Kinetics of Liquid Phase Photocatalyzed Reactions: An Illuminating Approach[†]

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Analysis of photocatalyst kinetics to date have relied largely on Langmuir−Hinshelwood rate forms, which assume equilibrated adsorption of reactants and, correspondingly, a slow, rate-controlling surface step. Alternatively, and more generally, a pseudo-steady state analysis based upon the stationary state hypothesis for reaction intermediates may be applied. We show here that only this second approach is consistent with the reported intensity dependence of apparent adsorption (and desorption) binding constants, as well as the catalytic rate constant. In consequence, we show that for at least some photocatalyzed reactions, adsorption/desorption reaction equilibria are not established during reaction, because the substantial reactivity of an adsorbed active species (e.g., hole (h+), radical (*OH), etc.) causes a continued displacement from equilibrium of the adsorbed reactant concentration.

1. Introduction

Analyses of liquid-phase kinetics for suspended or immobilized solid photocatalysts, especially TiO_2, have relied largely on Langmuir−Hinshelwood (LH) rate forms, which assume equilibrated adsorption of reactants and imply existence of a subsequent slow, rate-controlling surface step. The form of the rate equation, rate $= kKC/(1+KC)$, we demonstrated early in the photocatalysis literature to fit the kinetic data for disappearance of many water pollutants, such as halocarbons (Figure 1a,b).[1]

Alternatively, and more generally, a pseudo-steady state analysis for reaction intermediates may be applied. We will show that only this second approach is consistent with the recently reported intensity dependences of the Langmuir−Hinshelwood rate constant, k_{LH}, *and* that of the apparent adsorption constant, $K_{a,app}$, and its reciprocal the apparent desorption constant, $K_{d,app}$. In consequence, we expect that for most photocatalyzed reactions, reactant adsorption/desorption equilibria are not established during reaction, because the substantial reactivity of an active center (e.g., hole (h+), radical (•OH), electron (e−), etc.) causes a continued displacement of the adsorbed reactant concentration from the coverage corresponding to liquid−surface equilibrium.

Consideration of the various active centers in photocatalysis, namely, electrons (e−), holes (h+), and hydroxyl radicals (OH) leads to the conclusion that all photocatalytic kinetics ought to routinely require this pseudo steady state kinetic analysis. This result says that comparison of reaction rate parameters between different labs and research papers will require taking note of the intensity, inasmuch as we predict that *both* the Langmuir Hinshelwood rate constant and apparent adsorption/dissociation constants are functions also of intensity. Further, as indicated below, we predict that k_{LH} and $K_{d,app}$ will both be functions of the same power (e.g., 1.0 or 0.5) of the intensity. The intensity dependence in the rate equation arises because the photon absorption rate is the ultimate driver for formation of each of these active center species.
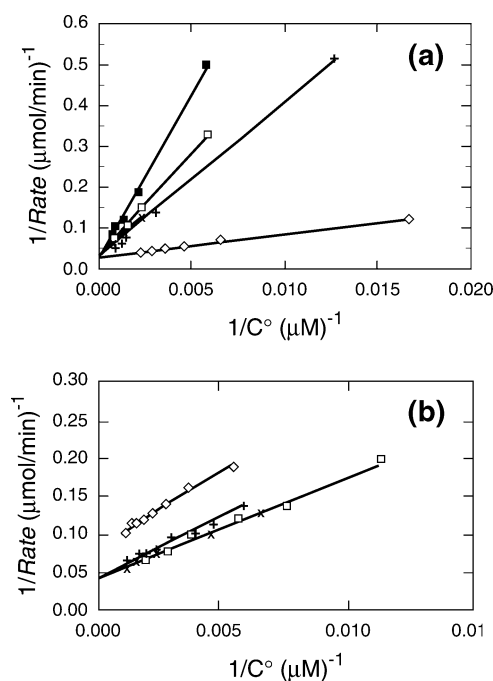
Figure 1. (a) Langmuir−Hinshelwood plots for chloroform (□), dichloromethane (×), perchloroethylene (◇), chloroacetic acid (■), and dichloroacetic acid (+). (b) Langmuir−Hinshelwood plots for tribromomethane (□), dibromomethane (×), 1,2-dibromoethane (◇), and 1,1-dibromomethane (+). From ref 1, used with permission. © 1990 Elsevier.

2. Background

This paper establishes an improved understanding of the kinetics of heterogeneous, photocatalyzed reactions by demonstrating the ubiquity of need to use a steady state approximation, rather than the more commonly applied slow step approximation, in liquid phase catalysis involving illuminated photocatalysts, in particular of titanium dioxide, by far the most commonly used photocatalyst material.

The Langmuir−Hinshelwood kinetic model finds widespread use in this emerging field of heterogeneous photochemistry, dating back to our earlier liquid phase reports.[2−5] Papers finding
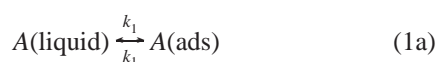
utility with this rate form have included photocatalyzed oxidation of water contaminants such as organic dyes, hydrocarbons, chlorinated hydrocrbons, nitrogen−hydrocarbon species, and dissolved metals and complexes. Similarly, reductive chemistry utilizing the LH rate forms are reported for conversions of dissolved metals, chlorinated hydrocarbons, nitroaromatics, and dioxygen. Earlier reports utilizing this rate form for liquid-phase kinetic studies include those of Cunningham,[6] Hoffmann,[7] and Anderson.[8]

Its popularity and its importance continues: of the 225 photocatalysis papers citing the phrase "Langmuir−Hinshelwood" in the abstract or keywords, 100 have appeared in the interval 2000−2003.[9] Thus, the generality of this form is widespread and its use is growing. The currency and breadth of this kinetic form is further indicated for the year 2003, with at least 27 citations of the LH form. Examples include photocatalyzed conversion of dyes,[10−15] biocides and herbicides,[16−18] selenium,[19] humic acid,[20] surfactant,[21] ferrate,[22] and paper mill effluent.[23] Its use in correlating gas phase studies is also common. Our focus in this paper will be the liquid phase, inasmuch as the identity of active centers (h+, OH, and e−) appears more broadly established than gas−solid results to date.

We paraphrase an earlier warning of the electrochemist Gileadi: "The Langmuir isotherm now has all the hallmarks of a classical law of physical chemistry: it is most useful now, more than 50 years after its conception, it has been applied to a wide variety of systems, and the conditions under which it was derived are hardly ever true". The same may be said of the Langmuir−Hinshelwood rate form. We showed earlier[1] that photocatalysts kinetics involving any of four possible hydroxyl radical mechanisms as the slow step would give rise to the LH rate form. The interest in photocatalytic rate models derived from mechanism is substantial: this 1990 paper has been cited more than 440 times to date.[9]

2.1. Langmuir−Hinshelwood Kinetics and the Rate Determining Step. To establish our argument, we briefly review the Langmuir−Hinshelwood approach, which in its simplest form assumes one relatively rapid reaction achieving adsorption equilibrium, followed by a single, slow surface reaction step (rate determining step). Thus

$$A(\text{liquid}) \underset{k_{1}}{\overset{k_{1}}{\rightleftarrows}} A(\text{ads}) \qquad (1a)$$

$$A(\text{ads}) \underset{(\text{slow})}{\overset{k_{2}}{\longrightarrow}} \text{products} \qquad (1b)$$

and the rate of reaction, $-r_A$, is given by

$$-r_A = k_{LH}\theta_A \qquad (2)$$

where n_c = catalytic surface sites per volume and θ_A = reactant equilibrium coverage (Langmuir isotherm):

$$\theta_A = \frac{(k_1/k_{-1})C_A}{1 + (k_1/k_{-1})C_A} = \frac{K_{ads}C_A}{1 + K_{ads}C_A} \qquad (3)$$

The governing rate expressed in terms of the fundamental rate constants is thus

$$-r_A = \frac{k_{LH}(k_1/k_{-1})C_A}{1 + (k_1/k_{-1})C_A} \qquad (4)$$

2.2. Flaws in the Langmuir−Hinshelwood Slow Step Photocatalysis Model. While the Langmuir−Hinshelwood rate form is widely cited in photocatalysis, flaws have appeared in
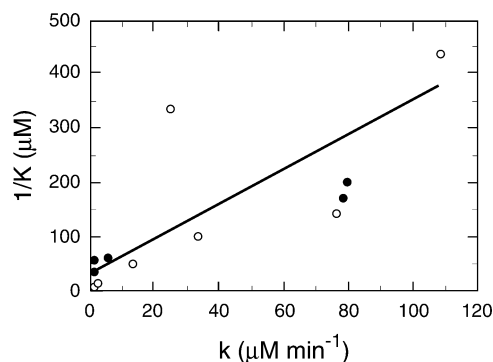

Figure 2. Plot of $1/K_{a,app}$ vs k_{LH} for phenol (○) and 4-chlorophenol (○). Adapted from ref 25.

the routine acceptance of this rate equation. Discordances of the following kinds have appeared over the past decade: (1) While adsorption isotherm and reaction rate may each follow the same analytic form, i.e., a saturation function of the Langmuir adsorption isotherm form,

$$\theta_A = \text{reactant coverage} = KC/(1 + KC)$$

and of the Langmuir−Hinshelwood kinetic rate form,

$$\text{rate} = k_{LH}K'C/(1 + K'C)$$

the dark adsorption equilibrium constant K is not found to be the same as the apparent adsorption constant K' in the rate equation. (2) Some reactions and adsorption systems have different analytic forms, as noted earlier.[24,25] (3) As also noted by Hoffmann et al.,[25] the LH parameters k and K collected from nine different studies of phenol and 4-chlorophenol have positive correlations (Figure 2). Our earlier OH-based analysis of multiple mechanisms assumed reactant adsorption/desorption equilibria and thus did not predict any such correlation. The present pseudo steady state analysis we show below contains this prediction and is thus consistent with this prior correlation. (4) Several recent papers[26−28] have explored the influence of *both* reactant concentration C and light intensity I in the same photocatalyzed reaction. These three papers in particular find that the rate constant in the Langmuir−Hinshelwood rate form, k_{LH}, *and* the apparent binding constant K' *both* depend on light intensity. Since the isotherm dark adsorption constant, K, is the ratio of the adsorption rate constant to the desorption rate constant (in the dark), it should be independent of intensity if it appears in the rate equation. Thus, we have a contradiction identified by the few papers which have substantially explored both variables of concentration and intensity with an LH analysis. (5) Emilene et al.[26] published their paper with an understated title "Factors affecting the efficiency of a photocatalyzed process in aqueous metal-oxide dispersion: Prospect of distinguishing between two kinetic models". This singularly quantitative study found the LH rate parameters for phenol oxidation to vary as follows: k_{LH} proportional to intensity and K' inversely with intensity. The authors eventually found that a pseudo steady state approach could give results consistent with these variations and focused on trying to resolve which of two mechanisms, Langmuir−Hinshelwood or Eley−Rideal, was correct. The focus of their paper is evident from the subtitle "Prospect of distinguishing between two kinetic models".

Remarkably, in this last paper, the phrase "pseudo steady state" analysis (rather than "slow" or "rate determining step") appears nowhere in their title or abstract. We claim that their result is not singular, but is to be expected for virtually all

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photocatalyzed reactions. We also show that the pseudo steady state model can arise from either an LH or ER mechanism (as we showed earlier for a slow rate determining step analysis.[1] In the limit as the forward reaction step becomes faster than the reactant desorption step, the LH mechanism becomes indistinguishable from the ER mechanism. Finally, we establish the more general result that both k_{LH} and $1/K'$ will vary with intensity to the same exponent, which may be 0.5 or 1.0, according to the intensity regime.

2.3. Pseudo Steady State Hypothesis in Photocatalysis. We hypothesize that a pseudo steady state approach can explain the apparent anomalies cited above. In particular, we will show below that (1) the steady state hypothesis yields rate equations in which *both* the reaction rate constant and the apparent binding constant (or its more convenient reciprocal, the apparent dissociation constant K'', depend on light intensity *raised to the same exponent,* and that (2) this dependence requires that the adsorption equilibrium constant on catalytic sites *not* be the same as the apparent binding (or dissociation) constant in the rate equation, again in agreement with prior discrepancies cited for the adsorption equilibrated, slow reaction step model.

Because our hypothesis is expected to apply to all photocatalyzed reactions involving a (catalyzed) step that reacts an active center with an adsorbed reactant, we establish a broadly general, thus widely applicable, improvement in kinetic modeling of reactant destruction. As most of the several thousand papers on photocatalytic conversions involve water or air pollutants, it is *reactant destruction* that is most often the priority purpose of photocatalysis. We will apply our argument to liquid-phase systems, as the active centers here are better established to date than for air treatment. Initial rate data will be our primary source of confirmation, with exception noted later.

We now show that invocation of a pseudo-steady state for the same three steps of adsorption, desorption, and reaction always leads to a positive dependence of both k_{LH} and $K_{d,app}$ on intensity, as recently reported.

We begin with the simplest network which, following Turchi and Ollis,[1] assume that reaction of adsorbed reactant with a surface hydroxyl radical occurs in eq 1b above:

$$A(ads) \xrightarrow[k_{LH}=k_2(OH)]{} products \qquad (5)$$

The pseudo steady state hypothesis applied to the surface coverage of reactant, θ_A, assumes that $d(\theta_A)/dt = 0$, where

$$d\theta_A/dt = k_1(C_A)(1 - \theta_A) - k_{1\theta A} - k_2(OH)\,\theta_A = 0 \quad (6)$$

In consequence, we have a steady state reactant coverage given by eq 7:

$$\theta_A = \frac{\left(\dfrac{k_1}{k_{-1}+k_2(OH)}\right)C_A}{1+\left(\dfrac{k_1}{k_{-1}+k_2(OH)}\right)C_A} = \frac{K_{a,app}C_A}{1+K_{a,app}C_A} \qquad (7)$$

Since the reaction rate is given by rate $= k_2(OH)\theta_A$, we expect that both the apparent rate constant, k_{LH}, and binding constant, $K_{a,app}$, depend on intensity through the concentration of hydroxyl radicals, (OH).

Two common circumstances arise:[1] low intensity, $k_2(\cdot OH)$ varies as $I^{1.0}$; and high intensity, $k_2(\cdot OH)$ varies as $I^{1.5}$. Thus the apparent adsorption and dissociation constants in the rate equation are now expected to exhibit an intensity dependence:

$$K_{diss}^{app} \equiv \frac{1}{K_{ads,}^{app}} = \frac{k_{-1}+\alpha I^n}{k_1} \qquad (8a)$$

Equation 8a also indicates that the adsorption and desorption constants on the catalytic sites in the dark are given by

$$K_{diss} \equiv \frac{1}{K_{ads}} \equiv \frac{k_1}{k_{-1}} \qquad (8b)$$

Thus, a general expectation is that

$$K_{diss}^{app}(\text{illumination}) > K_{diss}(\text{dark}) \qquad (9a)$$

and

$$K_{ads}^{app}(\text{illumination}) < K_{ads}(\text{dark}) \qquad (9b)$$

The general intensity dependence of the photocatalyzed reaction is given by eq 10, obtained by combining eqs 2, 5, 7, and 8a:

$$-r_A = k_{LH\,c}\theta_A$$

$$= k_2(OH)\frac{C_A}{\left(\dfrac{k_{-1}+k_2(OH)}{k_1}+C_A\right)}$$

$$-r = \frac{(\alpha I^n)\dfrac{n}{c}C_A}{\dfrac{k_1+\alpha I^n}{k_1}+C_A}$$

$$= \frac{k_{cat}^{app}\cdot K_{diss}^{app}}{K_{diss}^{app}+C_A} \qquad (10)$$

Thus, the pseudo steady state approach predicts that *both* the apparent rate constant, k_{cat}^{app}, and dissociation constant, K_{diss}^{app}, depend on intensity, I, *raised to the same exponent*. In contrast, the slow step approximation represented by rate equation 4 depends on intensity only through the rate constant, k_{LH}. We now discuss the results in light of the experimental literature.

Example 1. Phenol Oxidation. Emeline, Ryabchuck, and Serpone[26] recently reported on the photocatalyzed oxidation of phenol in water. They fitted all data for each fixed intensity to the LH rate form, then explored the variation in the resulting Langmuir−Hinshelwood rate parameters, k_{LH} and K_{ads}^{app}, with intensity. They reported (Figure 3) that k_{LH} varies as $I^{1.0}$ and K_{ads}^{app} varies as $I^{-1.0}$, thus k_{diss}^{app} varies as $I^{1.0}$. Thus, k_{LH} and K_{diss}^{app} have the same intensity dependence, as predicted from the present steady state analysis.

However, their dark adsorption constant, K_{ads}, gives a behavior contrary to that suggested from equations (9a,b). In particular, a plot of K_{diss} vs I calculated from Emilene et al.[26] data shows that $K_{diss} \rightarrow 0$ as $I \rightarrow 0$, thus K_{diss} (dark) $= 0$ in eq 9a, whereas these authors report a measured dark adsorption constant K_{ads} (dark) $= 3.14 \times 10^3$ M, hence $K_{diss}^{app} = 1/K_{ads}$ 3.2×10^{-4} M^{-1}, a value greater than any of the K_{diss} (illumination) values. We return later to this apparent discrepancy.

Example 2. Acetophenone Oxidation. Xu and Langford[27] measured the photocatalytic rate of disappearance of a "poorly adsorbed" reactant, acetophenone, in water at pH 6.2. They also
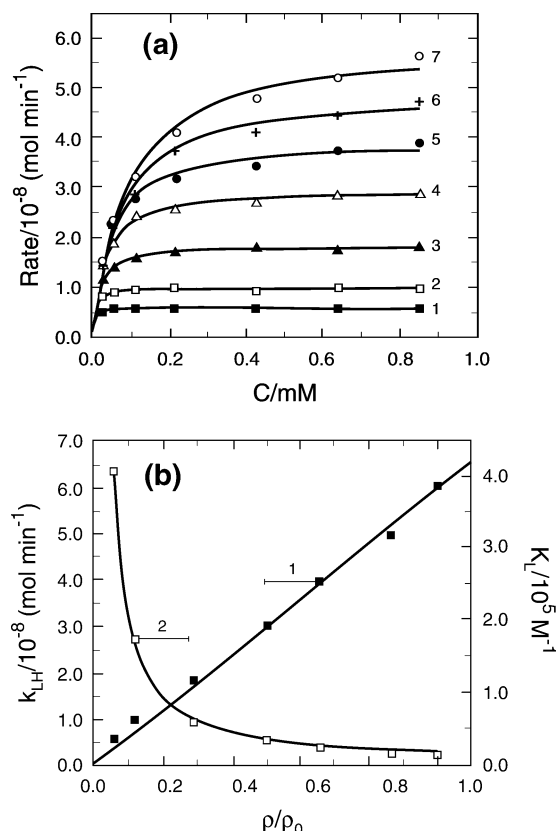
Figure 3. (a) Dependencies of the rate of phenol photodegradation on phenol concentration at different photon flow of actinic light at 365 nm, $[I(\max) = 1.1 \pm 0.3) \times 10^{17}$ photons/cm²-s] (b) Dependencies of rate constant k_{LH} (left axis) and K_L (right axis) on photon flow of 365 nm light. From ref 26, used with permission. © 2000 Elsevier.

Figure 4. Plot of calculated $K_{d(app)}$ and k_{LH} for acetophenone degradation vs intensity, I (top) or square root of intensity, (bottom). First order dependence passing through origin provides a better fit to data for k_{LH}; K plots are ambiguous.

fitted all fixed intensity data to the LH form, and reported that "The results shows that K (adsorption) decreases at higher light intensity, while k_{LH} increases...". Just three intensity values were examined: $I = 0.81$, 1.40, and 2.14×10^{-7} Einsteins s⁻¹. They also measured acetophenone adsorption in the dark ($I = 0$).

They estimated the LH parameters through calculating $\Delta C/\Delta t$ values for several early times. We extrapolate their Figure 5 results for k_{LH} and K_{ads} vs Δt back to $t = 0$ and obtain values descriptive of the initial rate (only acetophenone present). These extrapolation values are plotted in Figure 4 vs I and $I^{0.5}$. This figure shows that k_{LH} could plausibly fit either a first order or half order dependence on I over the limited range examined. The data for K_{ads} is scattered, and thus inconclusive. A square root plot for intensity is almost as good as these two parameters. We can say simply that it is possible these data are consistent with k_{LH} and K_{ads} having the same dependency on I, as predicted previously (low intensity $k_2(\cdot OH)$ varies as $I^{1.0}$; high intensity $k_2(\cdot OH)$ varies as $I^{1.5}$) and from eq 8a.

An obvious inconsistency is again found. Xu and Langford[27] reported that $K_{ads}(\text{dark}) = 2.44 \times 10^4$ dm³ mol⁻¹, which is less than any of the K_{ads} values reported for $K_{ads}(\text{illumination})$, hence

$$1/K_{ads}(\text{dark}) = K_{diss}(\text{dark}) > K_{diss}(\text{illumination})$$

which appears to be inconsistent with eq 9a.

Thus, both Emeline et al.[26] and Xu and Langford[27] find K(dark) > K_{app} for all concentrations and intensities explored. Two possible explanations suggest themselves: (1) The number of active catalyst sites are much fewer than the total surface adsorption sites. Thus, the K_{diss}^{app} value measured under illumination does not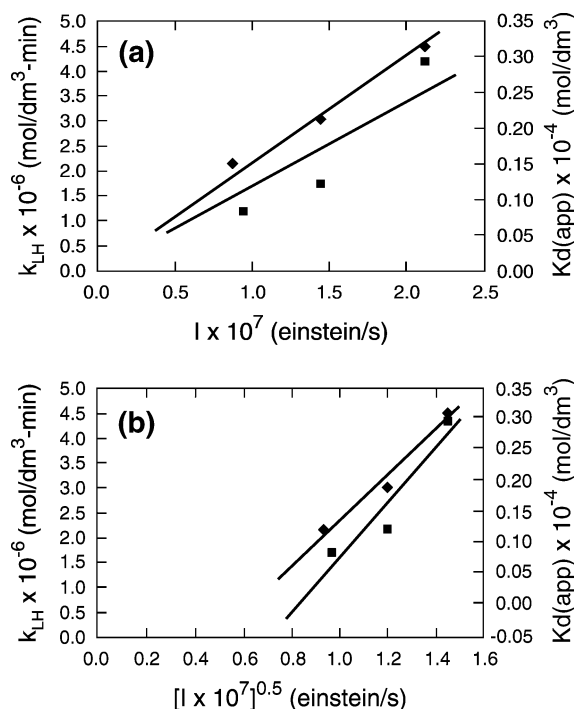 characterize the generally accessible surface probed by dark adsorption measurements. (2) The active sites exist only under illumination, and the species involved (e.g., Ti(III) sites, etc.) do not exist appreciably in the dark, so again dark adsorption sites do not characterize the photocatalytially active sites.

The data for both Emeline et al.[26] and Xu and Langford[27] extrapolate at low intensities to give $K_{d,app}(\text{dark}) = (k_1/k_1) = 0$, hence $k_1 = 0$. This result indicates a mechanism involving adsorption followed by reaction, i.e., two irreversible steps in series:

$$A \xrightarrow{k_1} A_{ads} \xrightarrow{k_2'} \text{products}$$
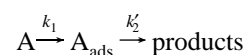
Such mechanisms are well established in enzyme catalysis. For example, the decomposition of hydrogen peroxide by the enzyme catalase is virtually diffusion controlled (i.e., every reactant collision with the active site results in reaction).[29]

Example 3. Methyl Viologen Oxidation. Martyanov and Savinov[30] explored oxidation of methyl viologen (MV) in TiO₂ slurries. Their curves for MV oxidation rate vs MV concentration fit the LH form, with K(M⁻¹) values shown below. We calculate the corresponding $K_{d,app}$ as the reciprocal of their K(M⁻¹) values and plot these versus the square root of intensity, which is appropriate since these authors found a calculated quantum yield to vary as the reciprocal of the square root of intensity, implying that their measurement were made in recombination dominated regime. Plotting the calculated $K_{diss}(app)$ vs I yields (two data points only for each line)

$$K_{diss,app} = 0.38 + 1.36(I)^{0.5} \quad pH = 9.0$$

$$K_{diss,app} = 0.25 + 0.74(I)^{0.5} \quad pH = 5.6$$

These forms have a positive intercept and positive slope, consistent with our proposed eq 11 above, derived from the

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pseudo-steady state assumption. However, their provision of only two points for each line indicates a need to revisit their conditions to better establish the order of the intensity dependence in $K_{d,app}$.

The similarity of these two curves is consistent with our hypothesis that $K_{diss,app}$ should vary as intensity to a power = 0.5 when recombination dominates, or to power 1.0 when surface reaction dominates. This behavior of $K_{diss,app}$ with I is only consistent with a pseudo steady state treatment of reactant on the photocatalyst, and is inconsistent with equilibrated adsorption/desorption of reactant. Thus, we disagree completely with these authors' assertion[30] that "the photocatalytic reaction cannot disturb the dark adsorption−desorption equilibrium" on the catalytic site. Indeed, our entire argument is that the demonstrated dependence of $K_{d,app}$ upon I can only be due to "disturbing" the adsorption−desorption process from equilibrium.

Example 4. Phenol Oxidation. We reconsider the correlative behavior (Figure 2) between k_{LH} and $1/K_{ad,app}$ noted from a literature survey of Hoffman et al.[25] As our derivation above shows that

$$k_{LH} = k_2(OH)$$

and

$$1/K_{a,app} = K_{d,app} = (k_{-1} + k_2\,(OH))/k_1 = (k_1 + k_{LH})/k_1$$

we predict that a plot of $1/K_{a,app} = K_{d,app}$ vs k_{LH} should be linear, of positive slope $1/k_1$ and of positive intercept k_{-1}/k_1, all properties of the correlation reported in Figure 2 below. We note that this plot will now allow us to evaluate individually the fundamental adsorption and desorption rate constants for reactant on the catalyst surface. For example, the slope of this figure is

$$\text{slope} = 1/k_1 = (420-30/(120-0) = 3.25\ \text{min}$$

thus providing the rate constant value $k_1 = 0.31\ \text{min}^{-1}$. For comparison, Chen et al. report first-order kinetics for DCE (1,2-dichloroethane) adsorption to fit $k_1 = 0.0815$ to $0.0871\ \text{min}^{-1}$.

The desorption rate constant, k_1, is then given by

$$k_{-1}/k_1 = \text{intercept} = 30\ (\text{microM})$$

thus

$$k_{-1} = 30\ k_1\ (\text{microM min}^{-1}) = 9.3\ \text{microM min}^{-1}$$

The new analysis allows evaluation not only of the intensity dependence and the rate constant for the active center step but also individually of the adsorption and desorption constants on the catalytic site. The availability of these values will allow a much stronger theoretical visitation in predicting rate constants of fundamental steps in the reaction mechanism.

Further, for systems where $K_{d,app}(\lim I \to 0)$ does not approach the dark dissociation constant, $K_d\ (= 1/K)$, we can say that the dark adsorption sites are not related to the presumably smaller number of photocatalytically active sites, as the latter involve only those regions proximate to the site containing [OH]. In particular, two of the papers cited above find $K_{d,app} \to 0$ as $I \to 0$, indicating that k_{-1} is approximately zero, and thus the reaction kinetics are approximated by two irreversible steps in series:

$$A_{soln} \to A_{ad} \text{ then } A_{ad} + [OH] \to \text{products}$$
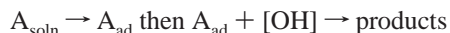
2.4. Alternative Forms to the Langmuir−Hinshelwood Scheme.

Alternative rate mechanisms are available. Emeline et al.[26] have shown that an Eley−Rideal (ER) mechanism may also give rise to the same apparent LH kinetic rate form in their study of phenol conversions. In this instance, an incoming, dissolved reactant arrives directly on an adsorbed radical [OH]. The example just discussed, which appear kinetically the same as two irreversible steps in series, is such a mechanism.

As indicated above, our earlier slow step analysis[1] included their ER possibility as one of four possible processes involving the active center, in this case (i) [OH]$_{adsorbed}$ reacts with reactant [R]$_{ads}$ (Langmuir−Hinshelwood bimolecular mechanism); (ii) [OH]$_{ads}$ reacts with reactant [R]$_{solution}$ (Eley−Rideal mechanism); (iii) [OH]$_{solution}$ reacts with [R]$_{adsorbed}$ (another Eley-Rideal mechanism); or (iv) [OH]$_{solution}$ reacts with [R]$_{solution}$. In all cases, our present insistence on a pseudo steady state analysis will always provide a positive dependence of k_{LH} and $K_{d,app}$ on intensity, because of the positive dependence of k_{LH} and $K_{d,app}$ on [OH], and thus on intensity. This dependence will exist for each of the four example mechanisms cited above.

3. Summary

Heterogeneous photocatalysis has survived well with use of the very simply Langmuir−Hinshelwood expression to describe reactant concentration influences on reaction rate, dissolved oxygen concentration, and the presence of competitive consumption of oxidants by a progression of intermediates, stable compounds. However, photocatalysis routinely involves the initial generation of reactive intermediates such as free electrons, holes, and hydroxyl radicals. The reactivity of the latter toward reactants in solution or adsorbed on the surface is such that we cannot expect reactant adsorption to be equilibrated. Thus the slow step approximation inherent in the original LH formulation is invalid in photocatalysis, and a pseudo steady state approach must be utilized in the kinetic equation for reactant itself, not just for the active intermediates. The now thrice observed dependence of $K_{d,app}$ upon intensity warns us that this may indeed be a general circumstance and that future comparisons of photocatalysis must include a deeper study to allow determination of all kinetic parameters of a fuller, more fundamental rate equation for photocatalyzed conversions.

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