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Catalytic Oxidation of Formic Acid in Aqueous Suspensions of Platinized Titanium Dioxide

Platinized titanium dioxide particles produce hydrogen when illuminated with bandgap light in the presence of aqueous solutions of many organic materials (*1–7*). This has been of interest in the chemical storage of solar energy. Many factors affect the rate of hydrogen produced from aqueous suspensions in this way (*4, 7, 8*). Oxygen is a powerful inhibitor of the reaction, precluding the use of aerated suspensions in most cases. Formic acid, however, gives hydrogen from dilute aqueous solutions at a rate that is relatively unaffected by the initial presence of oxygen. In investigating possible reasons for this it was noted that, when oxygen was added to a suspension of platinized titanium dioxide in dilute formic acid/sodium formate solution, carbon dioxide was formed rapidly even before the suspension was illuminated. Although the decarboxylation of carboxylic acids in the presence of illuminated suspensions of platinized titania has been the subject of a number of studies (*9–13*), nothing appears to have been reported on the decarboxylation in the dark. The dark reaction was therefore investigated and the results are reported here.

Titanium dioxide (Laporte, Tiona grade) was sieved and the 53 to 125-μm fraction selected. The BET method gave a surface area of 9.0 ± 0.9 $m^2\ g^{-1}$ for this material. The X-ray diffraction pattern showed lines that were characteristic of anatase but there was no trace of rutile. The TiO_2 was platinized by sodium chloride destabilization of colloidal platinum (*14*) to give a platinum loading of 0.4%. Platinized powder (0.2 g) was sonicated in 395 ml of water for 5 min and concentrated formic acid/sodium formate solution at pH 3.5 was added to give the required final concentration of formic acid in 400 ml. The suspension was contained in a glass photochemical reactor of ~450 cm^3 capacity. The reactor was fitted with a sintered glass disk and gas inlet at the base and an outlet from the gas space above the magnetically stirred suspension. The primary gas circuit was connected via a peristaltic pump to the automatic gas sampling valve of a Hewlett–Packard Model 5750 gas chromatograph fitted with Porapak Q columns and thermal conductivity detectors.

Helium was continuously passed through the reaction vessel by means of a secondary gas circuit. Helium was also used as the carrier gas in the chromatograph for the isothermal analysis at 40°C. Periodically, the gas in the free space above the suspension was sampled until no peaks were registered. The secondary gas circuit was then disconnected and the rate of formation of carbon dioxide in the gas space was followed. The chromatograph was calibrated against known volumes of carbon dioxide and oxygen added to the reactor. The TiO_2 was omitted in the calibration with oxygen.

In the absence of oxygen, the formation of carbon dioxide was negligible. When oxygen was added, carbon dioxide formation was observed together with oxygen disappearance. Results for a suspension containing 0.1 *M* formic acid at pH 3.5 (total concentration of both forms) is shown in Fig. 1.

The rate of carbon dioxide formation increased with increase in concentration of formic acid or oxygen. The amount of carbon dioxide formed was negligible in the absence of the Pt/TiO_2 catalyst. Inspection

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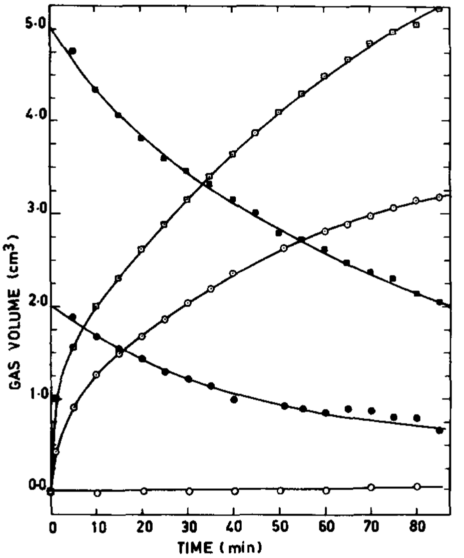

FIG. 1. Carbon dioxide formed and oxygen consumed in 0.1 *M* HCOOH Pt/TiO$_2$ suspension. Pt/TiO$_2$ (0.2 g) suspension (0.2 g TiO$_2$/400 ml), dark reaction, 25°C. (■, ●) oxygen, (□) carbon dioxide, initial oxygen volume = 5.0 cm^3; (⊙) carbon dioxide, initial oxygen volume = 2.0 cm^3; (○) carbon dioxide, initial oxygen volume = 0 cm^3.

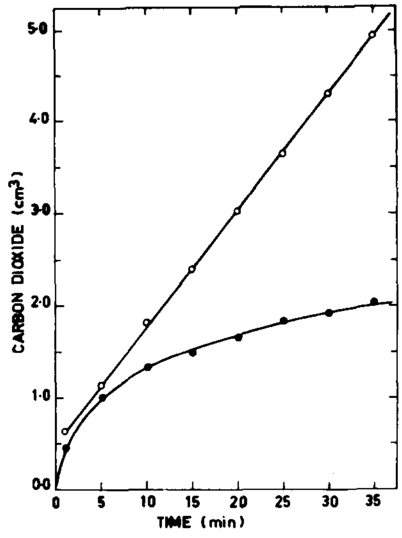

FIG. 2. Effect of light on formation of carbon dioxide from 0.1 *M* HCOOH at pH 3.5 and 25°C. Pt/TiO$_2$ (0.2 g) per 400 ml, 2 cm^3; O$_2$; 100-W Hg lamp, Pyrex glass filter. (○) Illuminated, (●) dark.

of the curves in Fig. 1 shows that approximately two molecules of carbon dioxide are formed for each molecule of oxygen consumed. It is therefore concluded that the reaction is

$$2\mathrm{HCOOH} + \mathrm{O_2} \xrightarrow{\mathrm{Pt/TiO_2}} 2\mathrm{CO_2} + 2\mathrm{H_2O} \quad (1)$$

$$\text{or } 2\mathrm{HCOO^-} + \mathrm{O_2} \longrightarrow 2\mathrm{HCO_3^-} \quad (2)$$

The same reaction stoichiometry was proposed (*15*) for the photocatalysis of formic acid oxidation by oxygen using unplatinized TiO$_2$ as the catalyst. In that study no dark reactions were found but a significant dark reaction has been reported for oxalic acid in aqueous suspensions of unplatinized TiO$_2$ (*16*). In the present study the rate of CO$_2$ formation using unplatinized TiO$_2$ was less than 3% of the initial rate using platinized TiO$_2$. No significant dark decarboxylation reactions were reported in the photo-Kolbe studies of acetic acid (*9, 12*) and benzoic acid (*10*) using platinized TiO$_2$ as the catalyst. By contrast, the dark reaction observed in the present study was quite significant when compared with the decarboxylation of the same system under illumination. When the suspension, containing initially 2 cm^3 of oxygen, was illumi-

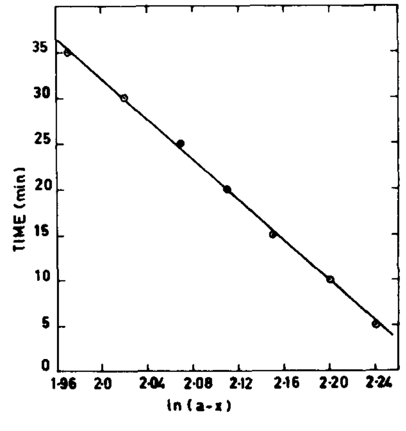

FIG. 3. First-order plot for decarboxylation of 0.3 *M* HCOOH at pH 3.5 and 25°C. Pt/TiO$_2$ (0.2 g) per 400 ml, 10 cm^3 O$_2$, dark reaction. a = 10.0, x = 0.5 (volume (cm^3) of CO$_2$ formed).

TABLE 1

Effect of Amount of Pt/TiO_2, O_2, and HCOOH Concentration on the Pseudo-First-Order Rate of Decarboxylation, pH 3.5, 25°C

Weight of Pt/TiO_2 (g)	O_2 (cm^3)	[HCOOH] (M)	$10^3 k'$ (min^{-1})
0.05	10.0	0.10	4.78 ± 0.05
0.10	10.0	0.10	6.66 ± 0.06
0.20	10.0	0.02	6.76 ± 0.05
0.20	10.0	0.10	6.98 ± 0.14
0.20	10.0	0.10	8.12 ± 0.13
0.20	10.0	0.30	8.94 ± 0.15
0.20	10.0	1.00	7.73 ± 0.24
0.20	30.0	1.00	7.29 ± 0.04
0.40	10.0	0.10	8.70 ± 0.03

nated with a 100-W medium-pressure Hg lamp, carbon dioxide was formed linearly with illumination time during the period from 1 to 35 minutes, achieving a volume of 5.0 cm^3. In the dark, under the same conditions, 2.0 cm^3 was formed. These results are shown in Fig. 2.

Consider now the specific reaction rate of the dark reaction. Since the formic acid/formate ion concentration is much greater than the oxygen concentration it is assumed that Reactions (1) and (2) are pseudo-first-order. The plot shown in Fig. 3 confirms the assumption. The reaction obeys first-order kinetics over a range of formic acid concentrations (0.02 to 1.0 M), oxygen volumes (10 to 30 cm^3), and weight of catalyst (0.05 to 0.40 g). The specific reaction rate constant, k', was estimated by the method of least squares. The results are shown in Table 1.

Since there is no decarboxylation in the absence of TiO_2 it is assumed that the reaction takes place on the surface of the TiO_2. There is no significant effect of the formic acid concentration on k' presumably because the surface of the particles is saturated with formate ions and or formic acid over the range of concentrations used. In the absence of catalyst k' is zero but the increase in k' over the range of 0.05 to 0.40 g per 400 ml is not linear. At higher loadings of catalyst it is possible that the particles conglomerate resulting in a diminished surface area per gram of catalyst.

It is evident from the foregoing that, within a few hours after the addition of platinized titania to an aerated solution of 0.1 M or greater, formic acid solution at pH 3.5 and 25°C, most of the oxygen will have been converted to carbon dioxide. If the suspension is exposed to light the rate of oxygen removal will be even more rapid. Therefore, it is clear that one reason formic acid/platinized titania suspensions give hydrogen at a high rate on illumination, even when oxygen is initially present, may be that the system is self-deoxygenating both in the dark and under illumination.

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