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Photocatalytic degradation of malonic acid in aqueous suspensions of titanium dioxide: an initial kinetic investigation of CO_2 photogeneration

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Abstract

The photocatalytic oxidation of malonic acid in aqueous suspensions of TiO_2 was investigated by following the formation of CO_2. The rate of formation of CO_2 is affected by the pH of the aqueous suspension, TiO_2 loading, malonic acid concentration, temperature, irradiation time, flow rate and light intensity. The disappearance of malonic acid fits a Langmuir–Hinshelwood kinetic model. Rate constants were calculated by including a correction term $\alpha(T)$ to take into account the decrease in the solubility of CO_2 with increasing temperature. The activation energy is 9.99 kJ mol^{-1}. A quantum yield of 0.26 for CO_2 formation was estimated from the proposed mechanism.

Keywords: Photocatalytic degradation; Malonic acid; TiO_2; CO_2

1. Introduction

In recent years, TiO_2 suspended in aerated water has been proven to be the most active photocatalyst with a band gap of 3.2 eV. The absorption of light with an energy greater than that of the band gap generates electron–hole pairs and subsequent oxidation–reduction processes.

So far, extensive work has shown that many organic compounds in aqueous solutions containing near-UV-illuminated suspensions of TiO_2 are oxidized completely to CO_2 [1]. In this work, we report a recent investigation of the photocatalytic oxidation of malonic acid ($HOOC–CH_2–COOH$), a representative member of the dicarboxylic acid family, in the presence of TiO_2. The possible photocatalytic oxidation of this compound to give CO_2 was followed and the initial kinetics of CO_2 photogeneration were studied. The disappearance of the acid and the formation of intermediate products were not analysed. In order to understand the mechanism of CO_2 formation, the effects of various factors, such as the catalyst concentration, flow rate, pH, concentration of malonic acid, temperature, irradiation time and light intensity, were investigated.

2. Experimental details

2.1. Materials

Degussa P25 grade titanium dioxide was a generous gift from Degussa Ltd., Turkey. It has a BET surface area of 50 ± 15 m^2 g^{-1} and an average particle size of 30 nm. X-Ray diffraction analysis showed that this material was mostly in the anatase form.

All chemicals used in the experiments were of laboratory reagent grade and were used without further purification.

2.2. The photochemical reactor

The experiments were carried out in a gas recycling reactor made of a Pyrex tube (length, 36.2 cm; outer diameter, 13 cm; inner diameter, 3.5 cm). It contained an inner glass tube with a thickness of 2 cm. The temperature of the system was controlled by a Julabo F40 Ultratemp 2000 water circulator connected to the inner glass tube. The suspension was contained in the annulus between the two tubes. The gas above the suspension was pumped using a Cole–Parmer peristaltic pump. A sintered glass disc, placed at the bottom of the reactor, provided for the circulation of air and prevented the settlement of the suspension. Tygon tubing was used for the connections. The reactor was placed in an irradiation box (length, 70 cm; width, 22 cm). Six 20 W black light fluorescent lamps (General Electric F 20 T 12/BLB) were used. Two together were attached to the right- and left-hand sides and the back of the box. It was possible to light them one by one. The front side of the box was designed to operate as a door and the reactor was attached to the front side in order to maintain a uniform geometry throughout the experiments. A fan was placed at the top of the box and air was continually

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circulated through the box in order to eliminate the heating effect of the lamps.

For most of the experiments described in this paper, stock solutions of malonic acid were prepared as 1×10^{-3} M at the natural pH (pH 3.4). The reaction mixture (200 ml) was mixed with the catalyst TiO_2 (1 g l^{-1}). A sonicator was used to ensure the uniform mixing of the TiO_2 suspension before mixing with malonic acid. Solutions were wrapped with Al foil and kept in the dark in order to prevent any interference from surrounding light before irradiation. The pH values of the reaction solutions were adjusted by adding $HClO_4$ or NaOH.

2.3. Analyses

A heated gas sampler (Shimadzu type HGS-2) was used to pass the gas samples into the gas chromatograph (GC) (Gow Mac). A GC equipped with a Porapak-N packed column and a thermal conductivity detector was used. The carrier gas was helium with a flow rate of 60 ml min^{-1}.

Calibrations were carried out using measured volumes of carbon dioxide added to the circulating gas phase loop under identical conditions with the experiments.

3. Results and discussion

3.1. Effect of catalyst concentration and flow rate

The dependence of CO_2 formation on the TiO_2 concentration was followed in the range 0.1–3.1 g l^{-1} (Table 1). Each point in Fig. 1 shows the result for 1 h irradiation. CO_2 formation increases with increasing TiO_2 concentration up to 0.8 g l^{-1}. With a further increase in TiO_2 concentration, the formation of CO_2 appears to reach a limiting value, representing the contribution of two main factors. One factor is the aggregation of TiO_2 particles at high concentrations, causing a decrease in the number of surface active sites. The other is that higher catalyst concentrations, because of the opacity and light scattering properties of the particles, can lead to a decrease in the passage of irradiation through the sample. Thus 1 g l^{-1} TiO_2 was chosen (near the beginning of the plateau) for further experiments.

The inset in Fig. 1 shows the results of CO_2 formation as a function of flow rate. Experiments were carried out at three different flow rates (Table 2). Although less CO_2 was formed at low flow rates, 288 ml min^{-1} was used in order to prevent the overflow of the solution from the reactor and escape to the Tygon tubing which passes through the peristaltic pump.

3.2. Effect of pH

The formation of CO_2 was determined as a function of the solution pH in the range pH 1.7–9. The results are plotted in Fig. 2.

Table 1
Effect of TiO_2 loading on CO_2 formation

TiO_2 (g l^{-1})	CO_2 (μmol)
0.1	0.66
0.2	1.6
0.3	1.6
0.7	2.3
1.4	2.4
2.1	2.3
3.1	2.2

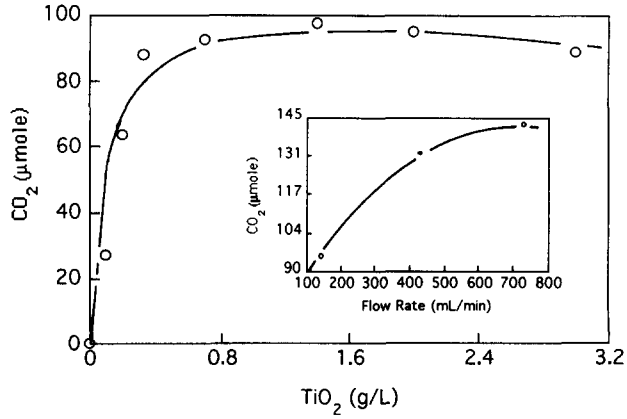

Fig. 1. Effect of the amount of TiO_2 on the formation of CO_2. The inset shows CO_2 formation as a function of the flow rate.

Table 2
Effect of flow rate on CO_2 formation

Flow rate (ml min^{-1})	CO_2 (μmol)
144	95.3
432	132
720	143

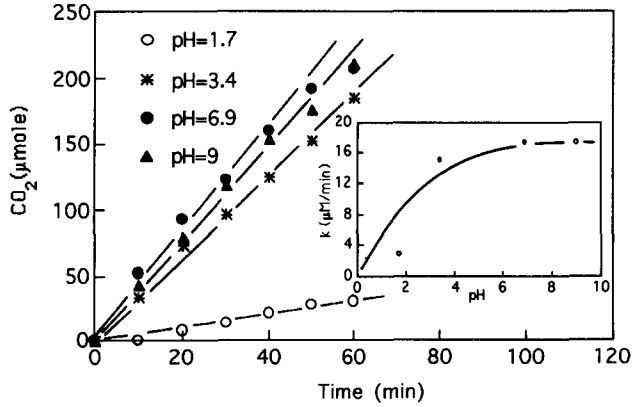

Fig. 2. Evolution of CO_2 at different pH values. The inset shows the effect of pH on the rate of CO_2 formation. Conditions: [malonic acid] = 1×10^{-3} M, T = 294 K, intensity = 1.8×10^{-7} einstein s^{-1}, [TiO_2] = 1 g l^{-1}, flow rate = 288 ml min^{-1}.

The ionizable hydrogens of malonic acid can be abstracted according to the pK_1 (2.85) and pK_2 (5.69) values [2]. The

Table 3
Effect of pH on the rate of CO_2 formation

k (μM min^{-1})	pH
2.86	1.7
15.1	3.4
17.3	6.9
17.4	9.0

following results (Table 3) were obtained when the rates of CO_2 formation were plotted against pH.

1) When the pH of the medium is below pK_1, the rate of formation of CO_2 is at its lowest. This can be explained by the presence of acid in its acidic form (i.e. no hydrogen is lost) which obstructs the formation of CO_2.
2) There is a small difference between the natural pH of the acid and its pK_1 value. Therefore, one of the hydrogens can be lost, enhancing the rate of CO_2 formation.
3) At pH $\approx$ 7, both ionizable hydrogens are abstracted, leading to the effective formation of CO_2.
4) The surface charge of TiO_2 is strongly influenced by the pH. The isoelectric point for TiO_2 in water is pH 6. At lower pH values, a positive surface charge is expected, and at higher pH values, a negative surface charge. At pH 9, the surface of TiO_2 will therefore be negatively charged. In addition, malonic acid exists in its dianionic form. Under these conditions, the predominant effect may lead to a decrease in the rate of CO_2 production. However, the decrease in CO_2 production does not occur to an appreciable extent. This implies that hydroxyl radicals may diffuse into the solution and react with malonic acid molecules.

3.3. Effect of irradiation time

The yield of CO_2 from 200 ml solutions of 1×10^{-3} M malonic acid at its natural pH, containing 0.2 g of TiO_2, was followed to extended irradiation times (Table 4) and, after irradiation for 150 min, the formation of CO_2 reached a plateau (Fig. 3).

Table 4
Effect of irradiation time on CO_2 formation

Time (min)	CO_2 (μmol)
0	0
10	33.2
20	73.1
30	96.2
40	124
50	152
60	185
80	217
100	260
120	289
140	320
160	320

A linear increase in the formation of CO_2 was observed during the first 60 min (Fig. 3, inset). Therefore, to compare different results and to shorten the duration of the experiments, we measured CO_2 formation for 60 min in all cases.

3.4. Effect of acid concentration

The effect of concentration on CO_2 formation was investigated in the $(0.01–1)\times10^{-3}$ M range by using slurries at natural pH and at a constant temperature of 21 °C. The rate of formation of CO_2 was assumed to be equal to the rate of disappearance of malonic acid for the examination of the effect of acid concentration on the CO_2 yield.

Fig. 4 shows the amount of CO_2 evolved, which increases linearly with the concentration of malonic acid.

The formation of CO_2 reaches a plateau in Fig. 5, indicating that the photogeneration of CO_2 obeys zero-order kinetics. The Langmuir–Hinshelwood (LH) model also holds for malonic acid (Fig. 5, inset); the rate expression can be written as

$$R = dC/dt = k(KC)/1 + KC$$

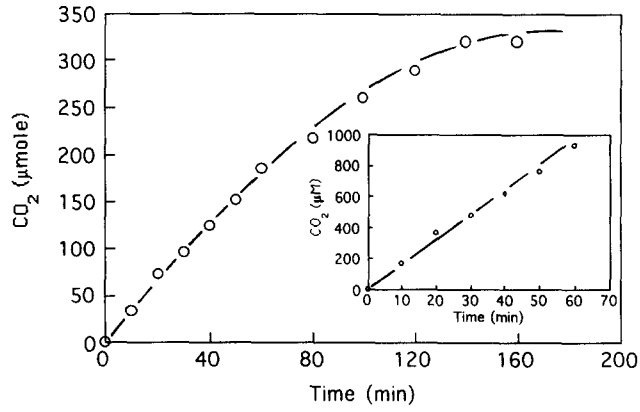

Fig. 3. Effect of irradiation time on CO_2 evolution. The inset shows the rate of CO_2 formation after 60 min irradiation time. Conditions: pH 3.4 (natural), [malonic acid] = 1×10^{-3} M, T = 294 K, intensity = 1.8×10^{-7} einstein s^{-1}, [TiO_2] = 1 g l^{-1}, flow rate = 288 ml min^{-1}.

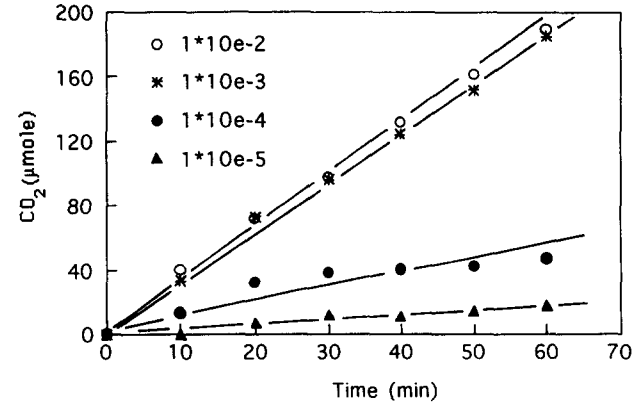

Fig. 4. The evolution of CO_2 as a function of malonic acid concentration. Conditions: pH 3.4 (natural), T = 294 K, intensity = 1.8×10^{-7} einstein s^{-1}, [TiO_2] = 1 g l^{-1}, flow rate = 288 ml min^{-1}.

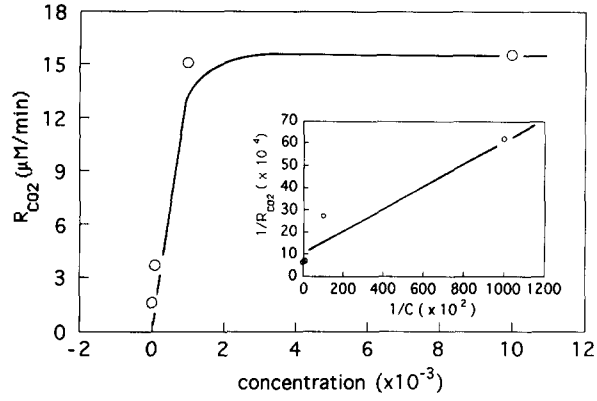

Fig. 5. Rate of CO_2 formation vs. malonic acid concentration. The inset shows $1/R_{CO2}$ vs. $1/C$.

Table 5
Effect of malonic acid concentration on the rate of CO_2 formation

R_{CO_2} (μM min^{-1})	C (M) ($\times 10^{-3}$)	$1/R_{CO_2}$ (min M^{-1}) ($\times 10^4$)	$1/C$ (M^{-1}) ($\times 10^2$)
15.5	10	6.45	1
15.1	1.0	6.67	10
3.69	0.1	27.1	100
1.61	0.01	62.1	1000

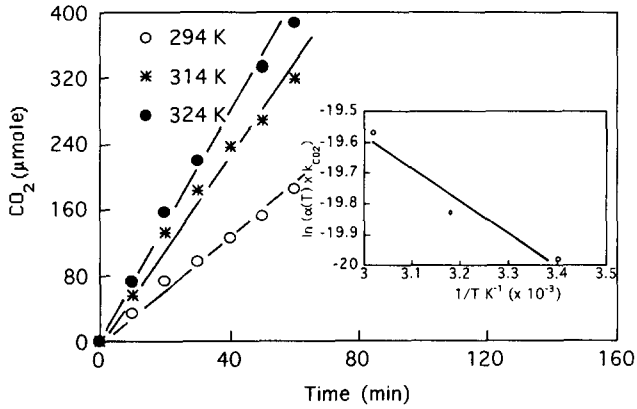

Fig. 6. The evolution of CO_2 at various temperatures. The inset shows an Arrhenius plot. Conditions: pH 3.4 (natural), [malonic acid] = 1×10^{-3} M, intensity = 1.8×10^{-7} einstein s^{-1}, [TiO_2] = 1 g l^{-1}, flow rate = 288 ml min^{-1}.

Table 6
Arrhenius data for malonic acid

$\ln[\alpha(T) \times k_{CO_2}$	$1/T$ (K^{-1}) ($\times 10^{-3}$)
−19.98	3.401
−19.83	3.181
−19.57	3.091

where C is the concentration of the acid, k is the reaction rate constant (8.97 μM min^{-1}) and K is the adsorption equilibrium constant (0.0214 μM^{-1}). The linearity of a plot of $1/R$ vs. $1/C$, where $1/k$ is the intercept and $1/kK$ is the slope, indicates that the LH model is valid [3]. The validity of the LH model confirms that the photo- oxidation occurs completely on the TiO_2 surface. The results are shown in Table 5.

3.5. Effect of temperature

The variation in CO_2 formation was followed at three different temperatures (21, 41 and 51 °C); it is found that increasing the temperature increases the reaction rate (Fig. 6). A correction term $\alpha(T)$ is needed to take into account the decrease in the solubility of CO_2 with increasing temperature. The temporal variation in the total number of moles of CO_2 ($N(CO_2)$) can be determined using the formula [4]

$$N(CO_2) = [CO_2](V_{HS}/V + V_{LP}K_{CO_2}T/294)/100$$
$$= \alpha(T)[CO_2]$$

where V_{HS} is the volume of the head space (0.150 l), V is the volume of one mole of gas at $T = 21$ °C and $P = 1$ atm (24.1 l), V_{LP} is the volume of the liquid phase (0.200 l) and K_{CO2} is the equilibrium constant for the process $CO_2(g) \rightleftharpoons CO_2(aq)$ and is equal to 3.9×10^{-2} mol l^{-1} atm^{-1} at 21 °C [5].

In this study, most of the experiments were carried out at $T = 21$ °C, and therefore $\alpha(T)$ is 14.02×10^{-5} mol/[CO_2]. At 41 °C, $\alpha(T)$ is 10.74×10^{-5} mol/[CO_2], and at 51 °C, $\alpha(T)$ is 9.83×10^{-5} mol/[CO_2].

The Arrhenius plot ($\ln[\alpha(T) \times k_{CO2}]$ vs. $1/T$) (Table 6) is shown in the inset of Fig. 6; the slope leads to the calculation of the activation energy as 9.99 kJ mol^{-1}.

3.6. Effect of light intensity

CO_2 formation from malonic acid was also investigated as a function of the light intensity. The light intensity was measured using a potassium ferrioxalate actinometer and was found to be 0.3×10^{-7} einstein s^{-1} in the wavelength region 300–400 nm. When the light intensity was increased, higher CO_2 formation was observed (Fig. 7).

When the reaction rates were plotted against the intensities of the lamps, no linear correlation was observed (Fig. 8);

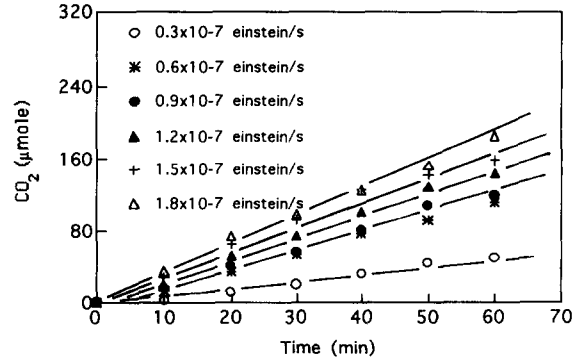

Fig. 7. CO_2 formation as a function of the lamp intensity. Conditions: pH 3.4 (natural), [malonic acid] = 1×10^{-3} M, $T = 294$ K, [TiO_2] = 1 g l^{-1}, flow rate = 288 ml min^{-1}.

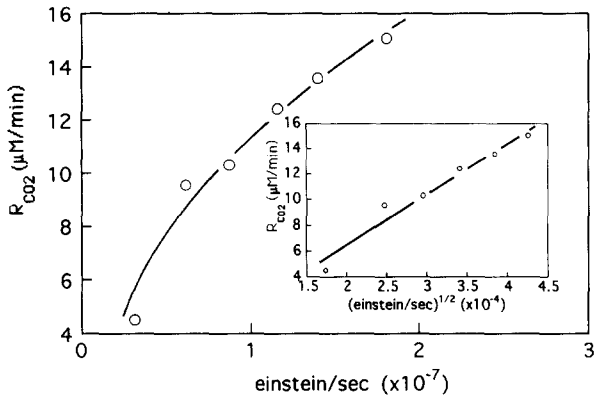

Fig. 8. Effect of light intensity on the rate of CO_2 formation. The inset shows the effect of the square root of light intensity on CO_2 evolution.

Table 7
Effect of light intensity on the rate of CO_2 formation

R_{CO_2} (μM min^{-1})	Intensity (einstein s^{-1}) (×10^{-7})	Intensity$^{1/2}$ (einstein s^{-1})$^{1/2}$ (×10^{-4})
4.51	0.3	1.73
9.54	0.6	2.45
10.3	0.9	3.00
12.4	1.2	3.46
13.5	1.5	3.87
15.1	1.8	4.24

however, a straight line was obtained when the square root of the intensity of the lamps was plotted (inset in Fig. 8). These results, also given in Table 7, can be explained in terms of the increased importance of electron–hole recombination at higher light intensities.

3.7. Postulated mechanism

The proposed reactions involved in the photo-oxidation of malonic acid (MA, malonic acid) were given as input to a program written in Fortran in IBM. The following mechanism can be proposed.

$$TiO_2 + h\nu \longrightarrow e^- + h^+ \quad (k_1)$$

$$MA \longrightarrow MA^- + H^+ \quad (k_2)$$

$$MA^- + H^+ \longrightarrow MA \quad (k_3)$$

$$MA^- + h^+ \longrightarrow MA^\bullet \quad (k_4)$$

$$MA^\bullet \longrightarrow R^\bullet + CO_2 \quad (k_5)$$

$$H^+ + e^- \longrightarrow H^\bullet \quad (k_6)$$

$$O_2 + e^- \longrightarrow O_2^{\bullet -} \quad (k_7)$$

$$O_2^{\bullet -} + H^\bullet \longrightarrow HO_2^- \quad (k_8)$$

$$HO_2^- + HO_2^- \longrightarrow O_2 + H_2O_2 \quad (k_9)$$

$$H_2O_2 + e^- \longrightarrow OH^\bullet + OH^- \quad (k_{10})$$

$$MA + OH^\bullet \longrightarrow R^\bullet + H_2O \quad (k_{11})$$

$$R^\bullet + H^\bullet \longrightarrow RH \quad (k_{12})$$

$$d[TiO_2]/dt = -k_1[TiO_2](h\nu) = \Phi I$$

$$d(e^-)/dt = -k_6[H^+](e^-) - k_7[O_2](e^-) - k_{10}[H_2O_2](e^-) + k_1[TiO_2](h\nu)$$

$$d(h^+)/dt = -k_4[MA^-](h^+) + k_1[TiO_2](h\nu)$$

$$d[MA]/dt = -k_2[MA] - k_{11}[MA][OH^\bullet] + k_3[MA^-][H^+]$$

$$d[MA^-]/dt = -k_3[MA^-][H^+] - k_4[MA^-](h^+) + k_2[MA]$$

$$d[H^+]/dt = -k_3[MA^-][H^+] - k_6[H^+](e^-) + k_2[MA]$$

$$d[MA^\bullet]/dt = -k_5[MA^\bullet] + k_4[MA^-](h^+)$$

$$d[R^\bullet]/dt = -k_{12}[R^\bullet][H^\bullet] + k_5[MA^\bullet] + k_{11}[MA][OH^\bullet]$$

$$d[CO_2]/dt = k_5[MA^\bullet]$$

$$d[H^\bullet]/dt = -k_8[O_2^{\bullet -}][H^\bullet] - k_{12}[R^\bullet][H^\bullet] + k_6[H^+](e^-)$$

$$d[O_2]/dt = -k_7[O_2](e^-) + k_9[HO_2^-][HO_2^-]$$

$$d[O_2^{\bullet -}]/dt = -k_8[O_2^{\bullet -}][H^\bullet] + k_7[O_2](e^-)$$

$$d[HO_2^-]/dt = -2k_9[HO_2^-][HO_2^-] + k_8[O_2^{\bullet -}][H^\bullet]$$

$$d[H_2O_2]/dt = -k_{10}[H_2O_2](e^-) + k_9[HO_2^-][HO_2^-]$$

$$d[OH^\bullet]/dt = -k_{11}[MA][OH^\bullet] + k_{10}[H_2O_2](e^-)$$

$$d[OH^-]/dt = k_{10}[H_2O_2](e^-)$$

$$d[H_2O]/dt = k_{11}[MA][OH^\bullet]$$

$$d[TH]/dt = k_{12}[R^\bullet][H^\bullet]$$

As a result, the CO_2 formation rate and quantum yield can be calculated as

$$R_{CO_2} = d[CO_2]/dt = \Phi I$$

where Φ is the quantum yield and I is the intensity; the overall quantum yield was found to be 0.26.

4. Conclusions

Our experimental results indicate that the rate of formation of CO_2 is pH dependent. The Langmuir-type plot obtained

confirms that the photo-oxidation reaction takes place on the surface of TiO_2. Taking into consideration the observation that an increase in temperature leads to a significant increase in the rate of CO_2 formation, the activation energy can be calculated as 9.99 kJ mol^{-1}. By increasing the number of lamps, the rate of CO_2 formation increases linearly. However, it should be noted that, at high intensities, the probability of electron–hole recombination also increases, which inhibits this linearity. In this case, the rate of CO_2 formation vs. the square root of intensity can be plotted as a straight line. The rate of CO_2 formation increases with increasing irradiation time; however, a limit is observed after 150 min when the formation of CO_2 reaches a plateau.

Acknowledgements

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