

## Chapter 2

# Kinetic Concepts of Heterogeneous Photocatalysis

**Abstract** The ABCs of empirical chemical kinetics are highlighted from the scratch. Aspects of dynamics regarding charge carrier trapping and recombination are essential part of this discussion. The effect of imposition of external constraints such as temperature of the reactivity solution, concentration of the subject compound, intensity and wavelength of light on photocatalytic degradation system is emphasised. Because of the crucial position of light intensity in heterogeneous photocatalysis, the principles of operation of important chemical actinometric systems are presented.

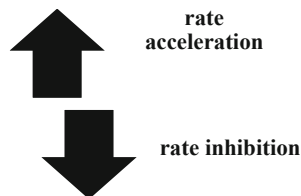
### 2.1 Background Sketch

Chemical kinetics addresses important issues in heterogeneous photocatalysis. Generally, it deals with the experimental determination and analysis of the quantity of a substance (usually concentration) as a function of time. In other words, chemical kinetics is concerned with reaction rate and throughput. Unlike in chemical equilibrium where the reactants and the products are in dynamic state of balance, chemical kinetics is concerned with either disappearance or appearance of chemical substances. The latter have direct consequences on reaction rate. A given chemical reaction may get accelerated or slowed down, for example by a positive catalyst or negative catalyst respectively as shown in Fig. 2.1. A simple example of this concept can be derived from common domestic techniques such as preservation using refrigeration method. The shelf life of batteries can be extended by lowering the surrounding temperature. The simple reason behind this observation is that the rate of decay of the electrolytes or sensitisers in the battery is slowed down by lowering the temperature. The following discussions will cover aspects of chemical kinetics including the factors that affect the rate of photocatalytic reactions.

Some aspects of catalysis such as the determination of rate are viewed from the standpoint of the principles of chemical kinetics. The rate of reaction is measured based on the property that is easiest to measure. This property can be colour, concentration or weight. As several products of varied structure and quantity can be formed during photocatalytic reactions, it is more convenient to measure reaction rates based on the disappearance of such a property.

The law of mass action is the central to the expression of reaction rates. The law is based on the fact that the rate of reaction increases proportionally with concentration.

**Fig. 2.1** Types of kinetic influences. Processes can be manipulated using a suitable catalyst to decline or increase in reaction rate, depending on the type of catalyst or reaction condition



This direct variation is expressed mathematically as a rate law and the constant of proportionality is termed rate constant.

Consider the photocatalytic transformation of a molecule A:



The rate of disappearance of A can be given by differential rate equation known as the differential rate law. A general differential rate law is given below.

$$r = \frac{-d[A]}{dt} = k[\text{reactant}]^n \quad (2.2)$$

where  $k$  is the rate constant and the power  $n$  is the order. A reaction is first, second or third order depending on the value of  $n$  (0, 1, 2 or 3 respectively). The parameter  $k$  as well can be first order, second order or third order rate constant. Rate constant can be utilised in comparing the rate of different reactions.

If time is measured in seconds the unit of  $r$  will be judged from Eq. (2.1) to be  $\text{mol dm}^{-3} \text{s}^{-1}$ . The unit of  $k$  however varies with the reaction scheme. For zero order the rate law is

$$r (\text{mol dm}^{-3} \text{s}^{-1}) = k[A]^0, \quad \text{or} \quad r = k$$

So for zero order reactions  $k$  is expressed in  $\text{mol dm}^{-3} \text{s}^{-1}$

Similarly, first order rate constant can be given by

$$k = \frac{r (\text{mol dm}^{-3} \text{s}^{-1})}{[A](\text{mol dm}^{-3})} \quad (2.3)$$

So, the unit of first order rate constant is  $\text{s}^{-1}$ .

For second order reactions

$$k = \frac{r (\text{mol dm}^{-3} \text{s}^{-1})}{[A]^2 (\text{mol dm}^{-3})^2} \quad (2.4)$$

Therefore the second order rate constant is expressed in  $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ . In this case, doubling the concentration of A results in quadrupling the rate of reaction.

For third order reactions,

$$k = \frac{r (\text{mol dm}^{-3} \text{s}^{-1})}{[A]^3 (\text{mol dm}^{-3})^3} \quad (2.5)$$

So the third order rate constant is expressed in  $\text{dm}^6 \text{mol}^{-1} \text{s}^{-1}$ . Since time is usually recorded in minutes during experiments many workers prefer to report rate constants with time in  $\text{min}^{-1}$ . Similarly, concentrations of substances with unknown molar masses have often been reported in ppm or  $\text{mgdm}^{-3}$ .

## 2.2 Decay Models in Photocatalysis

Various photocatalytic processes have been described by different kinetic models such as pseudo zero order, pseudo first order and second order models. As most of the processes studied are monitored based on the disappearance of the initial entities we refer to their kinetic schemes as decay models. The integral treatment of differential rate equations yields integrated rate laws which can display vividly the disappearance or decay profile of the original compound undergoing photocatalytic destruction. The commonest decay models that are observed in photocatalysis studies are the zero and the first order rate laws. Normally, the zero order is observed at surface saturation. Basically, the rate of a zero order reaction does not vary with concentration. In other words, a change in concentration does not result in any change in the reaction rate. In this case, the differential rate law for the disappearance of any reactant molecule A is given by

$$\frac{d[A]}{dt} = -k \quad (2.6)$$

So

$$d[A] = -kdt \quad (2.7)$$

Upon integration between the concentration limits  $[A]_0$  and  $[A]_t$  and time  $t = 0$  and  $t = t$  we have

$$\int_{[A]_0}^{[A]_t} d[A] = k \int_{t=0}^{t=t} dt \quad (2.8)$$

$$[A]_t - [A]_0 = -kt \quad (2.9)$$

Or

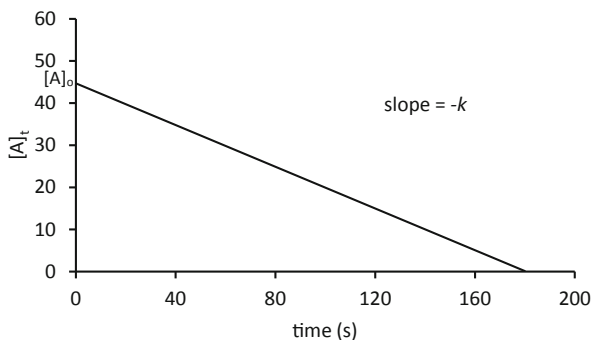
$$[A]_t = [A]_0 - kt \quad (2.10)$$

If Eq. (2.10) is compared with the equation of straight line  $y = mx + c$ , a plot of  $[A]_t$  against  $t$  will give a straight line whose intercept equals  $[A]_0$  and slope equals  $-k$  (Fig. 2.2).

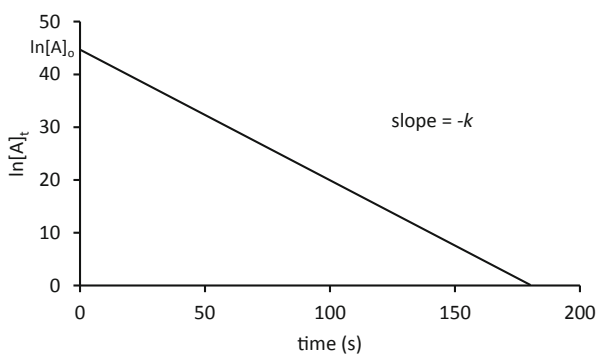
Conversely, the rate of first order reaction depends upon the concentration of single reactant. The rate of consumption of A is

$$-\frac{d[A]}{dt} = k[A] \quad (2.11)$$

**Fig. 2.2** Zero order kinetic fit for the disappearance of a reactant A with time



**Fig. 2.3** First order fit for the decay of reactant A with concentration varying in the range  $[A]_0$  to  $[A]_t$  and with time up to  $t$  seconds



By collecting concentration terms together we obtain the following:

$$\frac{d[A]}{[A]} = -k dt \quad (2.12)$$

If the concentration of A at time  $t=0$  s is  $[A]_0$  and at any other time  $t=t$  s the concentration is  $[A]_t$  the differential rate law can be integrated within those limits as follows:

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = k \int_{t=0}^{t=t} dt \quad (2.13)$$

$$\therefore \ln [A]_t - \ln [A]_0 = -kt \quad (2.14)$$

or

$$\ln [A]_t = \ln [A]_0 - kt \quad (2.15)$$

If Eq. (2.15) is compared with the equation of straight line  $y = mx + c$ , a plot of  $\ln[A]_t$  versus  $t$  should give a straight line whose slope is  $-k'$ . The intercept of the plot is  $\ln[A]_0$  (Fig. 2.3).

Eq. (2.15) can be presented in exponential form, to display the relationship between first order concentration decay and time.

$$\frac{[A]_t}{[A]_0} = e^{-kt} \quad (2.16)$$

This decay equation has found important applications in physical chemistry which include the dating of prehistoric lives.

## 2.3 Pseudo Order Reactions

The term ‘pseudo-’ has been commonly used to prefix the order of a reaction because in real fact one of the reactants in catalytic systems acts as a catalyst and its concentration remains more or less unchanged such that instead of having second-order reaction for example, a pseudo-first order reaction is observed (Auguliano et al. 2008). Similarly when the substrate is in large excess, the catalyst surface gets wholly covered all through and the disappearance of the substrate becomes negligibly dependent on concentration. At such saturation coverage, a pseudo zero order photocatalytic reaction will be observed (Theurich et al. 1996).

If a substance A is undergoes transformation such that its apparent concentration remains constant during the process, the following expression holds true.

$$\frac{d[A]}{dt} = -k[A] \quad (2.17)$$

Since  $[A]$  is constant the rate changes by a constant value which can be represented by

$$-\frac{d[A]}{dt} = -k' \quad (2.18)$$

$$d[A] = -k' dt \quad (2.19)$$

where  $k'$  is the observed or pseudo-zero order rate constant. If the concentration of A measured at time  $t = 0$  s is  $[A]_0$  and any time  $t = t$  s the concentration becomes  $[A]_t$  the differential rate law can be integrated within those limits as follows:

$$\int_{[A]_0}^{[A]_t} d[A] = -k' \int_{t=0}^{t=t} dt \quad (2.20)$$

$$[A]_t = [A]_0 - k't \quad (2.21)$$

On the other hand, if we consider the two reacting species A with B combining to form products



If the concentration of A and B at the start of the reaction be  $[A]$  and  $[B]$ . Then,

$$-\frac{d[A]}{dt} = k[A][B] \quad (2.23)$$

Assuming that  $[B] \gg [A]$  or in other words  $[B]$  is constant then

$$-\frac{d[A]}{dt} = k'[A] \quad (2.24)$$

$k'$  is the observed rate constant known as the pseudo-first order rate constant. Therefore, the major difference between pseudo first order rate equation and first order lies in the observed rate constant. If the concentration of A measured at time  $t = 0$  s is  $[A]_0$  and any time  $t = t$  s the concentration becomes  $[A]_t$  the differential rate law can be integrated within those limits as follows:

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = k' \int_{t=0}^{t=t} dt \quad (2.25)$$

$$\ln[A]_t - \ln[A]_0 = -k't \quad (2.26)$$

$$\ln[A]_t = \ln[A]_0 - k't \quad (2.27)$$

If Eq. (2.27) is compared with the equation of straight line  $y = mx + c$ , a plot of  $\ln[A]_t$  versus  $t$  should give a straight line whose slope is  $-k'$ . The intercept of the plot is  $\ln[A]_0$ .

## 2.4 Fractional Lifetimes

Within certain time of the start of chemical reaction, only a fraction of the original substance may be transformed. The time required for this transformation is known as fractional lifetime. The time taken for the original amount of reactant to transform is called the half-life. Half-life has been the conventional fractional lifetime preferred for use generally in chemical kinetics and is denoted usually by  $t_{1/2}$ . It should be noted that half-life is not characteristic of a given reactant as different reactants can have the same half-life.

For first order reactions the integral rate law may be written in the following form

$$\ln \frac{[A]_0}{[A]_t} = kt \quad (2.28)$$

where  $[A]_0$  and  $[A]_t$  are the concentrations of a reactant A at time  $t = 0$  and at  $t = t$

At half-life  $[A]_t = \frac{[A]_0}{2}$  and Eq. (2.28) becomes:

$$\ln 2 = kt_{1/2} \quad (2.29)$$

and

$$t_{1/2} = \frac{\ln 2}{k}$$

or

$$t_{1/2} = \frac{0.6932}{k} \quad (2.30)$$

The concentration term has therefore been eliminated on the way to half-life equation, which implies that the half-life of first order reactions is independent of the concentration of the reactant.

The half-life of second order reactions can be derived from the integrated second order rate law:

$$-\frac{1}{[A]_t} + \frac{1}{[A]_0} = -kt \quad (2.31)$$

If we apply the half-life condition that  $[A] = \frac{[A]_0}{2}$  Eq. (2.31) yields

$$-\frac{2}{[A]_t} + \frac{1}{[A]_0} = -kt_{1/2} \quad (2.32)$$

Therefore,

$$t_{1/2} = \frac{1}{k[A]_0} \quad (2.33)$$

The equation shows that the half-life of second order increases as the initial concentration of the reactant is increased.

For zero order reactions the integrated rate law is given by:

$$[A]_t = [A]_0 - kt \quad (2.34)$$

At half-life the integrated rate equation becomes:

$$\frac{[A]_0}{2} = [A]_0 - kt \quad (2.35)$$

$$\therefore [A]_0 = 2([A]_0 - kt_{1/2}) \quad (2.36)$$

$$t_{1/2} = \frac{[A]_0}{2k} \quad (2.37)$$

From the half-life of a reaction we can make conclusion regarding the rate of the reaction. Table 2.1 shows the classification of reaction rates based on their half-lives. The table can be useful in describing photocatalytic reaction rates so that those falling within the same category can be considered together.

**Table 2.1** Classification of rates of reaction based on half-life (Wright 2006)

Half-life (s)	Time span for near-completion	Rate classification
$10^{-15}$ to $10^{-12}$	ps or less	ultra fast rate <sup>a</sup>
$10^{-12}$ to $10^{-6}$	$\mu$ s or less	very fast rate
$10^{-6}$ to 1	s	fast rate
1 to $10^{-3}$	mins or hrs	moderate rate
$10^3$ to $10^6$	Weeks	slow rate
$> 10^6$	weeks or years	very slow rate

<sup>a</sup>added in this text after considering current developments in subsecond spectroscopy

## 2.5 Manifestations of Second Order Decay Kinetics in Photocatalysis

Second order reactions involving a single reacting entity (type I) can be represented by the chemical equation below:



Therefore the rate of disappearance of A is given by the equation:

$$-\frac{d[A]_t}{dt} = -k[A]^2 \quad (2.39)$$

Upon rearrangement of Eq. (2.39) we obtain

$$\frac{d[A]_t}{[A]^2} = -k dt \quad (2.40)$$

If  $[A]$  at time 0 s is  $[A]_0$  and at time  $t$  seconds is  $[A]_t$  we can integrate between those lower and upper limits of concentration and time

$$-\frac{1}{[A]_t} + \frac{1}{[A]_0} = -kt \quad (2.41)$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \quad (2.42)$$

A plot of  $1/[A]_t$  against time should give a straight line having intercept equal to  $1/[A]_0$  and slope  $k$ . Consistence of photocatalytic degradation reactions with second order model is not expected but this unusual case was reported in the photocatalytic degradation of Auramine O aqueous solutions over ZnO catalyst owing to constraints in fitting the kinetic data to other than the second order kinetics (Kumar et al. 2007).

The recombination kinetics of charge carriers has been widely proven to be consistent with type I second order model (Serpone et al. 1995; Colombo and Bowman 1996; Bauer et al. 2004). Information gleaned from the femtosecond spectroscopic study by Colombo et al. (1995a) showed close similarities in the electron-hole kinetics and recombination dynamics of wide band gap semiconductors regardless of



the photocatalyst used. In another study, Bahnemann et al. (1997) observed the recombination of trapped holes and electrons in colloidal  $\text{TiO}_2$  within the first 200 ns. Later on, Bauer et al. (2004) studied the relaxation processes of charge carriers in 20 nm nano-crystalline ZnO at laser excitation wavelength of 750 nm. Sharp and broad peak were obtained at 385 and 600 nm respectively. The narrow peak was linked to the recombination of photo-electron and hole. The workers observed that more than 50 % of the photoactivated charge carriers disappeared in less than 10 ps. Electron and hole were rapidly trapped in about 1 ps. On the other hand, trap-assisted recombination and exciton recombination occurred within time scale of 400 and 12 ps respectively.

The femtosecond measurements of the intensity dependence of electron-hole recombination by Colombo et al. (1995b) has revealed at least two processes involved in the consumption of semiconductor-based conduction band electrons. There is a first order reaction leading to trapped electrons  $e^-$ , most likely at the surface, which subsequently undergoes very rapid second order recombination. The rate of recombination has been generally given by Eq. (2.43).

$$r_{\text{rec}} = k_{-2}[e^-][h^+] \quad (2.43)$$

Since the same number of opposite charge carriers recombine in the semiconductor particle, the rate of recombination will proceed by type I second order below.

$$r_{\text{rec}} = k_{-2}[e^-]^2 \quad (2.44)$$

Other surface reactions of second order type include the hydroxyl radical oxidation of paracetamol which has been characterised with second order rate constant of  $1.7 \times 10^9 \text{ mol}^{-1} \text{ dm}^{-3} \text{ s}^{-1}$  (Yang et al. 2009). Columbo et al. (1995b) has shown that a third (or higher) order process takes place between charge carriers which leads to a long-lived species. The third-order reaction is believed to be a result of an auger process which leads to ejected electrons in deep trap states. Currently, there are no elaborate details of this third order process and to our knowledge no further investigations have been carried out.

Similarly, the mechanistic details of the second order recombination process at these microscopic scales are sketchy. However, Rothenburger et al. (1985) has monitored the dynamics of charge carrier trapping and recombination in semiconductor particle and has corroborated the charge carrier lifetime (i.e. 30 + 15 ps) and kinetic model (i.e. second order) by invoking stochastic kinetic models detailed below. In subsection 1.5.1 of Chap. 1 we have introduced transit time, which is required for charge carriers' diffusion to the surface. This parameter may vary proportionally with the radius of the semiconductor particle according to Fick's equation (Eq. 2.45) (Grätzel and Frank 1982).

$$\tau = \frac{r^2}{\pi^2 D} \quad (2.45)$$

where  $\tau$  is the transit time in subseconds,  $r$  is the radius of the semiconductor particle,  $D$  is the diffusion coefficient. The recombination kinetics can be modelled by a

quadratic birth and death process which implies that the exponential decay of the survival probability of a single electron-hole pair in a semiconductor particle with time. If the average lifetime of charge carrier is  $\tau = k^{-1}$  and  $x$  pairs are present in a particle, the first recombination event yielding a particle with  $(x - 1)$  pairs will occur after an average time given by Eq. (2.46).

$$\tau = \frac{1}{x^2 k} \quad (2.46)$$

where  $x^2$  is a factor that allows for the fact that  $x^2$  different choices can be made from an ensemble of  $x$  electrons and  $x$  holes.

The time differential of the probability that a particle contains  $x$  electron-hole pairs ( $x = 1, 2, \dots$ ) at time  $t$  is given by Eq. (2.47).

$$dP_x(t)/dt = k + 1)^2 P_{x+1} + l(t) - kx^2 P_x(t) \quad (2.47)$$

If the charge carriers are assumed to be Poisson-distributed, this differential equation can be solved subject to the initial conditions of Eq. (2.48) for  $P_x(0)$ .

$$\langle x \rangle(t) = \frac{\langle x \rangle_0}{1 + \langle x \rangle_0 kt} \quad (2.48)$$

The average number of charge pairs present at time  $t$ ,  $\langle x \rangle(t)$ , can be calculated by means of the function technique to give Eq. (2.49).

$$\langle x \rangle(t) = \sum_{n=1}^{\infty} c_n e^{-n^2 kt} \quad (2.49)$$

Where

$$c_n = 2e^{-\langle x \rangle_0 (-1)^n \sum_{n=1}^{\infty} \frac{\langle x \rangle_0^i}{(n+i)!} \prod_{j=1}^n (n-i-j)}$$

The parameter  $\langle x \rangle_0$  is the average number of pairs present at  $t = 0$ .

From the equations, two kinetic schemes may be observed. When  $\langle x \rangle_0$  is very small, Eq. (2.49) becomes an exponential and the charge carrier recombination follows a first-order rate law. Secondly, the equation approximates a second-order rate model (Eq. 2.48) at high average initial occupancy of the semiconductor particles by electron-hole pairs (Fig. 2.4).

Rothenberg et al's plot of  $\langle x \rangle_0 k \tau_i$  calculated from Eq. (2.49), against  $\langle x \rangle_0$  for values of  $\tau_i$  corresponding to first, second and third lifetimes (i.e.  $i = 1/2, 1/4$  and  $1/8$ ; the fraction of initial charge carrier pairs still surviving) yielded two different limits. For first order process  $\langle x \rangle_0 k \tau_i = -\ln i \langle x \rangle_0$ , which manifested as straight lines passing through the origin. The second order recombination process was described by  $\langle x \rangle_0 k \tau_i = (1/i) - 1$ , which appeared as horizontal lines on the plot that can approximate to second order curves.

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