

PHOTOCATALYSIS OF FORMIC ACID OXIDATION BY OXYGEN IN AN AQUEOUS MEDIUM

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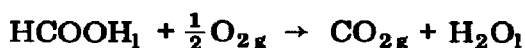
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Summary

A photochemical slurry reactor was used to carry out the photochemical oxidation of formic acid by oxygen in contact with anatase. Care was exercised to avoid limitations due to light absorption and to diffusion of oxygen from the gas phase to the catalytic surface. The influences on the kinetics of the concentrations of dissolved acid and oxygen and of the absorbed light intensity were measured, and a tentative mechanism is proposed.

1. Introduction

The reaction



is thermodynamically feasible ($\Delta G_{298}^\circ = -71.3$ kcal) but is kinetically very slow. A catalyst is required for the reaction to be carried out with a noticeable rate. When TiO_2 is used as a catalyst under ambient conditions, it has to be shone with light in order to be activated. The purpose of this work is to set up an experimental procedure which permits the study of such a photocatalysis, to avoid the possible diffusional limitations, to give the kinetic results gained in the chemical regime and finally to propose a tentative mechanism to account for these results.

2. Experimental procedure

2.1. Set-up

The experimental set-up basically consists of a photochemical slurry reactor, the catalyst being suspended in the aqueous solution of formic acid. A gaseous flow of oxygen or air is bubbled through this solution, which is

irradiated in the photoreactor with light coming from a high pressure mercury lamp (Philips H.P.K. 125) and recirculated via an external loop which includes a peristaltic pump, a refrigerator and a sampling valve. The kinetic measurements are based on the titration of the remaining formic acid with caustic soda. Because of the highly corrosive nature of formic acid, any metallic part has to be excluded from the set-up which is made entirely of Pyrex glass. The concentration of dissolved oxygen can be directly measured with a Beckman 777 oxygen analyser, based on the electroreduction and polarographic determination of oxygen.

2.2. Blank experiments

Even with an all-glass set-up and in the absence of catalyst, there is a reaction of HCOOH if the sheath between the lamp and the reactor is made of quartz. Indeed, a linear decrease with time (up to 60 h) of the concentration of formic acid is observed which corresponds to a zero order reaction (which increases for longer durations). These observations agree with previous results reported by Matsuura and Smith [1] on the photodecomposition of formic acid. The explanation lies in the fact that the 253.7 nm mercury resonance line excites formic acid (which absorbs at wavelengths shorter than 260 nm). If the photooxidation proper is to be studied, then these shorter wavelengths have to be excluded. This is why a Pyrex glass sheath which cuts off all wavelengths below 300 nm is used. It can then be checked that no photoreaction occurs in the absence of catalyst and that no reaction occurs in the dark in the presence of the catalyst.

2.3. Catalyst

The catalyst used is titanium dioxide, which presents the advantages of exhibiting a measurable photocatalytic activity and of chemical resistance to formic acid. However, the catalyst specifications are stringent.

(1) It must be in the form of a powder which should be easy to maintain suspended in the liquid.

(2) The crystallographic form anatase is a better catalyst than rutile if the literature observations are accepted [2 - 4].

The catalyst which gave us the best results in both respects was the commercial P 25 oxide from Degussa. It is a non-porous oxide, of approximate specific surface area $78 \text{ m}^2 \text{ g}^{-1}$ and hence of average particle diameter 20 nm, constituted mostly of anatase. Because the band gap of anatase is 3.23 eV [5], the corresponding light absorption edge is at 384 nm. From this value and that of the Pyrex glass absorption edge, the resulting wavelength "window" open for our experiments extends from 300 to 384 nm and therefore includes the mercury lines at 302.5, 313.0, 334.1 and 365.5 nm.

2.4. Reaction stoichiometry

From the absorption of CO_2 by a saturated basic solution, it could be checked that the amount of CO_2 formed is the same as the amount of oxidized HCOOH.

Under the experimental conditions used physical factors due to light absorption and interface transfers have to be discussed before any meaningful kinetic result can be given.

3. Physical factors (all these experiments were carried out at $T = 22\text{ }^{\circ}\text{C}$)

3.1. Influence of the catalyst mass

It is observed that the reaction rate r_V per unit volume is an increasing function of the catalyst mass m up to a limiting value $r_{V\text{lim}}$. If $\ln(1 - r_V/r_{V\text{lim}})$ is plotted as a function of m , a reasonably straight line is obtained (Fig. 1).

The interpretation rests upon the absorption of light by the catalyst. We shall take an oversimplified model (Fig. 2) in which we suppose that the light progresses radially. Consideration of a three-dimensional radiant flux [6] and of scattering [7] are obviously more rigorous approaches but lead to unnecessary complication in the present case.

We must take into account the fact that, because our photoreactor is shielded by an aluminium foil, the light reaching the outer wall is reflected back into the solution. The intensity which reaches the solution-glass interface is

$$I_1 = I_0 \exp(-\epsilon lc)$$

where l is the width of the annular space in the photoreactor and c is the

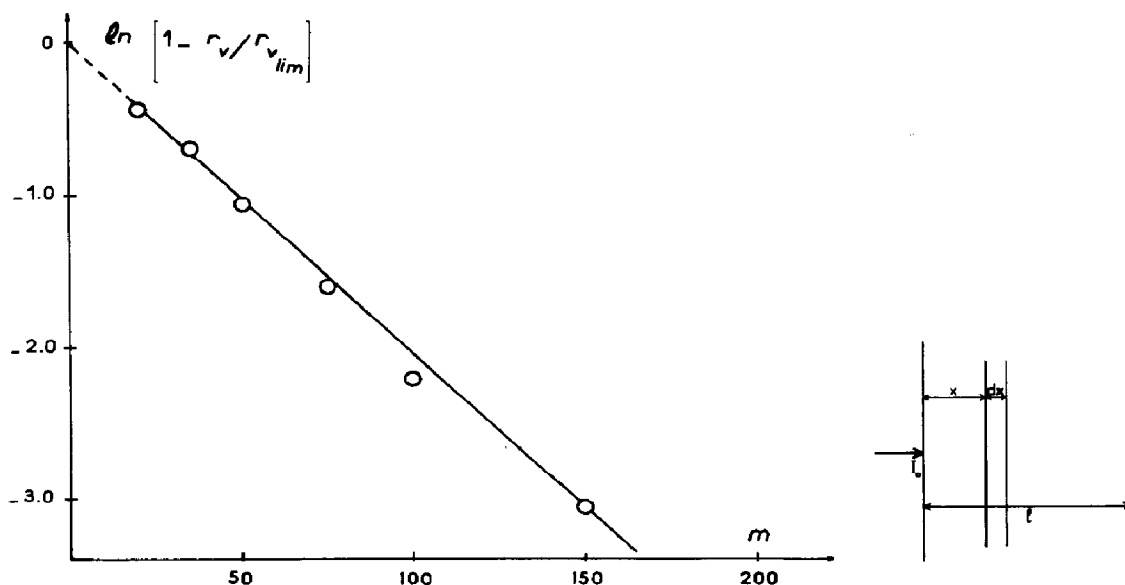


Fig. 1. $\ln(1 - r_V/r_{V\text{lim}})$ as a function of the catalyst mass m ($V = 80\text{ l h}^{-1}$, $c_{B1} = 8\text{ mg l}^{-1}$).

Fig. 2. The light absorption by an infinitesimal annulus of catalyst suspension.

mass of catalyst per unit volume of the solution. Independent absorption experiments showed that in the wavelength range considered $\epsilon = 0.95 \times 10^{-2} \text{ cm}^{-1} \text{ l mg}^{-1}$ so that, after an optical path $l = 5 \text{ cm}$ and with $c = 10 \text{ mg l}^{-1}$, $I_1/I_0 = 0.62$. This is the fraction of the initial intensity which is reflected, if absorption by the glass of the outer wall is ignored and if the aluminium reflectance is taken to be unity (both assumptions are again, of course, gross oversimplifications). If we then suppose that the infinitesimal rate in the annulus of width dx is proportional to the intensity dI_a absorbed by TiO_2 in its volume, we have

$$dr_v = kdI_a$$

with

$$dI_a = \epsilon c I_0 \exp(-\epsilon x c) dx + \epsilon c I_0 \exp\{-\epsilon c(2l - x)\} dx$$

Hence

$$dr_v = k\epsilon c I_0 [\exp(-\epsilon x c) + \exp\{-\epsilon c(2l - x)\}] dx$$

The integration between the limits 0 and l for x gives

$$r_v = kI_0 \{1 - \exp(-2l\epsilon c)\}$$

The limiting value of r_v when c increases is

$$r_{v \text{ lim}} = kI_0$$

and

$$\ln(1 - r_v/r_{v \text{ lim}}) = -2\epsilon l c$$

It is thus demonstrated that $\ln(1 - r_v/r_{v \text{ lim}})$ should be a linear function of the mass m of the catalyst with a slope (in absolute value) of

$$\frac{2\epsilon l}{V} = \frac{2 \times 0.95 \times 10^{-2} \times 5}{3} = 3.2 \times 10^{-2} \text{ mg}^{-1}$$

The experimental value is about $2 \times 10^{-2} \text{ mg}^{-1}$. The agreement can be considered to be fair if all the approximations made are taken into consideration.

3.2. Influence of the air flow rate

r_v is an increasing function of the air flow rate \bar{V} . If $1/r_v$ is plotted as a function of $1/\bar{V}^{1/2}$, a good straight line is obtained (Fig. 3).

The interpretation rests upon the examination of oxygen diffusion from the gas to the catalyst through the liquid, assuming that the main resistances are in the films which are on the liquid side and parallel to the interfaces (Fig. 4). The oxygen flux through the liquid can thus be expressed by

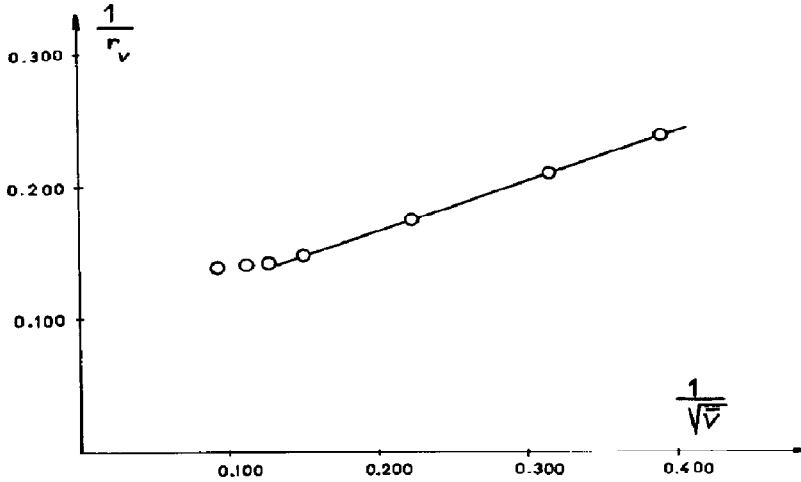


Fig. 3. The reciprocal of the reaction rate r_v as a function of the reciprocal of the square root of the air flow rate \bar{V} ($m = 300$ mg).

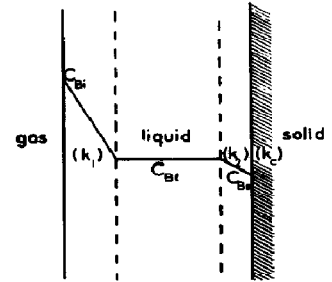


Fig. 4. A schematic diagram of the two-film model for oxygen diffusion through the liquid.

$$\begin{aligned} J &= k_1(c_{B_i} - c_{B_l}) \\ &= k_2(c_{B_l} - c_{B_s}) \\ &= k_c c_{B_s} \end{aligned}$$

where k_1 and k_2 are the mass transfer coefficients at the gas-liquid and liquid-solid interfaces respectively, and k_c is the rate constant of catalysis which is assumed for simplicity to be first order with respect to oxygen. It thus follows that

$$J = k c_{B_i}$$

with

$$\frac{1}{k} = \frac{1}{k_1} + \frac{1}{k_2} + \frac{1}{k_c}$$

(which expresses the additivity of resistances in series, as is usual for first order reactions). Let us allow only the first term on the right-hand side to be dependent on \bar{V} , and let us assume that [8]

$$\text{Sh}_1 = \frac{2}{\pi^{1/2}} \text{Pe}_1^{1/2}$$

where Sh_1 is the Sherwood number for gas-liquid dispersion:

$$\text{Sh}_1 = k_1 d_1 / \mathcal{D}$$

and Pe is the Péclet number:

$$Pe_1 = U_1 d_1 / \mathcal{D}$$

Let us assume that the diameter d of the bubbles is independent of \bar{V} , which is generally the case for most gas-liquid dispersions [9], and that the bubble ascension speed U_1 is proportional to \bar{V} . Then k_1 is proportional to $\bar{V}^{1/2}$ and J (and therefore r_V) is a homographic function of $\bar{V}^{1/2}$, which confirms the experimental result. When \bar{V} and thus k_1 are sufficiently large, the mass transfer at the gas-liquid interface is no longer rate determining.

A rough estimation of the transfer coefficient k_2 can be based on the literature data giving the Sherwood number as a function of the Péclet number for this type of transfer [10]. With a grain diameter $d_2 = 2 \times 10^{-6}$ cm, a velocity $U_2 = 1$ cm s⁻¹ and an oxygen diffusivity $\mathcal{D} = 2.4 \times 10^{-5}$ cm² s⁻¹, the Péclet number is

$$Pe_2 = \frac{d_2 U_2}{\mathcal{D}} = \frac{2 \times 10^{-6}}{2.4 \times 10^{-5}} \approx 8 \times 10^{-2}$$

The Sherwood number Sh_2 can then be taken to be 2 [10]; hence

$$k_2 = 2\mathcal{D}/d_2 = 24 \text{ cm s}^{-1}$$

This ensures a maximum rate which is by orders of magnitude larger than the observed rate. In fact the maximum flux is

$$J_{\max} = k_2 c_{B1}$$

For $c_{B1} \approx c_{Bi} = 2.8 \times 10^{-7}$ mol cm⁻³, $J_{\max} = 6.7 \times 10^{-6}$ mol s⁻¹ cm⁻². In a typical experiment the catalyst mass is 20 mg and corresponds to an external area of

$$A_2 = 6m/\rho d_2 \approx 16 \times 10^3 \text{ cm}^2$$

Hence the maximum rate of oxygen consumption is

$$r_{\max} = J_{\max} A_2 = 107 \times 10^{-3} \text{ mol s}^{-1}$$

or, for the formic acid consumption, $r_{\max} = 257 \text{ mol h}^{-1} \text{ l}^{-1}$, instead of an observed value of $6 \times 10^{-4} \text{ mol h}^{-1} \text{ l}^{-1}$. It is very likely that oxygen diffusion through the liquid-catalyst interface does not control the reaction rate.

4. Chemical kinetics

The following factors were determined with sufficiently large catalyst concentrations and air flow rates to avoid any physical limitation.

4.1. Influence of concentrations and of temperature

The order with respect to formic acid is zero. Moreover, the rate r_V was measured as a function of the oxygen concentration c_{B1} in the liquid.

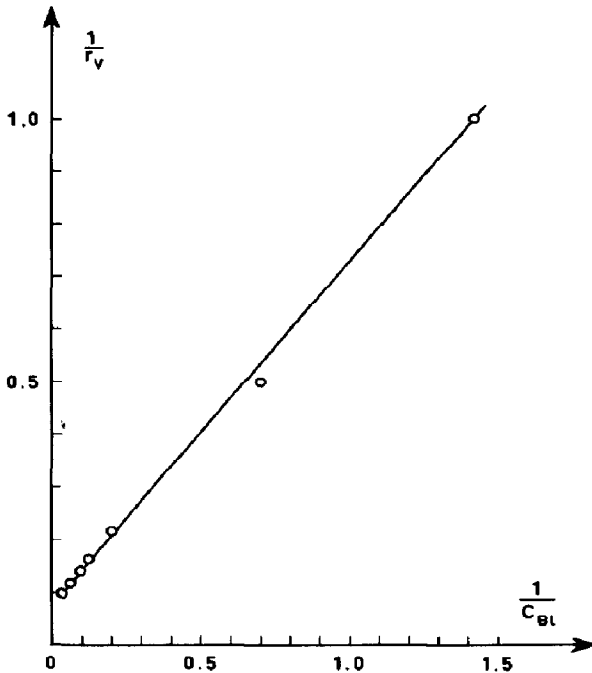


Fig. 5. The reciprocal of the reaction rate r_v as a function of the reciprocal of the concentration c_{B1} of dissolved oxygen ($m = 300$ mg).

Linearization of the curve is possible if $1/r_v$ is plotted against $1/c_{B1}$ (Fig. 5). An activation energy of about 4 kcal mol^{-1} was found.

4.2. Influence of light intensity

Let us suppose a suspension containing at the "concentration" c a species absorbing the incident light I_0 with a molar extinction coefficient ϵ_i at wavelength λ_i . If L is the optical length in the medium then, according to the Beer-Lambert law, the overall absorbed intensity is

$$I_{as} = \sum_i I_{0i} \{1 - \exp(-\epsilon_i c L)\}$$

the sum being extended over the entire range of incident wavelengths. In the case of the present photoreactor, which is annular and shielded by a reflecting surface, L is very large so that for all the values of $\epsilon_i \neq 0$

$$I_{as} = \sum_i I_{0i} = I_0$$

The absorbed intensity is thus equal to the incident intensity at the corresponding wavelengths and can therefore be determined by measuring the intensity I_{as} absorbed by an actinometric solution, *i.e.* an aqueous solution

of oxalic acid (0.1 mol l^{-1}) and uranyl sulphate (0.02 mol l^{-1}). The quantum yield of the reaction



is well known as a function of wavelength [11] but it is necessary to take into account the powers w emitted by the lamp at various wavelengths, as well as the transmittance θ of the Pyrex glass. This leads to the results presented in Table 1 and to the average quantum yield (0.53) in the range where the actinometric solution absorbs.

The number of moles of oxalic acid photodecomposed per second was found equal to 1.31×10^{-5} , so that the overall intensity absorbed by the actinometric solution is

$$I_{\text{aa}} = \frac{1.31 \times 10^{-5}}{0.53} = 24.7 \times 10^{-6} \text{ einstein s}^{-1}$$

However, all this intensity is not absorbed by the suspension, since it absorbs only between 300 and 384 nm. Thus, the sum of the xI_{aa} values for the first four wavelengths has to be considered, and is equal to $I_{\text{as}} = 14.8 \times 10^{-6} \text{ einstein s}^{-1}$.

It is now possible to study the influence of the absorbed intensity on the reaction rate by inserting metallic grids with more or less wide meshes between the lamp and the internal sheath and by comparing the results obtained with a grid (absorbed intensity, I_{as}^k ; reaction rate, r_{V}^k) with those obtained without any grid (I_{as} and r_{V} respectively). The equality of the ratios $I_{\text{as}}^k/I_{\text{as}}$ and $r_{\text{V}}^k/r_{\text{V}}$, and therefore the proportionality of the rate to absorbed light can be seen from Table 2. The proportionality constant, *i.e.* the quantum yield, was measured by determining the reaction rate under the same conditions as those used for I_{as} , *i.e.* $r_{\text{V}} = 8.33 \times 10^{-7} \text{ mol HCOOH s}^{-1}$. Thus

$$\phi = \frac{8.33 \times 10^{-7}}{148 \times 10^{-7}} = 0.056$$

This value compares well with those reported in the literature for analogous photooxidations: sulphite ion, $\phi = 0.16$ [12]; cyanide ion, $\phi = 0.06$ [3]; acetic acid, $\phi = 0.10$ [4].

4.3. Tentative interpretation

The partial reaction order of zero with respect to formic acid and the homographic dependence of r_{V} on the oxygen concentration can be interpreted in the most straightforward way by a Langmuir-Hinshelwood mechanism, with the intervention of two different types of adsorption sites s_1 and s_2 for the two reactants, according to the partial sequence

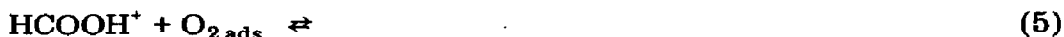
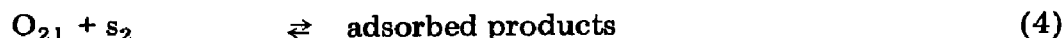
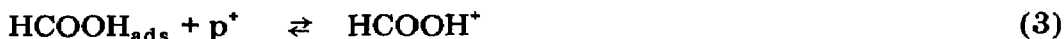


TABLE I

λ (nm)	w (W)	$w \times 10^6$ (einstein s^{-1})	θ	$w_i = w\theta \times 10^6$ (einstein s^{-1})	$x = \frac{w_i}{w_{i\text{tot}}}$ (%)	ϕ	ϕx	$xI_{sa} \times 10^6$ (einstein s^{-1})
302.5	1.9	4.80	0.30	1.44	3.06	0.57	1.74	0.76
313.0	3.6	9.42	0.70	6.59	14.02	0.56	7.85	3.47
334.1	1.5	4.19	0.82	3.44	7.32	0.53	3.88	1.81
365.5	6.2	18.95	0.88	16.68	35.50	0.46	16.33	8.78
403.7	2.1	7.09	0.90	6.38	13.58	0.56	7.60	
435.8	3.8	13.84	0.90	12.46	26.52	0.59	15.65	
Totals		58.29		46.99	100.00		53.05	14.82

TABLE 2

Grid	I_{as}^k/I_{as}	r_V^k/r_V
1	0.60	0.61
2	0.35	0.37



If step (5) is rate determining, then

$$r = k_5 [\text{HCOOH}^+] [\text{O}_{2\text{ads}}]$$

From the quasi-equilibrium (3)

$$[\text{HCOOH}^+] = K_3 [\text{HCOOH}_{\text{ads}}] [p^+]$$

and from the quasi-equilibrium (2)

$$[\text{HCOOH}_{\text{ads}}] = \frac{K_2 c_{A1}}{1 + K_2 c_{A1}} c_{s_1}$$

(c_{s_1} is the total concentration of sites s_1) which reduces to $[\text{HCOOH}_{\text{ads}}] = c_{s_1} = \text{constant}$ if $K_2 c_{A1} \gg 1$. Hence

$$r = k_5 K_3 c_{s_1} [\text{O}_{2\text{ads}}] [p^+]$$

Substituting the value for $[\text{O}_{2\text{ads}}]$ derived from the quasi-equilibrium (4), *i.e.*

$$[\text{O}_{2\text{ads}}] = \frac{K_4 c_{B1} c_{s_2}}{1 + K_4 c_{B1}}$$

and assuming that $[p^+]$ is proportional to the absorbed light intensity, since it results from step (1), leads to the experimental results.

However, this does not constitute a proof of the proposed mechanism [13]. For instance, it can be suggested [14] that the rate-controlling step is the reaction in the liquid phase of an active form of oxygen formed at the catalyst surface, as it seems to have been found for CdS [15].

5. Conclusions

The photocatalytic oxidation of a dissolved species by gaseous oxygen poses a number of questions bound to the three-phase system and to its illumination. In non-photoreactive systems these questions are well known,

e.g. for hydrogenations with Raney nickel catalysts (other examples are given in a very recent review [16]). Of course, the intervention of light introduces a complication. These preliminary questions must be answered before any certain kinetic results can be reached. The interpretation of the kinetics by a mechanism shall be considered to be tentative as long as a direct proof of the intermediates has not been given; a direct proof is not as easy to obtain in the presence of a liquid as it is for conventional catalysis in contact with a gas.

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Nomenclature

A	formic acid
B	oxygen
<i>c</i>	concentration
<i>d</i>	diameter
\mathcal{D}	diffusivity of oxygen in solution
<i>I</i>	luminous intensity
<i>J</i>	molal flux
<i>k</i>	rate constant or transfer coefficient
<i>K</i>	equilibrium constant
<i>l</i>	optical length
<i>L</i>	optical length
<i>m</i>	catalyst mass
Pe	Péclet number
<i>r</i>	reaction rate
Sh	Sherwood number
<i>U</i>	velocity
<i>V</i>	volume
\dot{V}	volume flow rate
<i>w</i>	power

Greek symbols

ϵ	extinction coefficient
λ	wavelength
θ	transmittance
ϕ	quantum yield

Subscripts

a	absorbed intensity
ads	adsorbed species

g	in the gas phase
i	at interface
l	in the liquid phase
lim	limiting value
max	maximum value
V	per unit volume

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