\cdot OH \qquad (1)$$
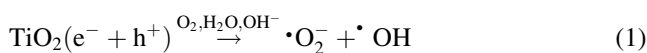
The mechanisms of OH formation have been discussed in the literature [3,4]. The hydroxyl radical is an extremely potent oxidizing agent capable of oxidizing almost all organic compounds. The redox potential for OH has been assigned a value of +2.8 V [5].

In the present work we studied the photocatalytic oxidation of oxalic acid, a representative member of the dicarboxylic acid family, in the presence of TiO$_2$. The mechanism of photocatalytic degradation of this compound, to CO$_2$, was followed and some kinetic parameters were calculated.

Oxalic acid was chosen because its radiolysis and reactivity toward OH radicals has been investigated in detail [6,7], and also because it is a water pollutant resulting from some industrial treatment processes (textile industry, metal-lurgy etc.). Moreover, as indicated by the potential of the redox couple H$_2$C$_2$O$_4$ (aq)/CO$_2$(g) -0.49 V [8] it is easy to oxidize.

2. Experimental details

The solutions were prepared from analytical grade chemicals (BDH or Merck) without further purification. Doubly distilled water saturated with oxygen was used. The pH of oxalic acid solutions was 3.5 and was adjusted with HClO$_4$.

Oxalic acid concentration was determined by the spectrophotometric method with copper benzidine [9] or by using conventional permanganate titration. All the experiments were carried out using 2 mg cm^{-3} suspensions of TiO$_2$ (Degussa P-25, predominantly anatase, specific area of 50 m^2 g^{-1}, non-porous).

Photocatalytic degradation of oxalic acid was studied using the flow system of the total organic carbon analyzer – SGE Anatoc instrument. Oxidation is carried out by illumination with near-UV light (300–400 nm) in the presence of a photocatalyst. Oxidation occurs through photocatalysis during the liquid's passage through glass coils surrounding the near-UV light sources. The lamps used are 8 W blacklight fluorescent tubes. The lamps are mounted horizontally in the center of the reaction coils to obtain maximum efficiency. The carbon dioxide generated by the degradation of organic compound is determined via measurement of conductivity, and exhibits linear response over a wide concentration range. Calibration relies on establishing

the relation between carbon mass in the sample and conductivity measurement. Benzoic acid was used as a calibration standard. Commonly, samples were measured over the mass range of 10–100 µg of carbon. The sample pH should be adjusted to a value of 3.5. At pH 3.5 the formation of CO_2 is favored by at least 99.5% vs. 0.5% of the HCO_3^-.

3. Results and discussion

Photocatalytic degradation of oxalic acid in the presence of O_2 over TiO_2 powder dispersed in aqueous solution was investigated by measuring CO_2 formation as a function of the illumination time at pH = 3.5, and at constant temperature of 22°C. Oxalic acid is present in ionic form in the solution of pH 3.5. The reason for this is the dissociation of oxalic acid, which occurs with $pK_1 = 1.25$ and $pK_2 = 4.28$ [7]. At pH 3.5 the fraction of oxalic acid present as $HC_2O_4^-$ exceeds 85%.

Results obtained show that the photocatalytic decomposition of oxalic acid gives only carbon dioxide. The evolution of CO_2 as the final product of the photodegradation was investigated in the 0.3–4.0 µmol range of oxalic acid. Fig. 1 shows the typical curves of the evolution of CO_2. The maximum amount of CO_2 evolved increases with the increase of oxalic acid concentration. Dashed lines show the carbon mass corresponding to complete conversion of oxalic acid to CO_2. This may also be concluded from the data in Table 1, where the correlation between the initial concentration of oxalic acid, determined spectrophotometrically, and the maximum of CO_2 evolved is presented. It is noteworthy that in all cases, the amount of CO_2 evolved reflects that there is a one-to-two correspondence between the moles of oxalate and CO_2 evolved as measured by the TOC analyzer. The observed reaction time for complete disappearance became less with the decrease of the initial amount (from about 4 min to about 9 min in the studied range of oxalic acid amounts).
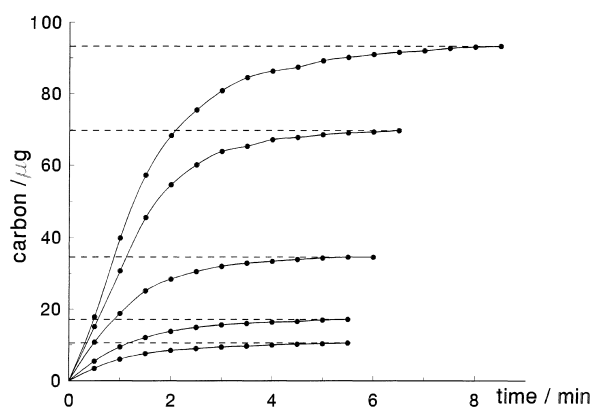

Fig. 1. Effect of irradiation time on the CO_2 evolution for five different initial amounts of oxalic acid. Dashed lines show yield corresponding to total oxidation of oxalic acid.

Table 1
Correlation between amounts of oxalic acid, carbon dioxide and initial oxidation rates

$H_2C_2O_4$/µmol	CO_2/µmol	CO_2/µmol min^{-1}
0.30	0.65	0.445
0.45	0.88	0.542
0.50	1.07	0.643
0.55	1.17	0.819
0.75	1.46	0.897
0.85	1.52	0.903
1.35	2.87	1.667
1.95	3.99	1.833
2.90	5.81	2.583
3.85	7.78	3.333

Published reaction mechanisms for the oxidation of organic compounds over titanium dioxide suspended in oxygenated aqueous solution involve reaction with OH radicals produced by the reaction of photogenerated holes with adsorbed water molecules or hydroxyl ions [3,10]. It is known that OH radicals react rapidly with most organic solutes. It is also known that oxygen reacts efficiently with the photoelectrons forming O_2^- (or HO_2) radicals, and should inhibit the electron–hole recombination.

According to these considerations and the obtained results, the following reaction mechanism may be proposed for the photooxidation of oxalic acid at the surface of TiO_2 catalyst: oxalic acid reacts with OH radicals

$$HC_2O_4^- + {}^\bullet OH \rightarrow OH^- + {}^\bullet COOH + CO_2 \qquad (2)$$

Free radicals formed in reaction Eq. (2) disappear by reaction with oxygen

$$^\bullet COOH + O_2 \rightarrow {}^\bullet HO_2 + CO_2 \qquad (3)$$
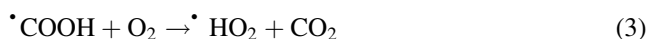
Recombination of HO_2 radicals leads to H_2O_2 formation,

$$^\bullet HO_2 + {}^\bullet HO_2 \rightarrow H_2O_2 + O_2 \qquad (4)$$
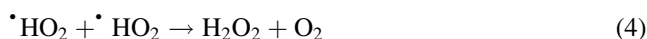
but hydrogen peroxide was not found as a final product of photocatalytic degradation. The consumption of H_2O_2 during the photooxidation resulted from the reaction with electrons and OH radicals [11,12].

Postulated mechanism of the photocatalytic degradation of oxalic acid closely corresponds to the published data concerning the radiolysis of oxalic acid solution [6]. Herrmann et al. [8] predicted the mechanism involving the reaction of the photoactivated species O_{ads}^* with adsorbed $HC_2O_4^-$ ions. They suggest that degradation occurs by an attack of the C–C bond with the production of an intermediate leading to the formation of an unstable bicarbonate ion. We assume that the OH radical attacks C–C bond leading to the formation of COOH radical, which disappears by reaction with oxygen. This conclusion is in accordance with the observation of Muthu et al. for the photodegradation of oxalic acid by fullerenes [13].

The release of CO_2 was found to follow first-order kinetic law up to about 75–80% decomposition of oxalic acid. It occurs during the first 2 min of illumination (Fig. 2). The
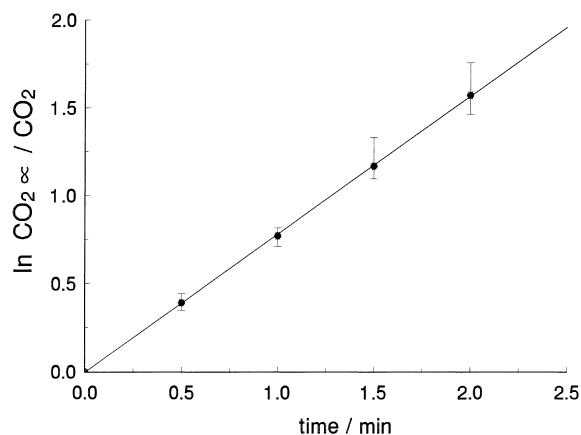
Fig. 2. Plot of ln $[CO_2]_\infty/[CO_2]$ vs. irradiation time for 10 different initial amounts of oxalic acid in the range of 0.3–4.0 μmol.

Fig. 3. Reciprocal initial degradation rate vs. reciprocal initial amount of oxalic acid.

numerical values of the points in Fig. 2 were calculated from expression

$$\ln\frac{[CO_2]_\infty}{[CO_2]} = k^*t \tag{5}$$

in which $[CO_2]_\infty$ is the measured amount of CO_2 for the complete destruction of oxalic acid and $[CO_2]$ is actual amount. Each point represents the mean value obtained upon substitution of the values of $[CO_2]_\infty$ and $[CO_2]$ measured for 10 different initial amounts of oxalic acid. The obtained values are independent on the initial amount of oxalic acid within experimental accuracy. A linear relationship between $\ln[CO_2]_\infty/[CO_2]$ and illumination time demonstrates a good approximation for the data of degradation of oxalic acid in the studied range. From the slope of the plot in Fig. 2, obtained by the method of linear regression ($r = 0.999$), reaction rate constant k^* was calculated as 0.78 min^{-1} ($t_{1/2} = 53.3$ s). Under the present conditions obtained value is independent of the initial concentration, but the overall rate of reaction increases as the oxalic acid concentration increases (from 0.25 to 3.03 μmol $H_2C_2O_4$ min^{-1} in the studied range of concentrations). This effect can be explained by assuming that at low substrate concentrations the number of catalytic sites is not a limiting factor of the degradation rate which is proportional to the substrate concentration, as well as that the competition between reaction intermediate and substrate for active sites does not exist [14,15].

The photodegradation kinetics of many organic compounds in TiO_2 dispersions under UV illumination has often been modeled to the simple Langmuir–Hinshelwood equation [3,10,16]

$$R = -\frac{dC}{dt} = \frac{kKC}{1+KC} \tag{6}$$

a linear transform of which gives:

$$\frac{1}{R} = \frac{1}{k} + \left(\frac{1}{kK}\right) \times \left(\frac{1}{C}\right) \tag{7}$$

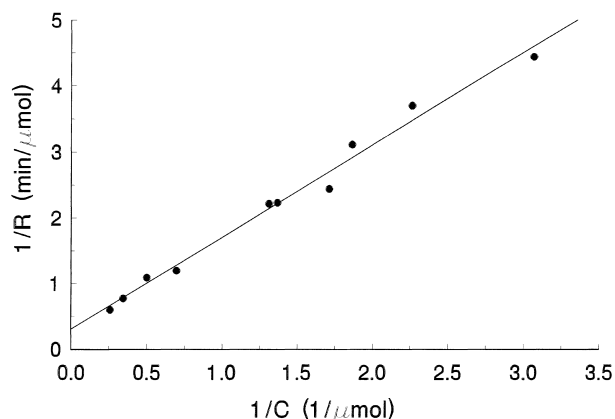where R denotes initial rate of disappearance of organic substrate, C is its initial concentration, k is the rate constant and K is adsorption constant of the reactant concentration C. The linearity of a plot of $1/R$ vs. $1/C$ indicates that the Langmuir–Hinshelwood model is valid.

The rate of disappearance of oxalic acid was assumed to be proportional to the rate of CO_2 formation for the examination of the effect of the initial amount of oxalic acid to the initial oxidation rates. The initial rates of formation of CO_2 at different oxalic acid amounts were obtained from the straight lines of the curves in Fig. 1. From the slopes of these lines initial oxidation rates, expressed as μmol of CO_2 formed per minute, were determined and the initial oxidation rates of oxalic acid against the initial amount of oxalic acid were calculated (Table 1, columns 2 and 3).

Fig. 3 shows the plot of the reciprocal initial rates vs. reciprocal initial amount of oxalic acid. The plot based on Eq. (7) fitted satisfactory. The correlation coefficient obtained is 0.993. The values corresponding to k and K, obtained from the intercept and the slope of the plot in Fig. 3, are 3.20 μmol min^{-1} and 0.22 μmol^{-1}, respectively. The k value represents the limiting oxidation rate for the oxalic acid, and K value reflects the tendency for the oxalic acid to be adsorbed by TiO_2.

The obtained data confirm that the Langmuir–Hinshelwood kinetic model is appropriate for the interpretation of the CO_2 photogeneration rate during the oxalic acid and similar organic compounds' degradation at low concentrations [8,17–20]. Further experiments with higher oxalic acid concentrations are in progress.

References

[1] O. Legrini, E. Oliveros, A.M. Braun, Chem. Rev. 93 (1993) 671.

[2] D.F. Ollis, E. Pelizzetti, N. Serpone, in: N. Serpone, E. Pelizzetti (Eds.), Photocatalysis – Fundamentals and Applications, Wiley, New York 1989, p. 603.

[3] C.S. Turchi, D. Ollis, J. Catal. 122 (1990) 178.

[4] L. Sun, J.R. Bolton, J. Phys. Chem. 100 (1996) 4127.

[5] A.J. Bard (Ed.), in: Encyclopedia of Electrochemistry, Marcel Dekker, New York 1974, p. 191.

[6] Z.D. Draganic, I.G. Draganić, M.M. Kosanić, J. Phys. Chem. 68 (1964) 2085.

[7] Z.D. Draganić, M.M. Kosanić, M.T. Nenadović, J. Phys. Chem. 71 (1967) 2390.

[8] J.-M. Herrmann, M.-N. Mozzanega, P. Pichat, J. Photochem. 22 (1983) 333.

[9] Z.D. Draganić, Anal. Chim. Acta 28 (1963) 394.

[10] R.W. Matthews, J. Catal. 111 (1988) 264.

[11] A.L. Lingen, J.F. Rabek, A. Kaminska, M. Scoponi, Coord. Chem. Rev. 125 (1993) 195.

[12] R.- a Doong, W.- h Chang, J. Photochem. Photobiol. A: Chem. 107 (1997) 239.

[13] S. Muthu, P. Muruthamuthu, P.R. Vasudeva Rao, Fullerene Sci. Technol. 1 (1993) 481.

[14] F. Sabin, T. Turk, A. Vogler, J. Photochem. Photobiol. A: Chem. 63 (1992) 99.

[15] K.E. O'Shea, I. Garcia, M. Augliar, Res. Chem. Intermed. 23 (1997) 325.

[16] K. Rajeshwar, J. Appl. Electrochem. 25 (1995) 1967.

[17] R.W. Mathews, Wat. Res. 24 (1990) 653.

[18] J.G. Sczechowski, C.A. Koval, R.D. Noble, in: D.F. Ollis, H. Al-Akabi (Eds.), Photocatalytic Purification and Treatment of Water and Air, Elsevier, Amsterdam 1993, p. 645.

[19] Y. Inel, A.N. Ökte, Toxicol. Environ. Chem. 55 (1995) 115.

[20] Y. Inel, A.N. Ökte, J. Photochem. Photobiol. A: Chem. 96 (1996) 175.