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A mechanistic study of the photoelectrochemical oxidation of organic compounds on a TiO_2/TCO particulate film electrode assembly

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Abstract

The photo-oxidative degradation of sodium benzene sulfonate, 2-phenoxyethanol, ethyleneglycol, diethyleneglycol, acetic acid and formic acid, was examined on a TiO_2 particulate film immobilized on a transparent conductive oxide (TCO) glass electrode assembly. The photocurrents generated during the photodegradation of these organic compounds were monitored. Formation of intermediate species (acetic acid and formic acid) during the temporal course of the photo-oxidative process(es) appears to have a direct effect on the photocurrents.

Keywords: TiO_2/TOC electrode; Photoelectrochemical oxidation; Ethyleneglycol; Sodium benzenesulfonate; 2-Phenoxyethanol

1. Introduction

The photo-oxidative degradation of organic pollutants mediated by TiO_2 particles provides an attractive method for the purification and treatment of water and air [1]. In recent years we have reported extensively on the photodecomposition of such organic substrates as surfactants [2], pesticides [3] and cyanide [4]. To date, aqueous titania suspensions have proven relatively effective. This notwithstanding, however, a disadvantage of such suspensions in practical treatment processes is the need to ultimately remove the TiO_2 particulates by filtration, centrifugation, coagulation or flocculation. Any treatment process that avoids such additional costly operations will prove economically beneficial.

A TiO_2 particulate thin film exhibits interesting photochemical and photoelectrochemical properties [5–7]. Application of an external anodic bias to drive the photogenerated electrons to the counter-electrode compartment in a TiO_2 particulate film electrode assembly in which titania particles are fixed on a transparent conductive oxide (TCO) glass plate leads to minimization of electron–hole recombination and to promotion of charge separation following irradiation of the assembly [6,7]. We and others have demonstrated that these TiO_2/TCO electrodes exhibit photocatalytic activities that are similar to titania suspensions in the photodegradation of surfactants [8] and chlorophenols [9]; they are thus preferable to suspension systems from the standpoint of removal of TiO_2 particles. This type of thin-film electrode assembly also provides a convenient method for accelerating the photocatalyzed degradation of pollutants on application of an external bias.

Because of complications typically inherent in a reaction system, the mechanism(s) of the photocatalyzed mineralization of organic substances and the details of the generation of photocurrents in a TiO_2 particulate film electrode system have not received wide attention [8,9]. In this work, we examine the photo-oxidation of some organic compounds on such an electrode assembly. The intermediates (formic acid and acetic acid) formed during the electrochemically assisted photocatalytic process have been identified. The effect of formic acid (and/or acetic acid) on the generation of photocurrents has been determined and the relevant mechanism(s) of photodegradation is briefly discussed.

2. Experimental section

The TiO_2/TCO particulate film electrodes were prepared using a procedure similar to that reported earlier [8]. TiO_2 particles (Degussa P-25, anatase) dispersed in an aqueous

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solution were loaded onto a 20×50 mm^2 transparent conductive oxide (TCO) glass plate (Asahi Glass Co. Ltd.; glass plate coated with fluorine-doped SnO_2) which was subsequently dried in air. The plate was brought to 400 °C at 1 °C min^{-1} in a furnace and then sintered for 2 h at 400 °C. The quantity of TiO_2 particles that coated an area of 20×30 mm^2 was about 5 mg.

All organic substrates used were generally of the highest purity available commercially: 2-phenoxyethanol, diethyleneglycol, formic acid and acetic acid were obtained from Wako Pure Chemical Ind. Deionized and once-distilled water was used throughout. The reactant solution (20 ml) was contained in a Pyrex glass photoreactor [8].

In the electrode assembly, the anode was a TiO_2/TCO plate and the counter-electrode (the cathode) was a Pt wire; the two compartments of the working and counter-electrodes were separated by a fine glass frit. The reference electrode was a Ag/AgCl electrode using an electrolyte such as NaCl, Na_2SO_4 or Na_2CO_3 connected to the assembly via a salt bridge consisting of a saturated NaCl and agar. The direct irradiation on the AgCl electrode was avoided by wrapping with aluminum foil as much as possible. Applied voltages were supplied from a potentiostatat. The UV illumination source was a mercury lamp (Toshiba SHL-100WQ, 75 W); the light intensity at 360 nm was 0.95 mW cm^{-2}. The potentials at the TiO_2/TCO electrode were measured with an electrometer. Temporal changes in the concentrations of the photodegraded organic substrates and formation of formic acid and/or acetic acid intermediates were monitored by high-performance liquid chromatography (HPLC), using the refractive-index detection method.

3. Results and discussion

3.1. Effect of electrolytes on photocurrent during the photodegradation of sodium benzene sulfonate and 2-phenoxyethanol

Photocurrents generated during the photodegradation of sodium benzene sulfonate (BS) and 2-phenoxyethanol (PE) in the presence of different electrolytes at various concentrations are displayed in Figs. 1(a)–1(d). In the photo-oxidation of BS, the effect of varying the NaCl concentrations on the size of the photocurrent is negligible for concentrations greater than 0.5 M (Fig. 1(a)).

At low concentrations (below 0.01 M) or in the absence of supporting electrolytes, the photocurrent decreased at more

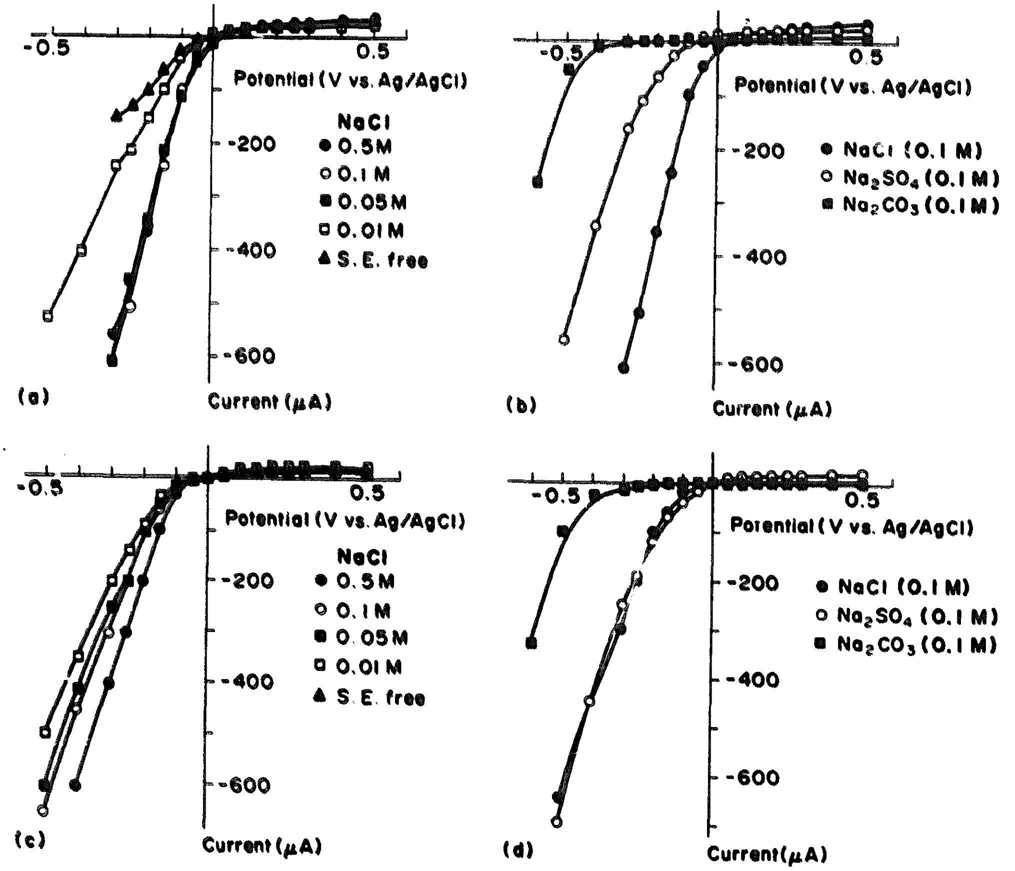

Fig. 1. Effect of the kind and concentration of electrolytes on the photo-current generated in the photodegradation of sodium benzene sulfonate and 2-phenoxyethanol. (a) The dependence of photocurrent vs. applied bias upon the concentration of NaCl in the decomposition of sodium benzene sulfonate (0.1 mM). (b) Photocurrent vs. applied bias in each electrolyte (0.1 M) of NaCl, Na_2SO_4 and Na_2CO_3 in the decomposition of sodium benzene sulfonate (0.1 mM). (c) Same as (a) but for 2-phenoxyethanol. (d) Same as (b) but for 2-phenoxyethanol.

negative electrode potentials; similar results were exhibited by Na_2SO_4 as the electrolyte. The dependence of photocurrents in the photodegradation of BS on the nature of electrolytes is illustrated in Fig. 1(b) at electrolyte concentrations of 0.1 M. Both anodic and cathodic photocurrents vary with the nature of the electrolyte for identical concentrations and identical electrode potentials: $NaCl > Na_2SO_4 > Na_2CO_3$. The latter electrolyte displayed a lower photocurrent because of hydrolysis of the carbonate anion that renders the solution alkaline to $pH \approx 11.5$; this influences the magnitude of the photocurrent.

Figs. 1(c) and 1(d) depict the photocurrents during the photodegradation of 2-phenoxyethanol. Variations in the concentration of NaCl electrolytes have only a slight effect on the cathodic photocurrent; however small the effect, the higher the concentration electrolyte, the greater the cathodic photocurrent. In the absence of electrolytes, photocurrent measurements were precluded owing to voltage overload. In the photo-oxidation of 2-phenoxyethanol, identical concentrations of NaCl and Na_2SO_4 (but not ionic strength) resulted in identical photocurrents; again sodium carbonate had a negative effect on the magnitude of the photocurrent, for reasons noted above (Fig. 1(d)).

3.2. Photocurrent variations in the photodegradation of organic substrates

Temporal variations in the photogenerated currents as a function of irradiation time at electrode potentials between +0.5 V and −0.1 V (vs. Ag/AgCl) are depicted in Figs. 2(a)–2(d). The photocurrent increased slightly with increasing irradiation time during the initial stages of oxidation of 2-phenoxyethanol (Fig. 2(a)) and then decreased gradually with further irradiation and further oxidation. We attribute the maximum photocurrent to formation of and subsequent oxidation of formic acid, HCOOH [8], the principal intermediate before evolution of carbon dioxide [9] (see also below). To verify the effect that HCOOH has on the photogenerated current in the photo-oxidation of organic substrates, we also examined the photo-oxidative decomposition of formic acid (Fig. 2(b)) under otherwise identical conditions to those for 2-phenoxyethanol.

Initially, a higher photocurrent was evident in the photo-oxidation of formic acid, which decreased rapidly as photodegradation of HCOOH continued. In another experiment (Fig. 2(c)) a solution of formic acid was added to a reactant solution of 2-phenoxyethanol that had been irradi-

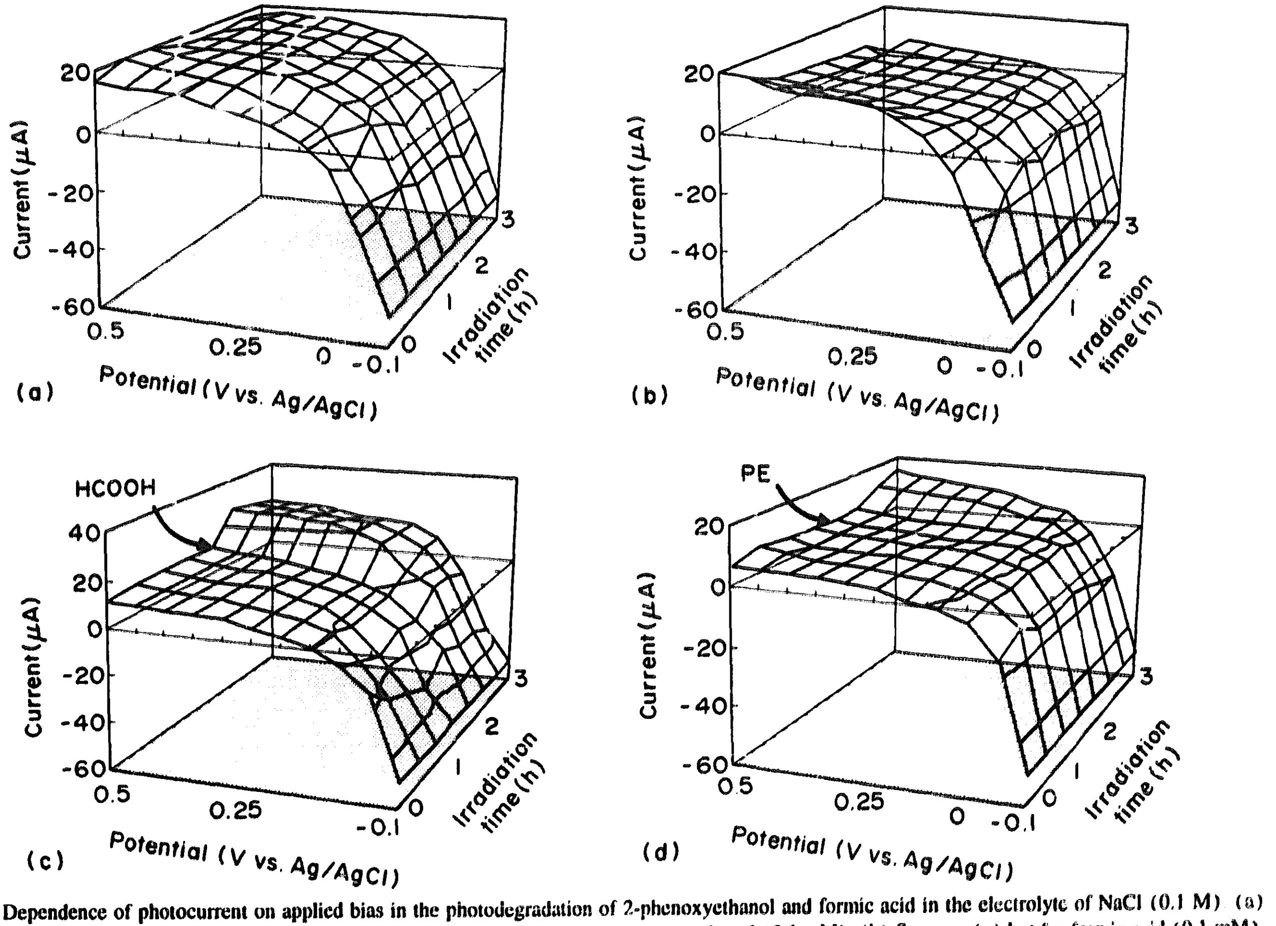

Fig. 2. Dependence of photocurrent on applied bias in the photodegradation of 2-phenoxyethanol and formic acid in the electrolyte of NaCl (0.1 M). (a) Photocurrent and applied bias against irradiation time in the decomposition of 2-phenoxyethanol (0.1 mM). (b) Same as (a) but for formic acid (0.1 mM). (c) Addition effect of formic acid (10 mM) after 2 h irradiation in the photo-oxidation of 2-phenoxyethanol (0.1 mM). (d) Addition effect of 2-phenoxyethanol (10 mM) after 2 h irradiation in the photo-oxidation of 2-phenoxyethanol (0.1 mM).

ated and undergone oxidation for about 2 h. The magnitude of the photocurrent increased suddenly and subsequently decreased gradually with further illumination. These observations clearly indicate that HCOOH has a direct influence on the size of the photocurrent observed in the photo-oxidation of 2-phenoxyethanol. Addition of a fresh sample (from a 10 mM stock solution) of this substrate to a similar reactant solution 0.1 mM in 2-phenoxyethanol after 2 h of irradiation showed a gradual increase in photocurrent (Fig. 2(d)). This is attributed to a gradual degradation of 2-phenoxyethanol along a pathway that implicates several steps to yield various hydroxylated aromatic intermediates, peroxides and aldehydes along the way to ultimately form HCOOH at longer times, such that the dramatic increase seen earlier on addition of HCOOH was not evident when this species formed gradually.

The photo-oxidation of formic acid leads to generation of photocurrent through the external circuit by a process summarized in reactions (1)–(3):

$$TiO_2 + h\nu \longrightarrow h_{tr}^+ + e_{tr}^- \quad (1)$$

$$h_{tr}^+ + HCOOH \longrightarrow HCOO^{\bullet} + H^+(H_2O) \quad (2)$$

$$HCOO^{\bullet} + TiO_2 \longrightarrow CO_2 + H^+ + TiO_2(e_{cb}^-) \quad (3)$$

where subscripts tr and cb mean "trapped" and "conduction band", respectively.

This current-doubling phenomenon reported earlier by others [10] evidently also takes place during the photo-oxidation of 2-phenoxyethanol and formic acid.

3.3. Formation of HCOOH and/or CH$_3$COOH as intermediates and their effect on photocurrent in the photo-oxidation of organic substrates

The temporal variations in photocurrent and in the concentration of HCOOH during its photo-oxidative decomposition are illustrated in Fig. 3. The photocurrent decreased from an initial value of 150 μA to 50 μA after 3.5 h of irradiation; decreases in the concentration of HCOOH with irradiation time displayed a parallel behavior, reaching 0.3 mM from an initial 1.0 mM value.

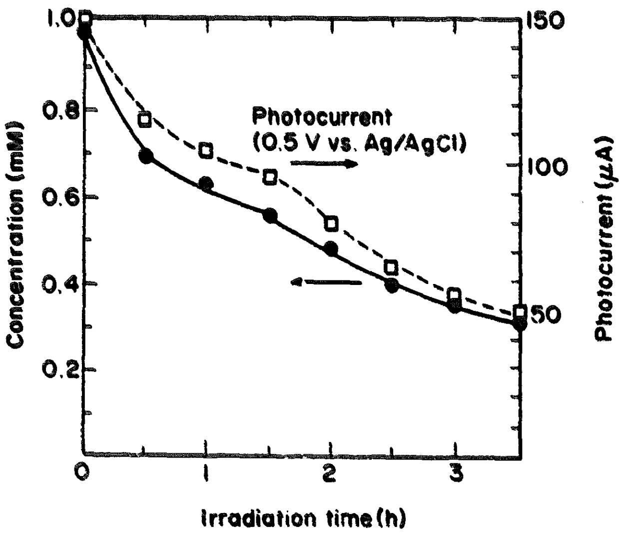

Fig. 3. Relationship between photocurrent and concentration of formic acid under a fixed bias of 0.5 V in the photodegradation of formic acid (initial concentration of 1 mM).

The behavior of acetic acid under otherwise identical photo-oxidative conditions is depicted in Fig. 4. The photogenerated current dropped from 50 μA (about one-third of that seen in a formic acid solution) to about 22 μA after 3.5 h of illumination, while the concentration dropped from 1.0 mM to about 0.4 mM. Note again the parallel behavior between the magnitude of the photocurrent and the extent of photo-oxidation: they decrease at about the same rate. Note also we saw no evidence of formation of formic acid in this time range.

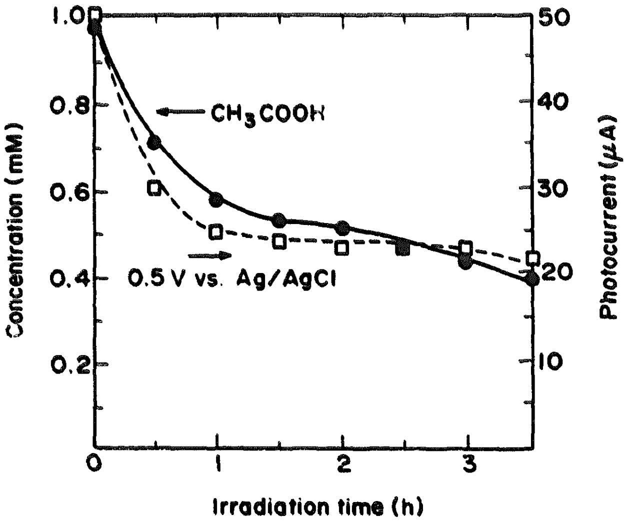

Fig. 4. Same as Fig. 3 but for the photodegradation of acetic acid (initial concentration of 1 mM).

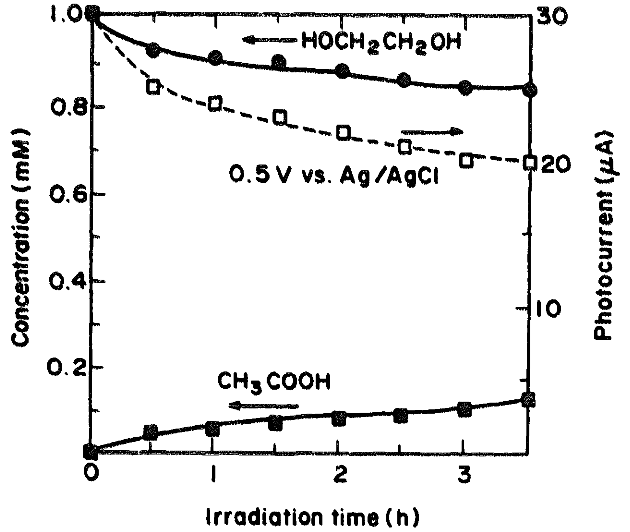

Fig. 5. Photocurrent for the disappearance of ethylene glycol and the formation of acetic acid under the constant applied bias of 0.5 V in the photodegradation of ethylene glycol (initial concentration of 1 mM) in the electrolyte of NaCl (0.1 M).

The results from the photodegradation of ethyleneglycol, $HO–CH_2CH_2–OH$, are summarized in Fig. 5. Relative to the photo-oxidation of HCOOH and CH_3COOH, both the size and the temporal variations of the photocurrent are smaller. The disappearance of ethyleneglycol is slower than for either formic or acetic acid, and its conversion to these two intermediate species is also a slow process. After about 3.5 h, approximately 17% of ethyleneglycol (0.1 mM) has been converted into intermediate species, amongst which acetic acid (detected early on) accounts for about 70% (0.12 mM; Fig. 5) of the quantity consumed. The photocurrent drops from 30 μA at time 0 to about 20 μA after 3.5 h. Under the prevailing conditions used, no formic acid was detected. This is probably due either to its slow formation from acetic acid (note that no HCOOH was detected in the photo-oxidation of CH_3COOH – Fig. 4) or perhaps to its too rapid decomposition.

The photodegradation of diethyleneglycol, $HOCH_2CH_2–O–CH_2CH_2OH$, is illustrated in Fig. 6. Similar to the ethyleneglycol system, oxidation of diethyleneglycol and loss of photocurrent were slower than for either formic acid or acetic acid decomposition. After 3.5 h of irradiation, about 24% of $(HOCH_2CH_2)_2O$ is degraded to give acetic acid; formic acid begins to form after a 1 h induction period. These two intermediate products account for about 80% of the quantity (mass balance) of diethyleneglycol oxidized.

Changes in photocurrent and formation of acetic acid in the photo-oxidation of 2-phenoxyethanol, $PhO–CH_2CH_2OH$, with irradiation time are indicated in Fig. 7. The photocurrent dropped from 30 μA to 19 μA after 3.5 h; acetic acid began to form after an induction period of 1 h. No formic acid was detected under our conditions. By analogy with the results from the photo-oxidation of $HO–CH_2–CH_2–OH$ (Fig. 5), we infer that formation of acetic acid originates from the oxidation of the ethanol fragment in the $PhO–CH_2CH_2OH$ substrate.

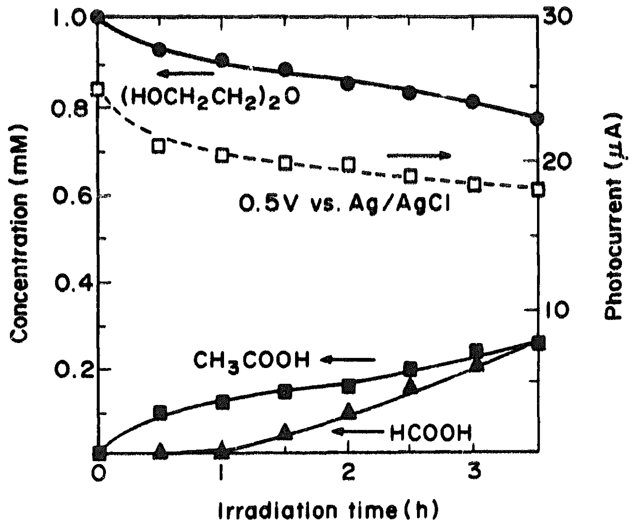

Fig. 6. Photocurrent for the disappearance of diethyleneglycol and the formation of formic acid and acetic acid under the constant applied bias of 0.5 V in the photodegradation of diethyleneglycol (initial concentration of 1 mM) in the electrolyte of NaCl (0.1 M).

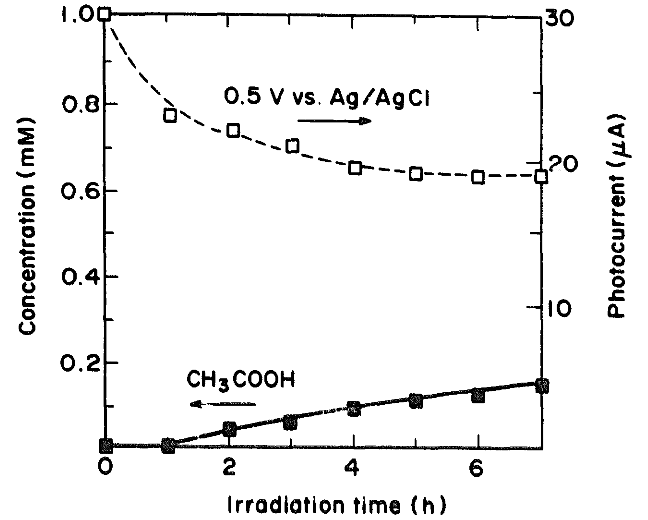

Fig. 7. Photocurrent and the formation of acetic acid under the constant applied bias of 0.5 V in the photodegradation of 2-phenoxyethanol (initial concentration of 1 mM) in the electrolyte of NaCl (0.1 M).

4. Concluding remarks

Organic compounds can be decomposed photoelectrochemically on a TiO_2/TCO electrode assembly. An external photocurrent is generated whose temporal behavior follows closely the temporal course of the disappearance of the initial organic substrate. In some cases, both acetic acid and formic acid were detected and identified. It is the formation of these intermediates that bears on the temporal variations in photocurrent.

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