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Competition Kinetics: An Experimental Approach

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Abstract

In this chapter, free radical kinetics with the help of competition kinetics and some experimental results calculated by competition kinetics to find out the rate constant of reactive species ($^{\bullet}OH$, e_{aq}^{-}, $^{\bullet}H$) with target compound, which is used by radiation chemists is briefly discussed. The competition kinetics method is well validated by taking ciprofloxacin, norfloxacin and bezafibrate as example compounds. The bimolecular rate constants of hydroxyl radical, hydrate electron and hydrogen atom has been calculated for example solute species (ciprofloxacin, norfloxacin and bezafibrate).

Keywords: competition kinetics, rate constants, norfloxacin, ciprofloxacin, bezafibrate
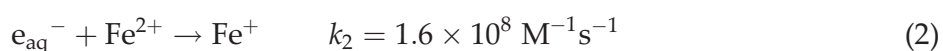
1. Introduction

Radiation chemistry involves extensive study of competition between fast reactions of transient species, reactive and intermediates. Such knowledge is useful to investigate the mechanism of a radiolytic reaction and to propose which process is taking place and which experimental condition is governing a reaction and to know the chemical kinetics of a radiolytic reaction under study.

Generally, in a chemical process, the reactant is converted to products in an individual step. However, in a radiation induced chemical reaction, all steps are taken into consideration including deposition of energy by a charged particle in the system and then formation of a final stable chemical product, and certainly will be a rather complex set of reactions [1]. In the following sections, we will briefly discuss the fast kinetics, i.e. competition kinetics to find the unknown rate constants of a compound with reactive species like hydroxyl radical ($^{\bullet}OH$) or hydrated electron (e_{aq}^{-}), by considering a reference compound whose rate constant with these reactive species is already known.

2. Competition kinetics

For detailed investigation of competing reactions, it is necessary to have a good knowledge about the rate constant data that will used to propose which reaction is predominant. For instance, the Fricke dosimeter contains three main active species (350 mol m^{-3} H$^+$, 1 mol m^{-3} Fe^{2+} and 0.25 mol m^{-3} O$_2$) that have very high rate constants with e$_{aq}^-$ and to find out the reaction mechanism involved in the dosimetry, it is necessary to investigate which solute(s) will mainly react with e$_{aq}^-$.

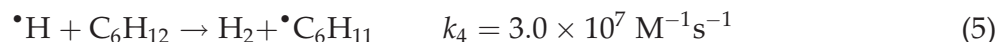The reactions and their corresponding rate constants are given as [1–3]:

$$e_{aq}^- + H^+ \rightarrow H \qquad k_1 = 2.3 \times 10^{10} \ M^{-1}s^{-1} \qquad (1)$$

$$e_{aq}^- + Fe^{2+} \rightarrow Fe^+ \qquad k_2 = 1.6 \times 10^8 \ M^{-1}s^{-1} \qquad (2)$$

$$e_{aq}^- + O_2 \rightarrow O_2^- \qquad k_3 = 1.9 \times 10^{10} \ M^{-1}s^{-1} \qquad (3)$$

The extent of reaction is proportional to the product k[solute] for each of the three solutes, that is,

$$e_{aq}^- + H^+: e_{aq}^- + Fe^{2+}: e_{aq}^- + O_2 = k_1[H^+] : k_2[Fe^{2+}] : k_3[O_2] = 5 \times 10^4 : 1 : 30 \qquad (4)$$

Alternatively, it can also be concluded that 99.94% of the hydrated electrons reacting with the three solutes will react with H$^+$, so under such conditions the reaction of e$_{aq}^-$ with Fe^{2+} and O$_2$ will be ignored. Therefore, it is compulsory to have an wide collection of rate constant data to apply kinetics for a radiation induced chemical reaction.

In Fricke dosimeter, hydrogen ions are considered as strong scavengers of hydrated electrons [4–6]. The effectiveness of a chemical scavenger depends upon the product k[scavenger] that must have a higher value than k[substrate]. For example, *tert*-butanol is used to scavenge hydroxyl radicals and by using concentration of 1 mol m^{-3} *tert*-butanol it has k[tert-butanol] = 6.0×10^5 s^{-1}. Therefore, *tert*-butanol would be an efficient scavenger for hydroxyl radical (can scavenger over 99% of the hydroxyl radical), if k[solute] for the reaction of hydroxyl radical with the solute is less than 6.0×10^5 s^{-1} [7]. Similarly, oxygen is used to scavenge hydrated electrons and hydrogen atoms from aqueous media [5, 8, 9] and for both the radical (e$_{aq}^-$ and •H) in air-saturated media, k[O$_2$] = 5×10^6 s^{-1}, so that oxygen can be expected to interfere in the radiolysis of aqueous media if k[solute] for the reactions of hydrogen atoms and hydrated electrons with the solute are of the same order as, or less than, 5×10^6 s^{-1}.

In case of radiolysis of organic species, their products also itself often act as scavengers and it is commonly found that the product yield is not in direct relation with the absorbed dose. To estimate the possible reasons of such effects, competition kinetics can be employed in an effective way if the radiolysis mechanism is known and the necessary rate constants are available. For example, cyclohexene is produced when cyclohexane is irradiated and both cyclohexene and cyclohexane have appreciable rate constants with hydrogen atoms, one of the radical specie produced during gamma radiolysis of aqueous media. The reactions are summarized below as:

$$\bullet H + C_6H_{12} \rightarrow H_2 + \bullet C_6H_{11} \qquad k_4 = 3.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1} \tag{5}$$

$$\bullet H + C_6H_{10} \rightarrow \bullet C_6H_{11} \qquad k_5 = 3.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1} \tag{6}$$

Under such conditions, the hydrogen atoms will be reacting equally with cyclohexane and cyclohexene when k_4 [cyclohexane] = k_5[cyclohexene] or in other words we can say that only when 1% of the cyclohexane has been converted to cyclohexene.

Furthermore, competition kinetics is also employed when measuring rate constants by pulse radiolysis using a reference compound.

2.1. Computation of bimolecular rate constant of $\bullet$OH with ciprofloxacin

Ciprofloxacin (CIP) belongs to a class of fluoroquinolone family and is used globally as a human and veterinary medication [10]. It has been very much concentrated that the event of these wide range antibiotics in the water bodies may position genuine dangers to the environment and human wellbeing by producing expansion of bacterial medication inactivation. The natural event of these fluoroquinolones anti-infection agents in numerous nations, similar to Switzerland, Australia and China have been affirmed in recent literature [10–13]. It has likewise been watched that most quinolone antibiotics are not completely utilized in the human body and accordingly are discharged and acquainted with the amphibian condition through wastewater sewages because of poor execution of ordinary water treatment plants [12, 14–16] bringing about adversative impacts to sea-going microorganisms and fish [17, 18]. Thus, it becomes necessary to advice alternative physiochemical techniques for effective removal of these contaminants and diminish their ecological effects [12, 19]. For this reason, the deterioration of ciprofloxacin (CIP) in water utilizing ionizing radiations was evaluated to examine the rate constant of $\bullet$OH with CIP. The degradation curves of CIP by gamma irradiation at various absorbed doses has been shown by **Figure 1**.

For computation of bimolecular rate constant of $\bullet$OH with CIP by competition kinetics, phenol was selected as reference compound that has second order rate constant of $6.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ with $\bullet$OH [20]. The sample solution of total 150 mL having CIP and reference compound phenol together in equivalent quantity was immersed with oxygen gas to change over e_{aq}^- and $\bullet$H to superoxide radical anions quickly [21], which are less responsive compared to $\bullet$OH.

$$CIP + \bullet OH \xrightarrow{k_{CIP}} \text{Products} \tag{7}$$

$$Phenol + \bullet OH \xrightarrow{k_{phenol}} \text{Products} \tag{8}$$

While, the notations, k_{CIP} and k_{phenol} denotes the bimolecular rate constants of $\bullet$OH with CIP and phenol, respectively. Keeping the condition that the dose rate (DR) was kept constant, the rate of decay of CIP is directly related to the rate constant and the concentration of $\bullet$OH [21]:

So,

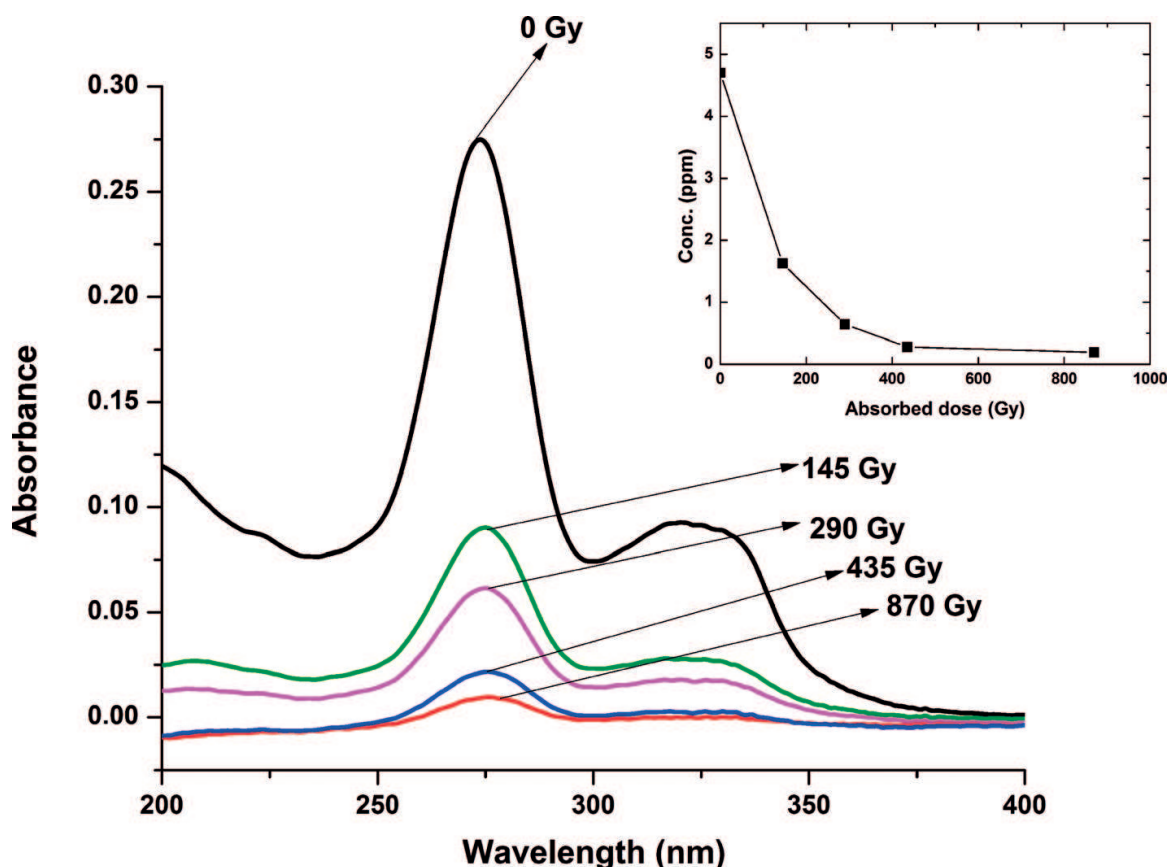$$-\frac{d[CIP]}{dD} = -\frac{1}{DR}\frac{d[CIP]}{dt} \tag{9}$$

Figure 1. The UV spectra of CIP solution observed by gamma irradiation at various absorbed doses ranging from 0 to 870 Gy. Inset shows the influence of gamma-irradiation on degradation of 4.6 mg L^{-1} of CIP solution [8].

Or,

$$-\frac{d}{dD}[CIP] = -\frac{1}{DR}k_{CIP}[CIP][^{\bullet}OH] \tag{10}$$

Similarly,

$$-\frac{d}{dD}[Phenol] = -\frac{1}{DR}k_{phenol}[Phenol][^{\bullet}OH] \tag{11}$$

While the absorbed ionizing dose and the total time for which irradiation was performed, are represented by "D" and "t," respectively. Subsequently, the original concentrations of both CIP and phenol are same. Therefore, the rate of decay of CIP to phenol would be equal to the ratio of their individual rate constants as follows [8]:

$$\frac{-\frac{d}{dD}[CIP]}{-\frac{d}{dD}[phenol]} = \frac{k_{CIP}}{k_{phenol}} \tag{12}$$

Or,

$$\ln\frac{[CIP]_D}{[CIP]_0} = \frac{k_{CIP}}{k_{phenol}}\ln\frac{[phenol]_D}{[phenol]_0} \tag{13}$$

In Eq. (13), at time 0, the concentration of CIP and phenol are represented by $[CIP]_0$ and $[Phenol]_0$, respectively; while after absorbed dose "D" of gamma irradiation, the corresponding concentration of CIP and phenol are represented by $[CIP]_D$ and $[Phenol]_D$, respectively.

When a straight line is plotted by taking $\ln \dfrac{[CIP]_D}{[CIP]_0}$ vs $\ln \dfrac{[Phenol]_D}{[Phenol]_0}$ a slope with $k_{CIP}/k_{Phenol} = 0.4012$ was obtained, so we have;

$$0.4012 = \frac{k_{CIP}}{k_{Phenol}} \tag{14}$$

Or,

$$k_{CIP} = 2.64 \times 10^9 \, M^{-1} s^{-1}. \tag{15}$$

Henceforth, the bimolecular rate constant of $^{\bullet}OH$ with CIP was calculated to be $2.75 \times 10^9 \, M^{-1} \, s^{-1}$. Dodd et al. [22] likewise ascertained apparent second order rate constant of with $^{\bullet}OH$-radical with CIP to be $4.1 (\pm 0.3) \times 10^9 \, M^{-1} \, s^{-1}$, which is somewhat higher than the esteem calculated in the current report [8].

2.2. Computation of $^{\bullet}OH$, e_{aq}^- and $^{\bullet}H$ with norfloxacin

Norfloxacin (NORO) may be called likewise chemotherapeutic antibacterial agent, furthermore is regularly utilized to medicine for urinary tract infections [23]. Its occurrence in surface water and wastewater overflows has been accounted for at follow ppb levels [12, 14, 24–27]. Even though, the detected concentration of NORO is very low and normally ranges from ng L^{-1} to µg L^{-1} in water bodies and µg kg^{-1} to mg kg^{-1} in soils and sediments, still these fluoroquinolone family are categorized as "pseudopersistant" contaminants because of their continuous and regular discharge into the water bodies [28, 29]. González-Pleiter et al. [30] concentrated on those unique united toxicities from claiming norfloxacin, amoxicillin, erythromycin, levofloxacin, furthermore anti-microbial prescription toward two maritime organisms, i.e. Cyanobacterium Anabaena CPB 4337. Similarly as a goal existing being and the green alga *Pseudokirchneriella subcapitata* as a non-target existing continuously. They assigned norfloxacin on a chance to be a greater amount dangerous on cyanobacterium over green alga. Furthermore, norfloxacin alone and additionally its mixture for different antibiotics might stance genuine idle danger to oceanic environment.

The presence of NORO in the fresh water bodies indicate that traditional wastewater or water treatment techniques are not efficient to remove NORO from aquatic environment due to its aromatic nature and its occurrence cause thoughtful health associated problems by using contaminated drinking water [31–33]. Therefore, it becomes an issue of interest to remove NORO from the aquatic environment.

In a typical experiment for gamma radiolysis of NORO, the apparent bimolecular rate constant of $^{\bullet}OH$, e_{aq}^- and $^{\bullet}H$ with NORO was assessed, using competition kinetics.

The following Eq. (14) was employed to measure the bimolecular rate constant of $^{\bullet}OH$, e_{aq}^- and $^{\bullet}H$, which are the main species produced during gamma radiolysis of aqueous media [21].

$$k_{\bullet OH/NORO} = \frac{\ln\left([NORO]_0/[NORO]_D\right)}{\ln\left([2-CP]_0/[2-CP]_D\right)} k_{\bullet OH/2-CP} \qquad (16)$$

2-Chlorophenol (2-CP) was selected as reference compound which have recognized rate constants with $\bullet OH$, e_{aq}^- and $\bullet H$ ($k_{\bullet OH/2-CP} = 1.2 \times 10^{10}\,M^{-1}\,s^{-1}$, $k_{e_{aq}^-/2-CP} = 1.3 \times 10^9\,M^{-1}s^{-1}$, $k_{\bullet H/2-CP} = 1.5 \times 10^9\,M^{-1}\,s^{-1}$) [20]. To permit only $\bullet OH$ to react with NORO, and scavenge e_{aq}^- and $\bullet H$, O_2 saturated sample (O_2 changes e_{aq}^- and $\bullet H$ to superoxide radical anions, which are less responsive opposite to $\bullet OH$) [20] was applied for computing the bimolecular rate of $\bullet OH$ with NORO. In the same way, the bimolecular rate constant of e_{aq}^- with NORO ($ke_{aq}^-/$NORO) was calculated by N_2-puging the sample solution added with 0.1 M iso-propanol (iso-propanol is used to scavenges both $\bullet OH$ and $\bullet H$) [20]. Similarly, the computation of bimolecular constant of $\bullet H$ with NORO ($k_{\bullet H/NORO}$) was made by N_2 saturating the solution of 0.1 M $tert$-butanol ($tert$-butanol is used to scavenge $\bullet OH$) [20] at pH 2.2. Low pH was maintained to get high yield of $\bullet H$ through reaction of e_{aq}^- with ^+H [34].

A linear plot with slope equal to $k_{\bullet OH/NORO}/k_{\bullet OH/2-CP}$ was observed by plotting $\ln([NORO]_0/[NORO]_D)$ vs $\ln([2-CP]_0/[2-CP]_D)$ at several absorbed ionizing doses. The same calculation was implemented for measurement of bimolecular rate constant of e_{aq}^- and $\bullet H$ with NORO, respectively. Applying the obtained slope values, the second order rate constants of $\bullet OH$, e_{aq}^- and $\bullet H$ with NORO were computed to be $(8.81\pm0.03) \times 10^9\,M^{-1}\,s^{-1}$, $(9.54 \pm 0.16) \times 10^8\,M^{-1}\,s^{-1}$ and $(1.10 \pm 0.20) \times 10^9\,M^{-1}\,s^{-1}$, respectively [5], which also indicates that $k_{e_{aq}^-/NORO}$ is lesser to $k_{\bullet H/NORO}$, or in other words the reactivity of e_{aq}^- to NORO is less than the reactivity of $\bullet H$ with NORO. Thus, in the removal of NORO by ionizing irradiation $\bullet H$ is of immense importance. The bimolecular rate constant of $\bullet OH$ with NORO in the current report is analogous with the study of Santoke et al. [35], in which they calculated the bimolecular rate constants of $\bullet OH$ with six common fluoroquinolones (orbifloxacin, flumequine, marbofloxacin, danofloxacin, enrofloxacin and model compound, 6-fluoro-4-oxo-1,4-dihydro-3-quinolone carboxylic acids) and was found to be in the range of $6.4 – 9.03 \times 10^9\,M^{-1}\,s^{-1}$.

2.3. Measurement of bimolecular rate constant of $\bullet OH$ with bezafibrate

Bezafibrate (BZF) is also the most commonly detected pollutant among various pharmaceuticals excreted into the sewage system and is categorized as persistent organic pollutants [36]. In drinking water its concentration has been noticed at the levels of 27 ng L^{-1} [37] in rivers at the concentrations level of 0.1–0.15 μg L^{-1} [37], in small streams in the range of 0.5–1.9 μg L^{-1} [37], in surface waters in the range of 3.1 μg L^{-1} [38], and up to 4.6 μg L^{-1} level in sewage treatment plant effluents. Owing to its high use and persistence nature, the elimination of BZF from aqueous media has emerged as a hot research topic. The qualitative and quantitative analysis of its degradation products besides its degradation kinetics is also of great concern. Keeping in view all these problems, the degradation of BZF was investigated by photo catalysis using hydrothermally synthesized TiO_2/Ti films with exposed {001} facets. Besides photo catalysis, there are other many advanced treatment options for efficient removal of BZF from aqueous media, such as nanofiltration techniques, ultraviolet (UV) radiation and advanced oxidation processes (AOPs) [39] and these have been thoroughly studied. In AOPs (the most reliable and efficient technique), as compared to other treatment techniques the pollutant of interest is

converted in to more stable, harmless inorganic species such as carbon dioxide, water and mineral salts. AOPs are categorized as ozonation (O_3), H_2O_2, O_3/H_2O_2/photocatalysis, and O_3/H_2O_2/UV photocatalysis [39, 40]. TiO_2 photocatalysis is considered as more auspicious and efficient technique among semiconductor photocatalysis [41, 42]. TiO_2 photo active material has shown a great potential in many applications, including water splitting to generate O_2 and H_2 [43, 44] water and wastewater treatment [45, 46], gas phase treatment [47, 48], as well as in solar cells [49]. So, in this case the degradation of BZF was performed by VUV photo active material with exposed {001} faceted TiO_2/Ti material.

For measurement of absolute bimolecular rate constant of •OH with BZF, *para*-chlorobenzoic acid (*p*-CBA) was used as probe molecule was calculated using *para*-chlorobenzoic acid (*p*-CBA) as probe molecule and by employing competition kinetics technique established by Pereira et al. [50] and given in Eq. (15).

$$k_{\bullet OH(s)} = \frac{k_{s(UV/H_2O_2)} - k_{s(UV)}}{k_{ref(UV/H_2O_2)} - k_{ref}} \times k_{\bullet OH(ref)} \qquad (17)$$

Where, $k_{\bullet OH}$, $k_{(UV/H_2O_2)}$ and $k_{(UV)}$ represent the second order rate constant of hydroxyl radical, UV/H_2O_2, fluence based rate constant of UV/hydrogen peroxide process and UV, fluence based rate constant of direct photolysis, respectively. The notations "s" and "ref" represents the substrate and reference compounds, which in our case is BZF and *p*-CBA, respectively. For the determination of •OH rate constant with BZF, two sets of experiments were performed. In one set of experiments, the solution containing 27.63 μM of BZF, 27.63 μM of *p*-CBA and 1 mM
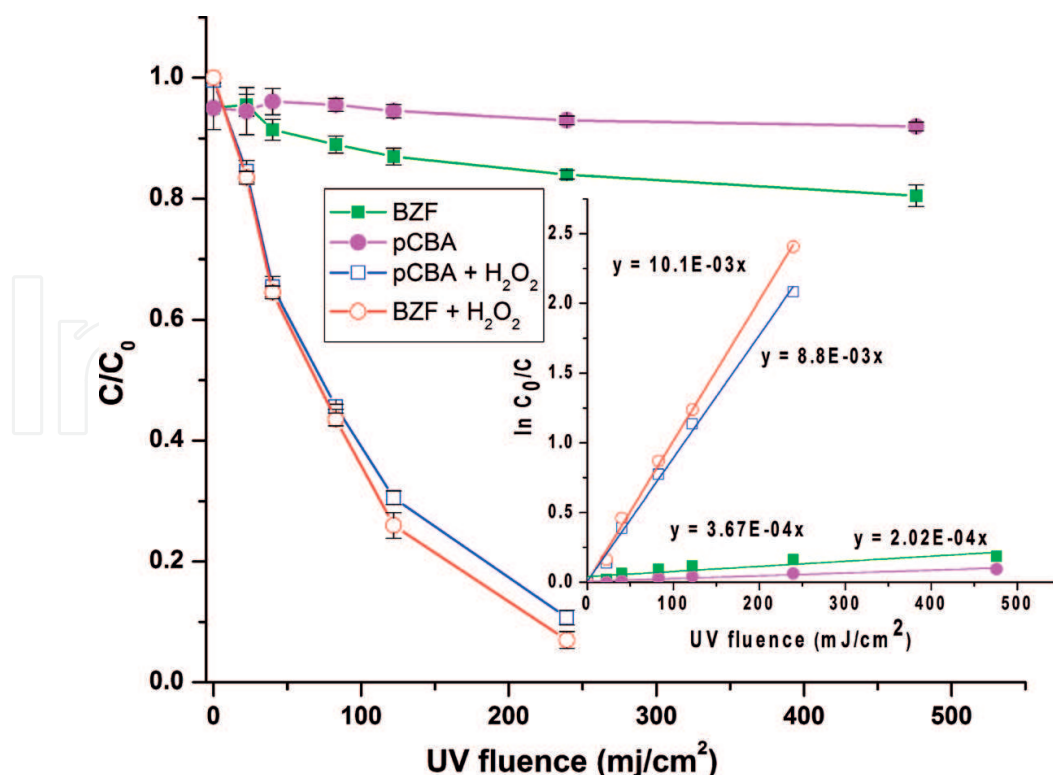

Figure 2. Determination of bimolecular rate constant of BZF with •OH; inset shows the degradation kinetics of BZF alone, p-CBA alone, BZF+ H_2O_2, pCBA + H_2O_2 exposed to UV-irradiation.

of H_2O_2 was exposed to UV irradiation, while another set of experiments was free of H_2O_2 to calculate k_{UV}. The concentration of H_2O_2 was kept higher for ensuring production of efficient $^\bullet$OH with UV-photocatalysis.

Figure 2 shows degradation curves for BZF and p-CBA, both BZF and p-CBA were found to follow pseudo-first order degradation kinetics. The second order rate constant of $^\bullet$OH with p-CBA is $5.0 \times 10^9 \, M^{-1} \, s^{-1}$ [20]. By substituting pseudo-first order degradation constants (k_{UV/H_2O_2} and k_{UV}) values in Eq. (15), the bimolecular rate constant of $^\bullet$OH with BZF was calculated and found out to be $5.66 \times 10^9 \, M^{-1} \, s^{-1}$.

3. Conclusions

The overall conclusion of this chapter is that, in radiation chemistry to have a good knowledge about the mechanism of a reaction mechanism it is necessary that one must have sufficient understanding about the free radical kinetics. In addition, competition kinetics model can be successful applied for the determination of unknown rate constants of reactive species with solute molecule. The competition kinetics can not only be applied for $^\bullet$OH rate constants with the solute but also for measurement of e_{aq}^- and $^\bullet$H with the target species. The competition kinetics method is validated by taking ciprofloxacin, norfloxacin and bezafibrate as example compounds. However, it should be make sure that competing reactions do not disobey the kinetics rules.

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