Can we adopt Langmuir-Hinshelwood mechanism for photocatalytic reaction kinetics?

references (for example; *: claiming Langmuir-Hinshelwood mechanism)

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2)   J. Cunningham and G. Al-Sayyed, *J. Photochem. Photobiol. A: Chem.*, **77**, 255-263 (1994).
3)   A. Mills and S. Morris, *J. Photochem. Photobiol. A: Chem.*, **71**, 75-83 (1993).*
4)   G. P. Lepore, B. C. Pant, and C. H. Langford, *Can. J. Chem.*, **71**, 2051-2059 (1993).*
5)   H. Al-Ekabi, N. Serpone, E. Pelizzetti, C. Minero, M. A. Fox and R. B. Draper, *Langmuir*, **5**, 250-255 (1989).*
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Langmuir (or Langmuir's) [adsorption] isotherm

This is originally, in 1916, introduced for the adsorption (v) from gas phase of pressure p to give saturation adsorption v_m with "adsorption (equilibrium) constant" b,

$$v = v_m bp / (1 + bp) \tag{1}$$

but, can be used for the liquid-solid phase adsorption, where p is replaced by concentration c.

Derived on the basis of assumptions: (1) unique adsorption site, (2) monolayer adsorption, and (3) no interaction between the adsorption sites.

Langmuir-Hinshelwood (L-H) mechanism

A representative reaction mechanism for surface reaction, derived by Langmuir and Hinshelwood (the original article could not be cited here).

Derived by assuming "bimolecular reaction" of **a** and **b**, both of which are adsorbed on the surface with the equilibrium constant, K_a and K_b and second-order rate constant k.

$$r = kns\theta_a\theta_b = kns \, (K_a K_b p_a p_b) / (1 + K_a p_a + K_b p_b)^2 \tag{2}$$

The surface adsorption site, with surface density of n, can adsorb both **a** and **b** molecules, and one site is surrounded by nearest neighboring sites of number of s.

In most of cases, this mechanism has been compared with the following Redeal-Eley machanism, both of which is derived by assuming that the surface reaction (of second-order kinetics), including at least one kind of surface-adsorbed species, is a rate-determining step.

N.B. If the component **b** does not participate in the reaction, i.e., first-order reaction of surface-adsorbed **a** proceeds, the rate may be expressed,

$$r = kn\theta_a = kn \, (K_a p_a) / (1 + K_a p_a), \tag{3}$$

which is formally very similar to basic Langmuir isotherm.   The first problem is whether we can call this equation (3) Langmuir-Hinshelwood mechanism.   Strictly speaking, L-H mechansim must contain the second-order, but not first-order, rate constant k.   The equation should be called kinetics with a rate-determining step of surface reaction of substrate **a** adsorbed with a Langmuiri isotherm.   Furthermore, as has been used in the field of catalyst science, L-H mechanism is employed as one of the possible mechanisms between L-H and the following R-E mechanism.

Redeal-Eley (R-E) machanism

Derived by assuming "bimolecular reaction" of **a** and **b**, the former of which is adsorbed on the surface with the equilibrium constant, K_a, but the latter remains in gas (or liquid) phase.

$$r = kn\theta_a\theta_b = kn\ (K_a p_a p_b)\ /\ (1 + K_a p_a) \tag{4}$$

The adsorption of component **a** is assumed to obey Langmuir isotherm, i.e., this R-E mechanism is also based on the Langmuirian adsorption.

To the best of my knowledge, there have been no reports claiming that a given photocatalytic reaction obeys R-E mechanism.

Photocatalytic reaction kinetics

Basic requirement for making rate expression(s) which corresponds photocatalytic reaction mechanism:

(1) photocatalytic reactions must be initiated by photoabsorption (photon flux I and absorption efficiency ϕ)
(2) excited electron (e⁻) and positive hole (h⁺) are formed (presumably the efficiency can be unity)
(3) e⁻ and h⁺ react with surface adsorbed species (second-order rate constants, k_e and k_h and surface concentration of their substrates, c_e and c_h)
(4) otherwise recombine each other to give no chemical reaction but heat ([first or second-order] rate constant k_r)
(5) if any chemical or photoinduced reaction(s) follows, its (their) kinetics must be included

cf. among a series of steps (1)-(4), it is impossible to adopt a concept of **rate-determining process (RDP)**, since this is not a sequential reaction processes with a bottle neck.

An approximation of rate equation is,

$$r = I\phi\ (k_e c_e + k_h c_h)\ /\ (1 + k_e c_e + k_h c_h + k_r), \tag{5}$$

derived on the assumption of independent consumption of e⁻ and h⁺ and a first-order recombination rate constant k_r.

If the term $k_e c_e + k_h c_h$ is large enough to neglect k_r, rate r should reach to $I\phi$, i.e, quantum efficiency of unity.   However, the quantum efficiency reported so far was at most 50 or 60 %

and a few % in average, suggesting that the recombination (k_r) can not be neglected in any case. On the other hand, if the term k_r is large enough to neglect $k_e c_e + k_h c_h$, the rate is given by,

$$r = I\phi \, (k_e c_e + k_h c_h) \, / \, k_r. \tag{6}$$

Further approximation is made by assuming predominant reaction by e^- or h^+ to replace $k_e c_e + k_h c_h$ with kc. If a Langmuirian adsorption of reaction substrate with an adsorption equilibrium constant K and concentration in the bulk C is applied to give the concentration c, we obtain,

$$r = I\phi \, kn \, KC \, / \, k_r(1 + KC). \tag{7}$$

Thus, a linear relation of $1/r$ versus $1/C$ (or in another linearization, C/r versus C) is predicted. The plots give the adsorption constant K, which must coincide with that obtained from the apparent adsorption isotherm.

In the case of photocatalytic reaction of oxidation of organic molecules in the presence of molecular oxygen (O_2), it is probable that amount of both the substrate and O_2 gives influence on the rate, as was observed in ref. (3).