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Quantifying co-consumption of dissolved oxygen during photochemical transformation of phenols

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Kurzfassung

Photochemische Reaktionen spielen eine wichtige Rolle beim Abbau von organischen Schadstoffen in Oberflächengewässern. Diese Studie untersuchte die Zehrung von gelöstem Sauerstoff (O_2) während der photochemischen Reaktion von drei Phenolen mit Singulett-Sauerstoff ($^1O_2$) und Hydroxylradikalen (•OH). Die drei untersuchten Phenolverbindungen waren das Schmerzmittel Acetaminophen, die Aminosäure L-Tyrosin und eine Modellverbindung für natürliches organisches Material (2-Hydroxy-1,4-naphthochinon). Es wurden Experimente mit Bengalrose als Sensibilisator für Singulett-Sauerstoff bei zwei verschiedenen pH Werten und Fenton-Reaktionen für die Erzeugung von Hydroxylradikalen mit verschiedenen H_2O_2-Konzentrationen durchgeführt. Die Ergebnisse zeigen, dass die Verhältnisse von Sauerstoff- und Phenolverbrauch bei Experimenten mit Singulett-Sauerstoff grösser als 1 waren, was darauf hindeutet, dass diese reaktive Spezies nicht nur mit den Ausgangsverbindungen, sondern auch mit den Reaktionsprodukten reagiert. Im Gegensatz dazu wurden bei Experimenten mit Hydroxylradikalen Verhältnisse von Sauerstoff- und Phenolverbrauch von ungefähr 1 beobachtet. Dies zeigt, dass in diesen Experimenten der Abbau von Phenolen unabhängig von gelöstem Sauerstoff erfolgen kann. Diese Studie trägt zum Verständnis der Bedeutung von gelöstem Sauerstoff bei photochemischen Prozessen mit Beteiligung von Phenolen bei.

Abstract

Photochemical transformations play an important role in the degradation of organic contaminants in sunlit surface waters. This study investigated the co-consumption of dissolved oxygen (O_2) during the photochemical transformation of phenols involving singlet oxygen ($^1O_2$), and hydroxyl radical (•OH). Three phenolic compounds were selected for this study: a painkiller drug (acetaminophen), an amino acid (L-tyrosine), and a model natural organic matter compound (2-hydroxy-1,4-napthoquinone). Experiments were performed with rose bengal as a sensitizer for singlet oxygen at two different pH values and with Fenton reactions to generate hydroxyl radicals at different H_2O_2 concentrations. The results show that the ratios of dissolved oxygen and phenol consumption were greater than 1 for experiments with singlet oxygen, indicating that this reactive species not only reacts with the parent compounds, but also with the reaction products. In contrast, ratios of dissolved oxygen and phenol consumption for hydroxyl radical experiments were close to 1, showing that the degradation of phenols can occur independently of dissolved oxygen. This study contributes to understanding the importance of dissolved oxygen in photochemical processes involving phenols, which is not commonly investigated.

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List of Abbreviations

ACE - Acetaminophen

CDOM - Chromophoric dissolved organic matter

$^{3}CDOM^{*}$ - Triplet excited-state chromophoric dissolved organic matter

HNQ - 2-Hydroxy-1,4-napthoquinone

H_2O_2 - Hydrogen peroxide

•OH - Hydroxyl radical

$O_2^{\bullet -}$ - Superoxide anion

$^{1}O_2$ - Singlet oxygen

RB - Rose bengal

TYR - L-tyrosine

1 Introduction

Organic contaminants are carbon-based chemicals introduced to the environment through human activities. Pharmaceuticals and personal care products [1], industrial solvents (e.g., ionic liquids) [2], and pesticide [3] are commonly found in surface waters near wastewater treatment plant outlets and agricultural sites. Organic contaminants are a problem because they can persist in the environment for a long period of time, bioaccumulate in food chains, and negatively impact both human health and ecosystem functions. For example, polycyclic aromatic hydrocarbons, toluene, and chlorobenzene have been shown to be related to an increased risk in cancer, reproductive difficulties, as well as damage to the nervous system, liver, or kidney [4]. After entering the environment, organic contaminants can undergo various physical, biological, and chemical processes, including photochemical transformation in surface waters [5, 6]. Transformation products of drugs like metformin, ranitidine, diltiazem, and acetaminophen are not only found to have higher concentrations than their parent compounds, but may also exhibit higher toxicity [7].

Photochemical processes play an important role in atmospheric and aquatic environments because they result in the transformation of both natural organic matter and anthropogenic organic contaminants via either direct or indirect photolysis [8, 9]. Photochemical processes are chemical transformations initiated by the absorption of photons, through which a reactant molecule becomes electronically excited and can then undergo a chemical transformation to photochemical products. During direct photolysis, a compound is transformed after it absorbs light in the solar spectrum (290-600 nm). Direct photolysis mechanisms include photoionization and bond breaking. The latter can proceed through electronically excited singlet or triplet states [10]. During indirect photolysis, photosensitizers such as chromophoric dissolved organic matter (CDOM), nitrate, nitrite, or transition metals absorb sunlight. The excited state species of these compounds then undergo reactions that lead to the formation of reactive intermediates, including superoxide ($O_2^{\bullet-}$), singlet oxygen ($^1O_2$), and hydroxyl radical (•OH) [11], which subsequently react with organic compounds in surface water [12]. Photochemical processes are important for the overall degradation and transformation of organic contaminants, especially if they are not easily biodegradable [9]. For example, the direct photolysis quantum yield for the dehalogenation of 4-chlorophenol in neutral aqueous solution can reach a high value of 0.68 [13]. Furthermore, indirect photolysis can significantly enhance the transformation rates of organic compounds. In the presence of 20 mg L^{-1} fulvic acid, the half-life of 17α-ethinylestradiol and 17β-estradiol in freshwater changed from 46 hours and 94 hours to 2.1 hours and 2.9 hours, respectively [14].

2 State of knowledge

2.1 Phenols

Phenols are a group of organic compounds that contain a hydroxy functional group attached to an aromatic ring. It is an important structure for both organic contaminants and natural organic matter. Phenols are widely used in many fields of chemical industry, including the manufacture of plastics, drugs, explosives, detergents, pesticides, and herbicides. etc [3, 15, 16]. They play a significant role as photooxidants that inhibit the oxidative degradation of organic materials, including biological aerobic organisms and commercial products [17]. Phenols react with oxidizing agents to form free radicals, which could contribute to the formation of diphenols or undergo further oxidation to form dihydroxybenzenes and quinones [17]. Phenol radicals are relatively stable, therefore, they can act as an effective radical scavenger and can also slow down the oxidation processes of organic contaminants [17].

The appearance of phenols in the environment is unavoidable due to their widespread use. Industrial effluent that contains mostly phenols or phenolic compounds is quite resistant to biological decomposition due to the stability of the benzene ring [18]. Because of their persistence, phenolic compounds can accumulate in tissues and be transported within living organisms and humans, before being excreted via body metabolic pathway [19]. Phenol exposure can disrupt the metabolic system of microorganisms, animals, and humans [19]. Especially in aquatic environments, the high solubility of phenols allows them to be introduced easily to the water system [20]. In sunlight-irradiated aquatic environments, the degradation of phenol occurs through both direct [21] and indirect photolysis, but mostly through reactions with photochemically produced intermediates (i.e., singlet oxygen, hydroxyl radical) [22, 23]. The influence of pH is critical because it affects the phenols' dissociation, chemical reactivity, and interactions with reactive oxygen species such as singlet oxygen. At acidic pH, phenols predominantly exist in their neutral or protonated forms (Ar-OH), and when the pH increases beyond the compound's pK_a, phenols undergo deprotonation to form phenolates (Ar-O-), which are much more reactive toward oxidation by singlet oxygen compared to their protonated forms [24]. Acetaminophen, L-tyrosine, and 2-hydroxyl-1,4-napthoquinone (HNQ) are the three phenols that were selected for this master's thesis.

Acetaminophen, also known as paracetamol, is the most commonly used analgesic worldwide, and is recommended as first-line therapy for all pain conditions [25]. It contains a hydroxy group with a pK_a of 9.5 [26] and an amide group, both attach to the benzene ring.

Acetaminophen is considered an emerging pollutant, and it was reported that up to 68% of acetaminophen is emitted by human urine [27]. Excreted acetaminophen will thus end up in wastewater and, if not treated properly, in surface water and can bioaccumulate in aquatic organisms [27]. Therefore, research on the fate and treatment methods of acetaminophen in the aquatic environment is very necessary and urgent, as the amount of use is increasing [26].

L-tyrosine is an aromatic amino acid that plays an important role in biological systems and industrial applications [28]. Natural tyrosine is derived from the metabolism of humans and animals [28]. However, in recent years, with the development of science and technology, tyrosine is considered as an important precursor in the production of valuable products such as supplements or medicines [28]. L-tyrosine has three functional groups: a phenol, an amine, and a carboxylic acid with pKa values of 10, 9.1, and 2.2, respectively [29].

HNQ, also known as lawsone, is the simplest form of natural occurring napthoquinone with red-orange pigment found in the leaves of henna plant [30]. It has been used for hair, skin, and nail coloring for centuries [31]. HNQ has also been used in various fields, such as pharmaceutical, cosmetic, cloth dyeing, and additives to vulcanized natural rubber [30, 31]. HNQ consists of a benzene ring fused with a quinone ring, to which a hydroxy group is bound. It has a pK_a value of 3.98 [32].

2.2 Oxygen and reactive oxygen species

2.2.1 Dissolved oxygen

The electronic ground-state of dissolved oxygen (O_2) is known as a primary oxidant, which accepts electrons during photochemical oxidation of organic compounds. Under sunlight irradiation, dissolved oxygen can be consumed, for example, through reactions with triplet-excited states of chromophoric dissolved organic matter ($^3CDOM^*$) [8]. O_2 plays a crucial role as a precursor for the formation of reactive oxygen species under sunlight irradiation, such as superoxide ($O_2^{\bullet -}$), singlet oxygen ($^1O_2$), and hydroxyl radicals (•OH).

2.2.2 Singlet oxygen

Singlet oxygen is a product of the energy transfer from $^3CDOM^*$ to dissolved oxygen in aquatic environments [33]. It is an important photooxidant for only a few numbers of organic compounds with certain functional groups, such as phenols [24].

In this study, rose bengal (RB) was used as a singlet oxygen sensitizer. Under visible light irradiation, RB absorbs a photon and undergoes intersystem crossing to an excited triple state ($^3RB^*$) [16]. $^3RB^*$ transfers energy to ground-state dissolved oxygen, producing singlet

oxygen. It is a more reactive form of dissolved oxygen [34], can react with phenols (Ar-OH) to oxidation products (eq.1). Overall, these reactions lead to the consumption of dissolved oxygen and phenols (i.e., acetaminophen, tyrosine, and HNQ).

$$RB + hv \rightarrow {}^3RB^* \xrightarrow{+O_2} RB + {}^1O_2 \xrightarrow{+Ar\text{-}OH} RB + products \quad \text{(eq.1)}$$

2.2.3 Hydroxyl radical (•OH)

Among reactive oxygen species, hydroxyl radical is the most reactive and can thus react rapidly with various organic compounds in water. In surface water, hydroxyl radicals are generated through two main pathways: Photochemical reactions of nitrate, nitrite, and CDOM [9, 35] and Fenton reactions between H_2O_2 and Fe^{2+} (see eq.2) [36]. The concentration of hydroxyl radicals in natural waters is usually very low, due to its very short half-life of only 10^{-9} s [37]. Therefore, assessing the impact of hydroxyl radicals on the photochemical transformation of organic compounds is also difficult. Hydroxyl radicals have the ability to decompose a wide range of natural organic matter and pollutants, contributing to the degradation of natural organic matter and pollutant concentrations in aquatic environments [38].

In this study, the Fenton reaction was conducted by the reaction of ferrous ion (Fe^{2+}) and hydrogen peroxide (H_2O_2), generating highly reactive hydroxyl radicals and ferric ions (Fe^{3+}) [36]. Subsequently, the hydroxyl radicals react with phenols (Ar-OH), leading to the formation of aryloxy radicals (Ar-O•) (see eq.3). The aryloxy radicals continue to react with dissolved oxygen to form products (see eq.4). While eq.4 shows the step that leads to the consumption of dissolved oxygen, eq.3 indicates that it directly results in the degradation of phenolic compounds.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^- \quad \text{(eq.2)}$$

$$\bullet OH + + Ar\text{-}OH \rightarrow Ar\text{-}O\bullet + H_2O \quad \text{(eq.3)}$$

$$Ar\text{-}O\bullet + O_2 \rightarrow Products \quad \text{(eq.4)}$$

3 Aims and Hypotheses

This thesis investigated the co-consumption of dissolved oxygen during the photochemical transformation of acetaminophen, L-tyrosine, and HNQ. Because the combination of dissolved oxygen and phenols is not commonly studied in photochemical research on contaminants, the primary aim of this study was to determine the ratios of dissolved oxygen and phenol consumption in experiments involving singlet oxygen and hydroxyl radicals.

Base on eqs. 1-4 shown in section 2.2, the following two hypotheses are proposed:

1. The ratio of consumed dissolved oxygen to phenol (O_2:phenol ratio) approaches 1 during photochemical degradation of phenols by singlet oxygen or hydroxyl radical.
2. Consumption rates of dissolved oxygen and phenols in experiments with singlet oxygen and acetaminophen or tyrosine increase with pH, while the rates in experiments with HNQ do not.

4 Materials and Methods

4.1 Chemicals

Acetaminophen (≥ 99%), L-tyrosine (≥ 99%), 2-hydroxy-1,4-napthoquinone (HNQ, 97%), rose bengal (95%), sodium sulfite (Na_2SO_3, ≥ 98%), hydrogen peroxide (H_2O_2, 30%), all from Sigma-Aldrich, as well as ammonium iron sulfate ($(NH_4)_2Fe(SO_4)_2$, ≥ 99%) from Merck were used as received. Ultrapure water produced with a PURELAB Chorus system (18.2 MΩ·cm, Elga Veolia), acetonitrile (HPLC grade, Fisher Scientific), sodium dihydrogen phosphate ($NaH_2PO_4 \cdot 2H_2O$, ≥ 99%, Acros Organics), disodium hydrogen phosphate (Na_2HPO_4 ,≥ 99%, Acros Organics), and amonium acetate (~5M in H_2O, Sigma-Aldrich) were used to make stock solutions, buffered solutions, and HPLC eluents. 10 mM hydrochloric acid (HCl, 32%, VWR) was used to make stock solutions of $(NH_4)_2Fe(SO_4)_2$ to slow down Fe^{2+} oxidation in ultrapure water.

4.2 Experimental setup

All glassware used in experiments with singlet oxygen or hydroxyl radicals was muffled at 550 °C for 5 hours after cleaning. Phosphate buffer solutions were prepared weekly by mixing 10 mM aqueous solutions of NaH_2PO_4 and Na_2HPO_4 until the desired pH was reached. Stock solutions of acetaminophen, tyrosine, HNQ, and RB were prepared weekly at a concentration of 1 mM in ultrapure water. Stock solutions of H_2O_2 (10 mM in ultrapure water) and $(NH_4)_2Fe(SO_4)_2$ (10 mM in diluted HCl) were prepared daily.

4.2.1 Experiments with singlet oxygen

Experiments to study the co-consumption of phenols and dissolved oxygen in the presence of singlet oxygen were conducted in completely filled 12-mL Exetainer vials (15.5 mm o.d., Labco Limited) sealed with screw caps and butyl rubber septa. For each experiment, seven vials were filled with 10 mM phosphate buffer at pH 7.0 or 8.4, 200 µM acetaminophen, tyrosine, or HNQ, and 1-10 µM RB. One vial was tightly wrapped in aluminum foil and used as a dark control. One additional vial, which had a temperature sensor spot glued to the

inside wall, was filled with phosphate buffer only. This vial served as a temperature control for dissolved oxygen measurement. Aluminum foil was wrapped around the vial where the temperature sensor was attached to limit light exposure of the sensor spot. Six out of seven vials along with the temperature control, were placed at an angle of approximately 35° in a solar simulator (Suntest CPS Atlas). After 15, 30, 60, 120, and 180 minutes of irradiation at a light intensity of 30 W m^{-2}, the concentration of dissolved oxygen was measured (see section 4.3.2) in one of the vials, which was subsequently opened to withdraw 0.5 mL into a 1-mL amber glass vial for HPLC analysis (see section 4.3.3). In the seventh vial, dissolved oxygen and phenol concentrations were measured without light exposure. Results from this vial were assumed to represent initial (t_0) concentrations. Control experiments without RB or without phenol were conducted occasionally. The experiments with acetaminophen and tyrosine were performed in duplicate at both pH levels, while experiments with HNQ were conducted in duplicate only at pH 7.0 and as a single replicate at pH 8.4.

Additional experiments were performed to quantify the second-order reaction rate constants of the three phenols with singlet oxygen. In these experiments, seven vials were completely filled with 10 mM phosphate buffer at pH 7.0 or 8.4, 100 µM of tyrosine together with 100 µM acetaminophen or HNQ, and 1-10 µM RB. One vial served as a dark control. All vials were irradiated in a solar simulator, and samples for HPLC analysis were taken as described above. Dissolved oxygen concentrations were not measured in these experiments.

Date evaluation including linear regression analysis was performed in Microsoft Excel. Errors reported for the slopes of linear regressions represent standard errors.

4.2.2 Experiments with hydroxyl radicals

Experiments to study the co-consumption of phenols and dissolved oxygen in the presence of hydroxyl radicals were conducted in eight completely filled 12 mL-Exetainer vials containing 200 µM acetaminophen, tyrosine, or HNQ and 0-750 µM H_2O_2 in ultrapure water. Experiments were performed in unbuffered solutions to avoid consumption of the generated hydroxyl radicals by buffer components. All vials were wrapped in aluminum foil to prevent light exposure. Subsequently, 60 µL of the $(NH_4)_2Fe(SO_4)_2$ stock solution was injected with a gas-tight glass syringe through the septum, and the solutions were vortexed for approximately 20 seconds. Two vials were used as controls, which contained only H_2O_2 but without $(NH_4)_2Fe(SO_4)_2$ or without both. After 120 minutes, the concentration of dissolved oxygen was measured in all vials (see section 4.3.2). For HPLC analysis (see section 4.3.3), all vials were opened. Samples were filtered with a 12-mL plastic syringe and a 2

µm polyamide filter (13 mm, Altmann Analytik). The first 5 mL was discarded, and 0.5 mL of the filtrate was transferred into amber glass vials. The experiments with acetaminophen were conducted in triplicate, while both tyrosine and HNQ were performed in duplicate.

4.3 Analyses

4.3.1 UV/vis photometry

To determine the absorption spectra of the three phenols investigated, a Lambda 35 UV/vis spectrometer (PerkinElmer) was used with a wavelength range from 200 to 800 nm. Solutions of acetaminophen, tyrosine, and HNQ were prepared at 100 µM in 5 mM phosphate buffer (pH 7.0) and measured in quartz glass cuvettes. Pure phosphate buffer was used as a blank, and correction of the measured wavelengths was performed with a holmium glass filter (Hellma Analytics). A spectral scan in the range of 200 nm to 800 nm showed a deviation between observed absorbance peaks and certified values of the holmium filter, which required a wavelength correction. Measured wavelengths were adjusted using a linear regression between observed and certified values.

4.3.2 Dissolved oxygen measurements

Dissolved oxygen concentrations were measured in closed Exetainer vials using a retractable fiber oxygen microsensor connected to a Firesting-Pro meter (Pyroscience) by piercing the septa of closed vials with the microsensor needle housing the fiber-optic sensor. After piercing the septa, the sensor tip was deployed to record the dissolved oxygen concentration and retracted before removal. The fiber-optic microsensor consists of a 230 µm optical fiber with an approx. 50 µm diameter sensor tip. The oxygen sensor was calibrated weekly with 300 mM Na_2SO_3 and daily with 100% air-saturated water for minimum and maximum dissolved oxygen concentration, respectively. In experiments, temperature compensation of the dissolved oxygen concentration measurements was performed with adhesive optical temperature sensor spots (5 mm diameter, Pyroscience), which were glued to the inside wall of the temperature control vial. The temperature sensor spots were calibrated daily with a teflon-coated temperature sensor (Pyroscience).

4.3.3 High-performance liquid chromatography (HPLC) analysis

The concentrations of the three phenols were determined by high-performance liquid chromatography (HPLC) on an Agilent 1260 Infinity II system with a wavelength detector set to 245 nm for acetaminophen, 225 nm for tyrosine, and 268 nm for HNQ. For all analyses, an Eclipse XBD-C18 column (4.6 x 250 nm, 5 µm, Agilent) was used with an isocratic mixture of ultrapure water (containing 5mM ammonium acetate) and acetonitrile

at a flow rate of 1 mL min^{-1}. Acetaminophen, tyrosine, and HNQ were measured at 10%, 5% and 15% acetonitrile, respectively. Injection volumes were set to 10 µL. For HPLC analysis, stock solutions of acetaminophen and HNQ were prepared at a concentration of 5 mM in acetonitrile, while tyrosine stock solutions were prepared at a concentration of 1 mM in ultrapure water. All the stock solutions were prepared weekly. Measurements were performed along with a 5-point calibration curve ranging from 50 to 250 µM. The resulting compound peaks were manually integrated.

5 Results and Discussion

5.1 UV-Vis absorption of phenols

UV-Vis photometry was performed with the three phenols to identify their wavelengths of maximum absorption for HPLC analysis. Acetaminophen exhibited two absorption peaks at 199 nm and 245 nm; tyrosine displayed three peaks at 196 nm, 225 nm, and 274 nm, while HNQ had peaks at 215 nm, 268 nm, and 452 nm. The wavelengths of maximal absorption were 199 nm for acetaminophen, 196 nm for tyrosine, and 268 nm for HNQ. Thus, 268 nm was used for HPLC analysis of HNQ. However, for acetaminophen and tyrosine, their maximal absorption wavelengths were below 200 nm, which often causes noisy HPLC baselines. Therefore, 245 nm and 225 nm were chosen instead for HPLC analysis of acetaminophen and tyrosine, respectively.

5.2 Second-order reaction rate constants with singlet oxygen

To determine the second-order reaction rate constants between phenols and singlet oxygen, a competition kinetic approach was used. This experimental approach was conducted by combining two phenols with RB in phosphate buffer. The results were used to compare the reaction rate of a compound with unknown reactivity to a compound with known reactivity. The natural logarithm of the normalized tyrosine concentration $\ln\left(\frac{[tyrosine]}{[tyrosine_0]}\right)$ was plotted on the x-axis as a reference compound, while the natural logarithm of the normalized acetaminophen concentration $\ln\left(\frac{[acetaminophen]}{[acetaminophen_0]}\right)$ or HNQ concentration $\ln\left(\frac{[HNQ]}{[HNQ_0]}\right)$ was plotted on the y-axis (Figure 1).

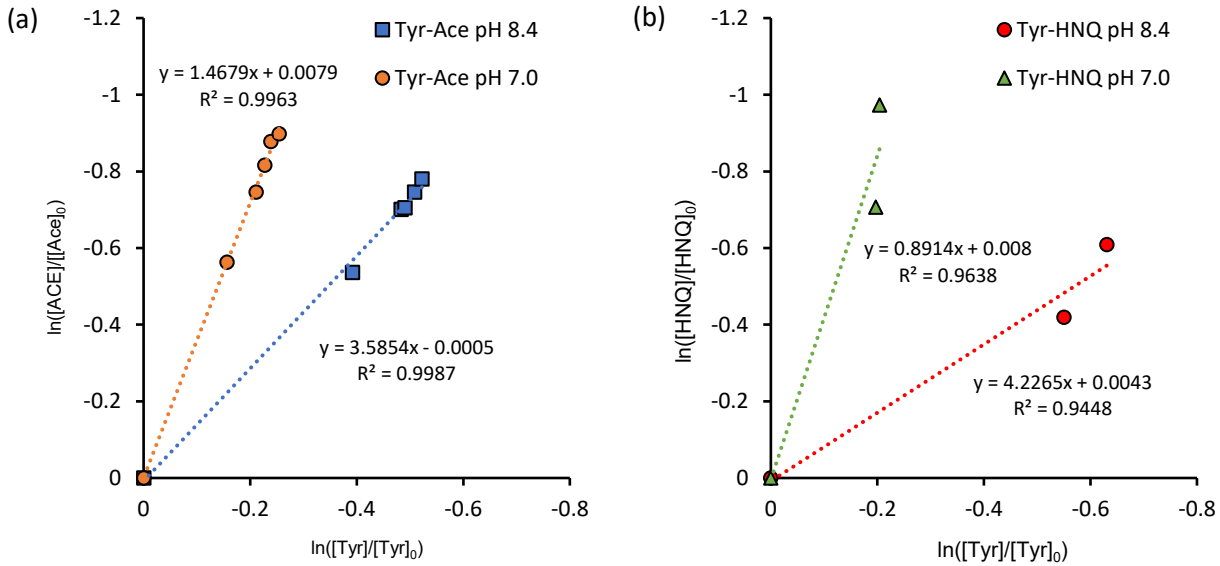

***Figure 1**: (a) Linear relationship between natural logarithms of normalized concentration of tyrosine and acetaminophen reacting with singlet oxygen. Experiments were conducted at pH 8.4 (blue squares) and pH 7.0 (orange circles). (b) Linear relationship between natural logarithms of normalized concentration of tyrosine and HNQ reacting with singlet oxygen. Experiments were conducted at pH 8.4 (red circles) and pH 7.0 (green triangles).*

The second-order reaction rate constant between tyrosine and singlet oxygen at pH 8.4 was previously determined to be $8.0 \times 10^6\ M^{-1}s^{-1}$[39] and used here as a reference to calculate second-order reaction rate constants of tyrosine and HNQ at the same pH using eq.5.

$$k_{1O2\_phenol} = slope \times\ k_{1O2\_tyrosine} \qquad \text{(eq.5)}$$

For example, to calculate the second-order reaction rate constant between acetaminophen and singlet oxygen at pH 8.4, an experiment was conducted in 10 mM phosphate buffer at pH 8.4 with 100 μM of each tyrosine and acetaminophen and 2 μM of RB. After different irradiation times, the concentrations of both tyrosine and acetaminophen were measured, and their natural logarithms of normalized concentrations were plotted as shown in Figure 1(a). From the slope of the linear regression, which is the ratio of second-order reaction rate constants of acetaminophen vs. tyrosine with singlet oxygen, the second-order reaction rate constant of acetaminophen with singlet oxygen at pH 8.4 was calculated as $(11.7 \pm 0.04) \times 10^6\ M^{-1}s^{-1}$. A similar experiment was performed with 100 μM of each tyrosine and HNQ but with only 1 μM of RB. However, due to the minimal change in tyrosine concentration after the first 30 minutes of irradiation, linear regressions between tyrosine

and HNQ were only based on the first three time-points. According to the results shown in Figure 1(b), the second-order reaction rate constant of HNQ with singlet oxygen at pH 8.4 was $(7.13 \pm 0.17) \times 10^6\ M^{-1}s^{-1}$.

For pH 7.0, there was no second-order reaction rate constant available as a reference, thus only the ratios of reaction rates between two phenols were calculated. The results from experiments at pH 7.0 in Figure 1 and Figure 2 show that acetaminophen reacted with singlet oxygen 3.6 times faster than tyrosine, while HNQ reacted 4.2 times faster than tyrosine.

5.3 Co-consumption of dissolved oxygen and phenols during reactions with singlet oxygen

Experiments were performed in 10 mM phosphate buffer at pH 7.0 with 200 μM acetaminophen and 10 μM RB. One vial was tightly wrapped in aluminum foil and used as a dark control. Additional controls were conducted occasionally, with one vial containing only acetaminophen in buffer. During 180 minutes of solar light irradiation, the concentrations of dissolved oxygen and acetaminophen decreased by 229 μM and 76 μM, respectively (see Figure 2a and 2b). During the first 30 minutes of the experiment, dissolved oxygen consumption followed pseudo-first-order kinetics (see Figure 3a) with a rate constant of 0.0249 min^{-1} (see Table 1). On the other hand, the concentration decrease of acetaminophen did not follow pseudo-first-order kinetics (see Figure 3b), and no further change in concentration was observed after 60 minutes of irradiation. A similar experiment was performed at pH 8.4, but with a reduced concentration of RB (2 μM). While acetaminophen concentrations also only decreased by 50 μM during the first 60 minutes (see Figure 2b), initial oxygen consumption at pH 8.4 was 1.56 times slower compared to pH 7.0 (see Figure 2a). Phenolic compounds tend to react faster with singlet oxygen at higher pH because deprotonated phenols react faster with singlet oxygen than their protonated form [40], leading to the faster decrease in phenol and oxygen concentration at higher pH. However, both dissolved oxygen and acetaminophen concentrations were consumed slower at pH 8.4 than at pH 7.0 because of the reduction in RB concentration, resulting in a lower singlet oxygen steady state concentration.

***Table 1**: Second-order reaction rate constants of the three phenols with singlet oxygen and initial pseudo-first-order reaction rate constants of O_2 consumption at pH 7.0 and 8.4. Calculations were based on data presented in Figures 1 and 3, and assumed the reaction rates of HNQ were the same at both pH. *Note that the second-order reaction rate constant of tyrosine with singlet oxygen at pH 8.4 was based on Mattheson et al. [39]*

Compounds	*pH*	*Second-order reaction rate constant (10^6 $M^{-1}s^{-1}$)*	*Initial pseudo-first-order rate constant of O_2 consumption (min^{-1})*
Acetaminophen	7.0	5.7 ± 0.05	0.0249 ± 0.0004
	8.4	11.7 ± 0.04	0.016 ± 0.0024
Tyrosine	7.0	1.6 ± 0.05	0.0231 ± 0.0017
	8.4	8*	0.0457 ± 0.0067
HNQ	7.0	7.1 ± 0.17	0.0263 ± 0.0055
	8.4	7.1 ± 0.17	0.0298 ± 0.0053

To assess the reactivity of tyrosine with singlet oxygen and compare it to other phenols, similar experiments were conducted, with 200 μM tyrosine instead of acetaminophen. Similar to acetaminophen, the decrease of dissolved oxygen also followed pseudo-first-order kinetics for the first 30 minutes of experiments (see Figure 3c), and the consumption of HNQ did not follow pseudo-first-order kinetics (see Figure 3d). Tyrosine had 3.6 and 1.5 times lower second-order reaction rate constants with singlet oxygen at pH 7.0 and 8.4, respectively (see Table 1). This trend was not reflected in the initial pseudo-first-order rate constants of dissolved oxygen consumption, which were almost identical at pH 7.0 and 2.9 times faster with tyrosine than with acetaminophen at pH 8.4. The total amount of dissolved oxygen and tyrosine consumed was higher at pH 8.4 than at pH 7.0 (see Figures 2c and 2d) and higher than in experiments with acetaminophen. The total consumption amount of dissolved oxygen and tyrosine also showed a large difference (249 μM and 92 μM) from that of acetaminophen (112 μM and 50 μM) at pH 8.4 (see Figures 2a, 2b, 2c, 2d). The consumption of acetaminophen and tyrosine in experiments suggests that products of acetaminophen appear to be more reactive and thus compete for singlet oxygen than products of tyrosine. However, this only explains the difference in phenol loss, while the difference in dissolved oxygen consumption is unclear.

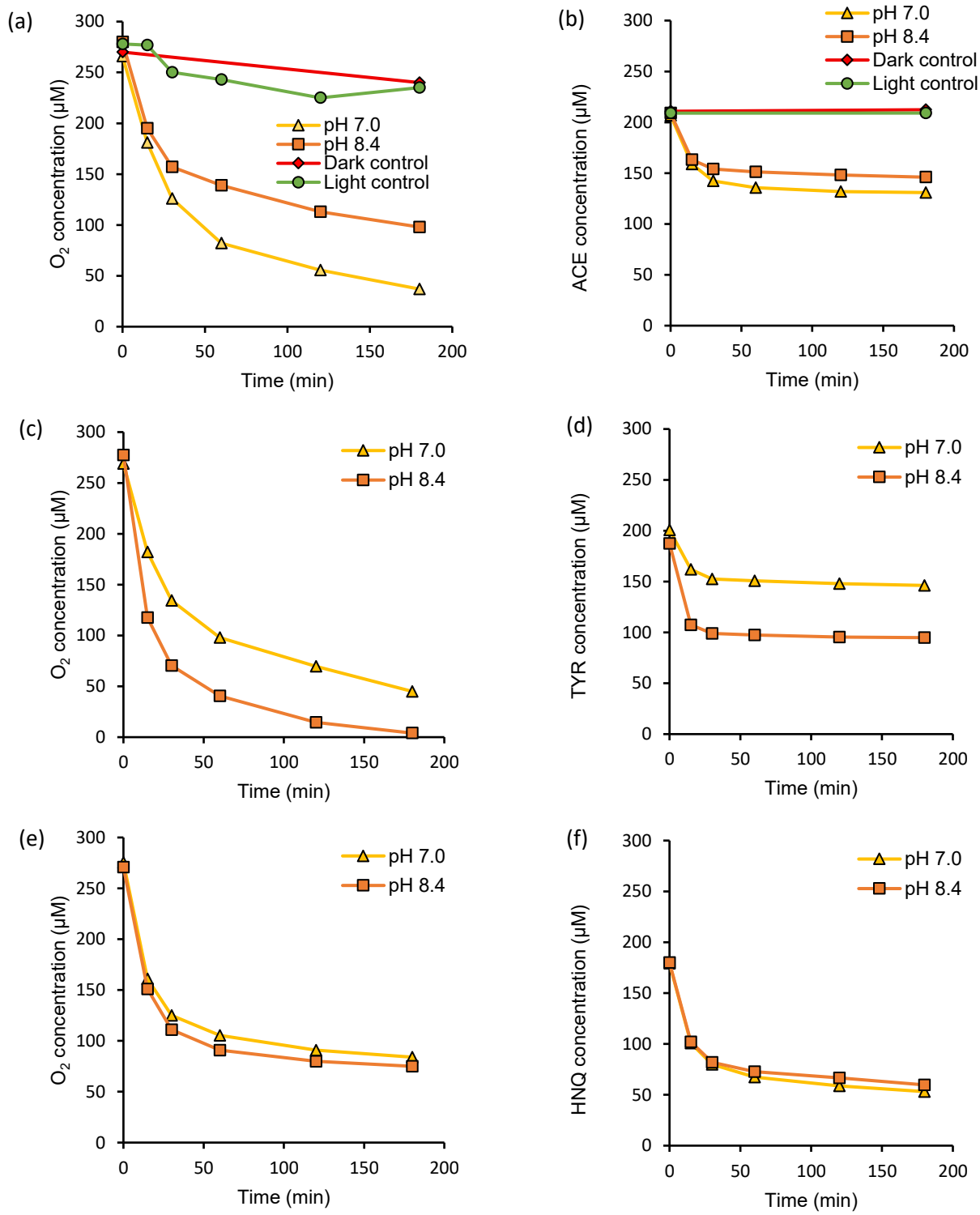

***Figure 2**: Concentrations of dissolved oxygen (a, c, e) and phenols (b, d, f) during singlet oxygen experiments with acetaminophen (a-b), tyrosine (c-d), and HNQ (e-f) at pH 7.0 (triangles) and pH 8.4 (squares). Red diamonds and green circles in (a) and (b) represent concentrations from dark controls and control experiment without RB, respectively.*

Experiments were also performed with 200 µM HNQ and 1 µM RB at pH 7.0 and 8.4. Different from the results of experiments with acetaminophen and tyrosine, the consumption of dissolved oxygen from HNQ followed pseudo-first-order kinetics (see Figure 3e), while the decrease of HNQ concentration nearly followed pseudo-first-order kinetics (see Figure 3f) with identical initial pseudo-first-order rate constants at both pH values (see Table 1), supporting the assumption made that the second-order reaction rate constant of HNQ is constant between pH 7.0 and 8.4. In accordance, the total consumption of dissolved oxygen and HNQ was almost identical under the two pH conditions (see Figures 2e and 2f).

While reaction rates describe how fast phenols react with singlet oxygen, they do not describe how many oxygen molecules are consumed for each phenol molecule consumed. To address this, stoichiometries were calculated between the loss of dissolved oxygen and phenols. According to eq.1, one mole of phenol should be consumed together with one mole of dissolved oxygen. Figures 4a-c indicate the different ratios between the concentrations of dissolved oxygen and phenols during 180 minutes of solar light irradiation. Acetaminophen and HNQ trends were identical at both pH conditions, but for tyrosine, differences were observed at the different pH values. For acetaminophen and tyrosine at pH 8.4, the O_2:phenol-ratios changed from approximately 2 to 3, while for tyrosine at pH 7.0, the ratios changed from approximately 2 to 4. In contrast, the O_2:phenol-ratios in experiments with HNQ stayed at around 1.5 for the whole 180 minutes of irradiation. Overall, these results indicate that singlet oxygen not only reacts with the parent phenols but also with reaction products, which results in O_2:phenol-ratios > 1 of these ratios, at least in experiments with acetaminophen and tyrosine. Further suggest that reactions with products become more important over time and are most important in experiments with tyrosine at pH 7.0.

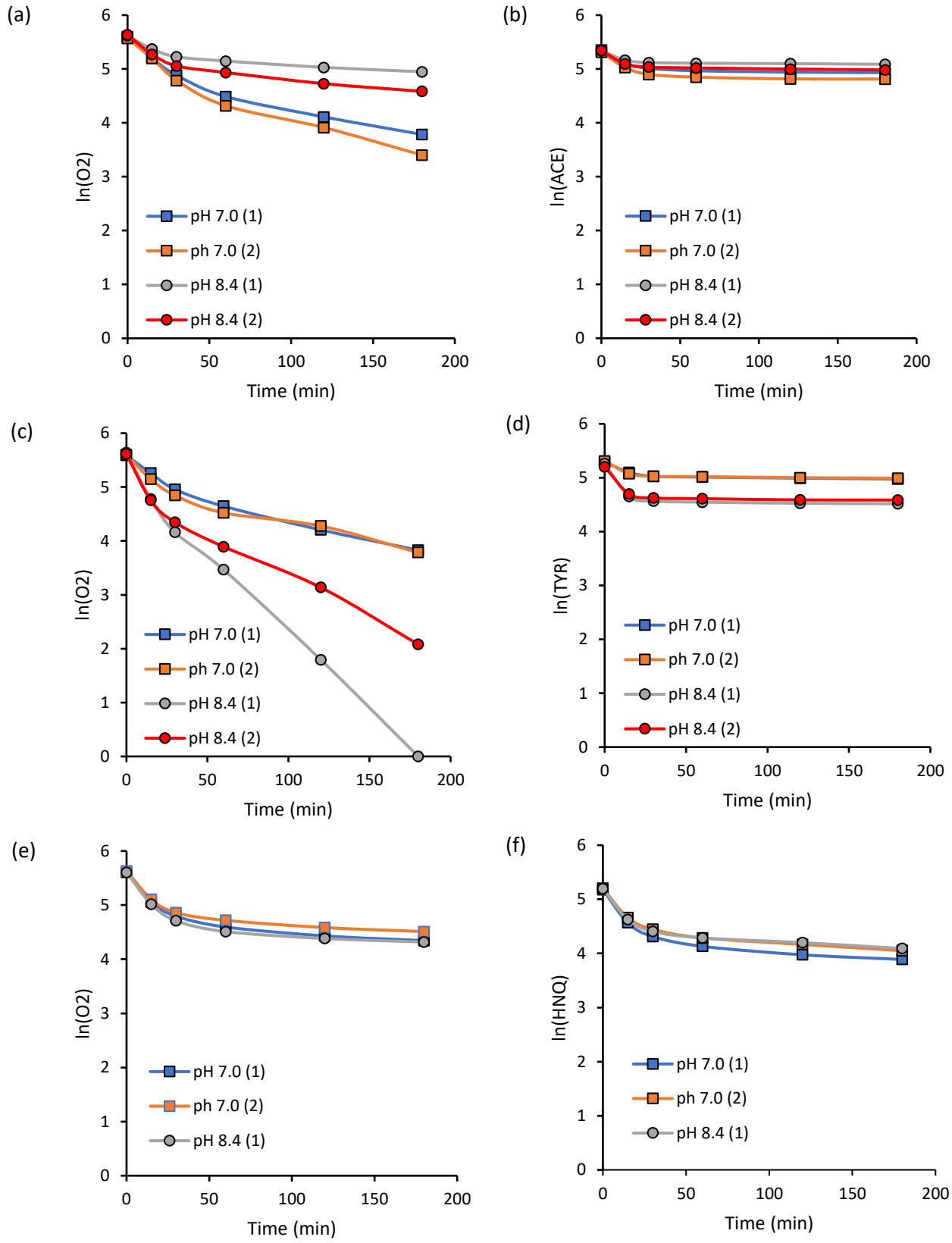

***Figure 3**: Natural logarithm of dissolved oxygen (a, c, e) and phenols (b, d, f) concentrations during singlet oxygen experiments with acetaminophen (a-b), tyrosine (c-d), and HNQ (e-f) at pH 7.0 (squares) and pH 8.4 (circles).*

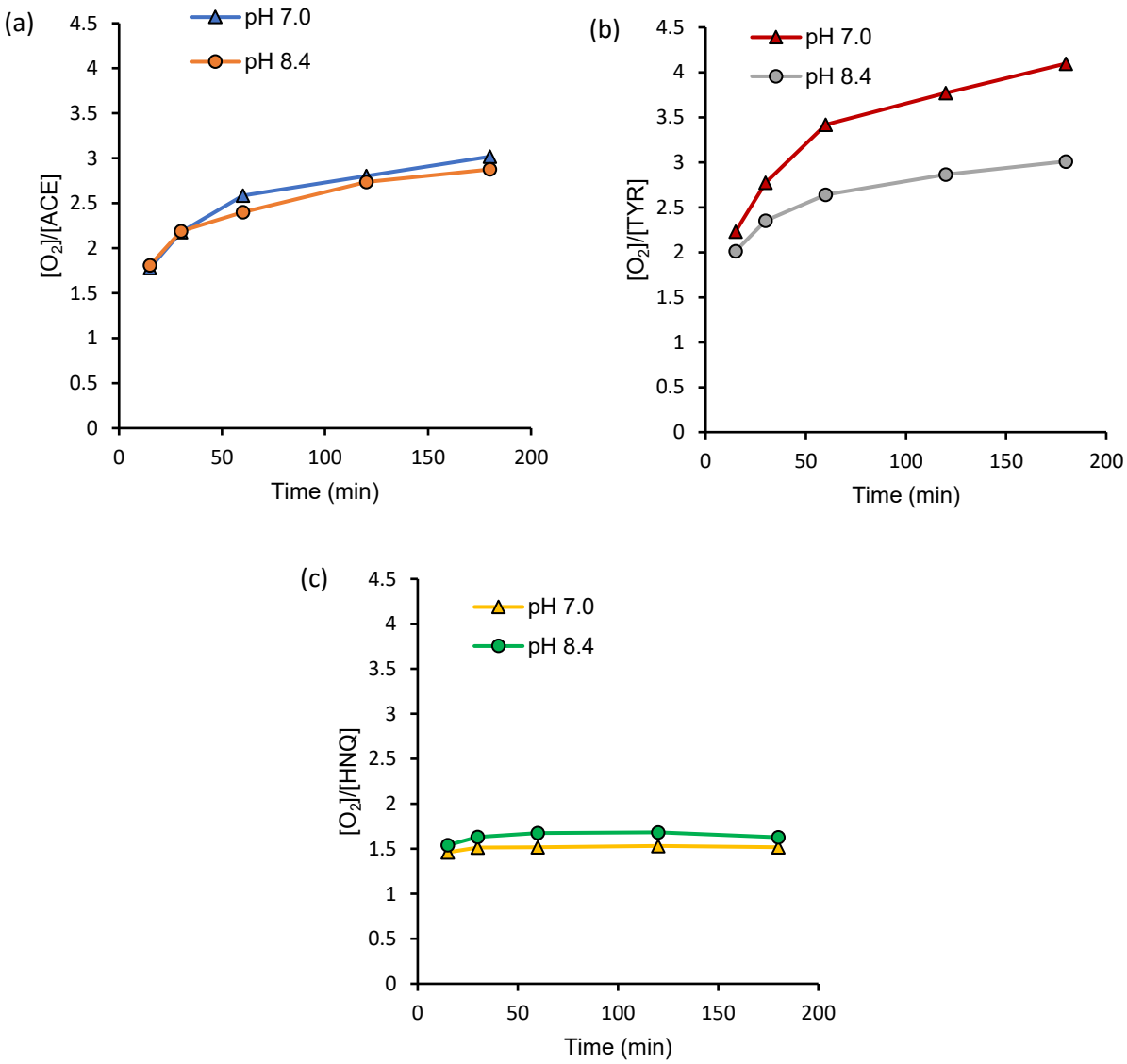

***Figure 4**: Ratios of dissolved oxygen concentration and acetaminophen (a), tyrosine (b), and HNQ (c) concentrations over time at pH 7.0 (triangles) and 8.4 (circles).*

5.4 Co-consumption of dissolved oxygen and phenols during reaction with hydroxyl radicals

Experiments with acetaminophen and hydroxyl radical were conducted in ultrapure water with 200 µM acetaminophen, 0 to 0.75 mM H_2O_2, and 50 µM Fe^{2+}. Two vials were used as controls, one containing only acetaminophen in ultrapure water, and the other containing both acetaminophen and H_2O_2 in ultrapure water. After 120 minutes, the concentration of dissolved oxygen decreased from 249 µM to 19 µM with an increasing H_2O_2 concentration from 0 mM to 0.75 mM (see Figure 5a), indicating a 0.31 µM of dissolved oxygen consumed per 1 µM H_2O_2 added. A similar trend was observed for the consumption of acetaminophen,

with a decreased of 212 µM in the same H_2O_2 concentration range (see Figure 5b), meaning 0.28 µM of acetaminophen was consumed per 1 µM H_2O_2 added.

Similar experiments were performed with 200 µM tyrosine. Tyrosine reacts 3.2 times more efficiently with hydroxyl radical than acetaminophen [41, 42]. Despite scattering results, when increasing the concentration of H_2O_2 up to 0.75 mM, the total consumption of dissolved oxygen was around 180 µM, showing that 0.24 µM dissolved oxygen was consumed per 1 µM H_2O_2 added (see Figure 5c). This was 1.3 times less than acetaminophen. On the other hand, the amount of tyrosine was almost completely consumed (200 µM) when 0.75 mM H_2O_2 was added, similar to acetaminophen (see Figure 5d), which was not expected based on the higher second-order reaction rate constant of tyrosine compared to acetaminophen.

***Table 2**: Second-order reaction rate constants of acetaminophen [41] and tyrosine [42] with hydroxyl radical.*

Compounds	*Second-order reaction rate constant (10^{10} $M^{-1}s^{-1}$)*
Acetaminophen	0.5
Tyrosine	1.6

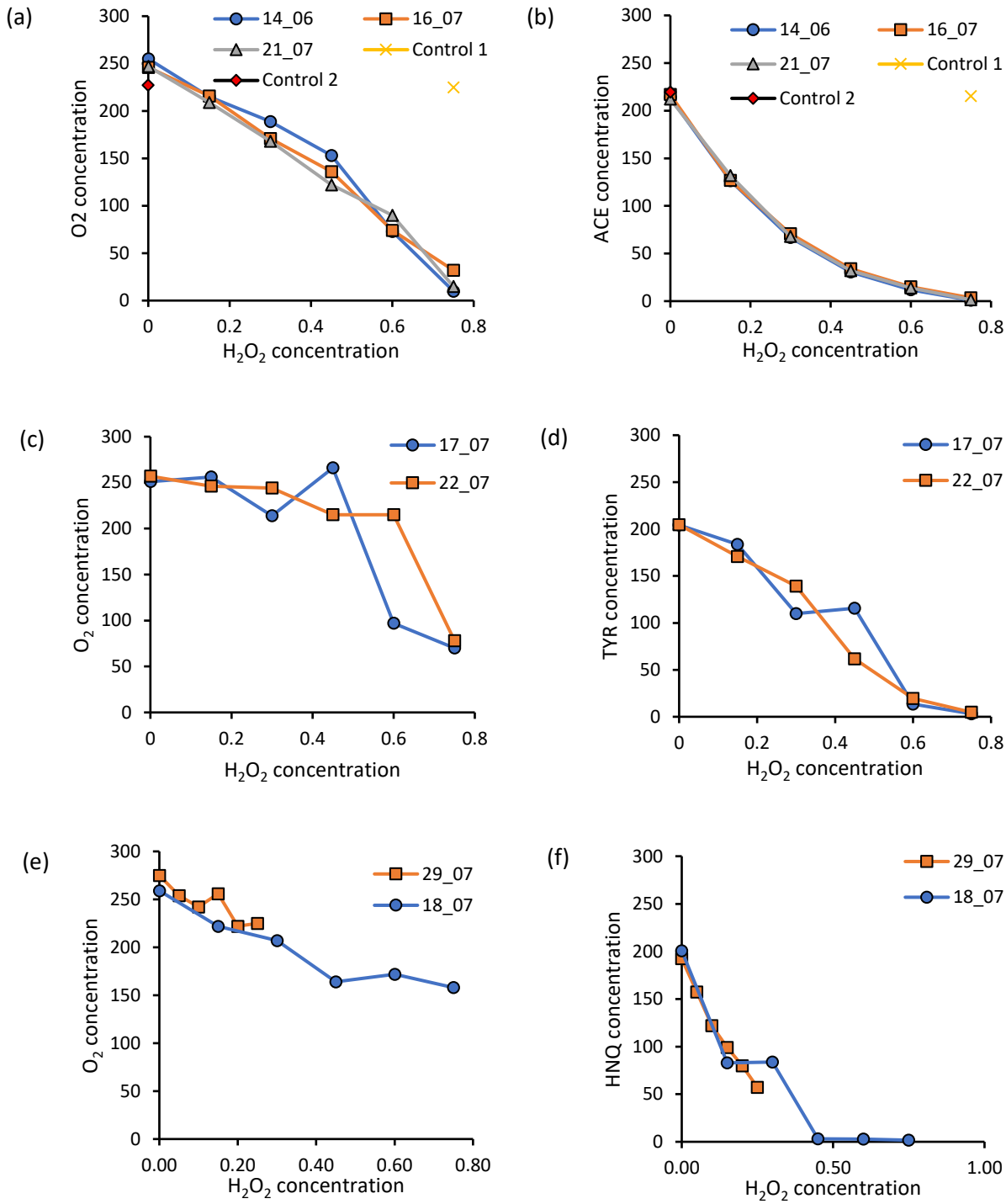

***Figure 5**: Concentrations of dissolved oxygen (a, c, e) and phenols (b, d, f) during hydroxyl radical experiments with acetaminophen (a-b), tyrosine (c-d), and HNQ (e-f) at different H_2O_2 concentrations (0 - 0.75 mM). Red diamond and yellow cross in (a) and (b) represent concentrations from controls containing only acetaminophen, and without Fe^{2+}, respectively.*

Different from acetaminophen and tyrosine, experiments with HNQ were conducted once with 0 to 0.75 mM H_2O_2 and once with 0 to 0.25 mM H_2O_2. The experiments showed that HNQ was completely consumed (199 µM) when adding 0.45 mM H_2O_2 (see Figure 5f), indicating that 0.4 µM of HNQ was consumed per 1 µM H_2O_2 added. However, the concentration of dissolved oxygen under the same conditions followed a similar trend as with tyrosine, at 0.23 µM of consumed dissolved oxygen per 1 µM H_2O_2 added (see Figure 5e). Overall, these results, when compared to acetaminophen and tyrosine, reveal that HNQ had the highest reactivity toward hydroxyl radical, followed by tyrosine and acetaminophen.

Stoichiometries were calculated between the loss of dissolved oxygen and phenols. According to eq. 3 and 4, one mole of phenol should be consumed together with one mole of dissolved oxygen. Figures 6a-c illustrate the different ratios between the concentrations of dissolved oxygen and phenols with the increase of H_2O_2 concentrations from 0 to 0.75 mM. The O_2:phenol-ratios for acetaminophen showed the most consistent increase between the individual replicates with an increase from 0.3 to 1.1, while O_2:phenol-ratios with tyrosine increased from 0 to 0.9 with substantial scattering. O_2:phenol-ratios with HNQ were relatively constant at approximately 0.4. Overall, these ratios were on average 3.4 times, 4 times, and 3.75 times smaller than those observed in singlet oxygen experiments with acetaminophen, tyrosine, and HNQ, respectively. This substantial difference can be due to the fact that hydroxyl radicals are much more reactive than singlet oxygen (see Tables 1 and 2). Hydroxyl radicals can react with phenols to form aryloxy radicals (see eq. 3). These aryloxy radicals do not always require dissolved oxygen to form products, which means the degradation of phenols can occur without consumption of dissolved oxygen. This directly leads to higher phenol consumption than dissolved oxygen consumption, resulting in O_2:phenol-ratios < 1.

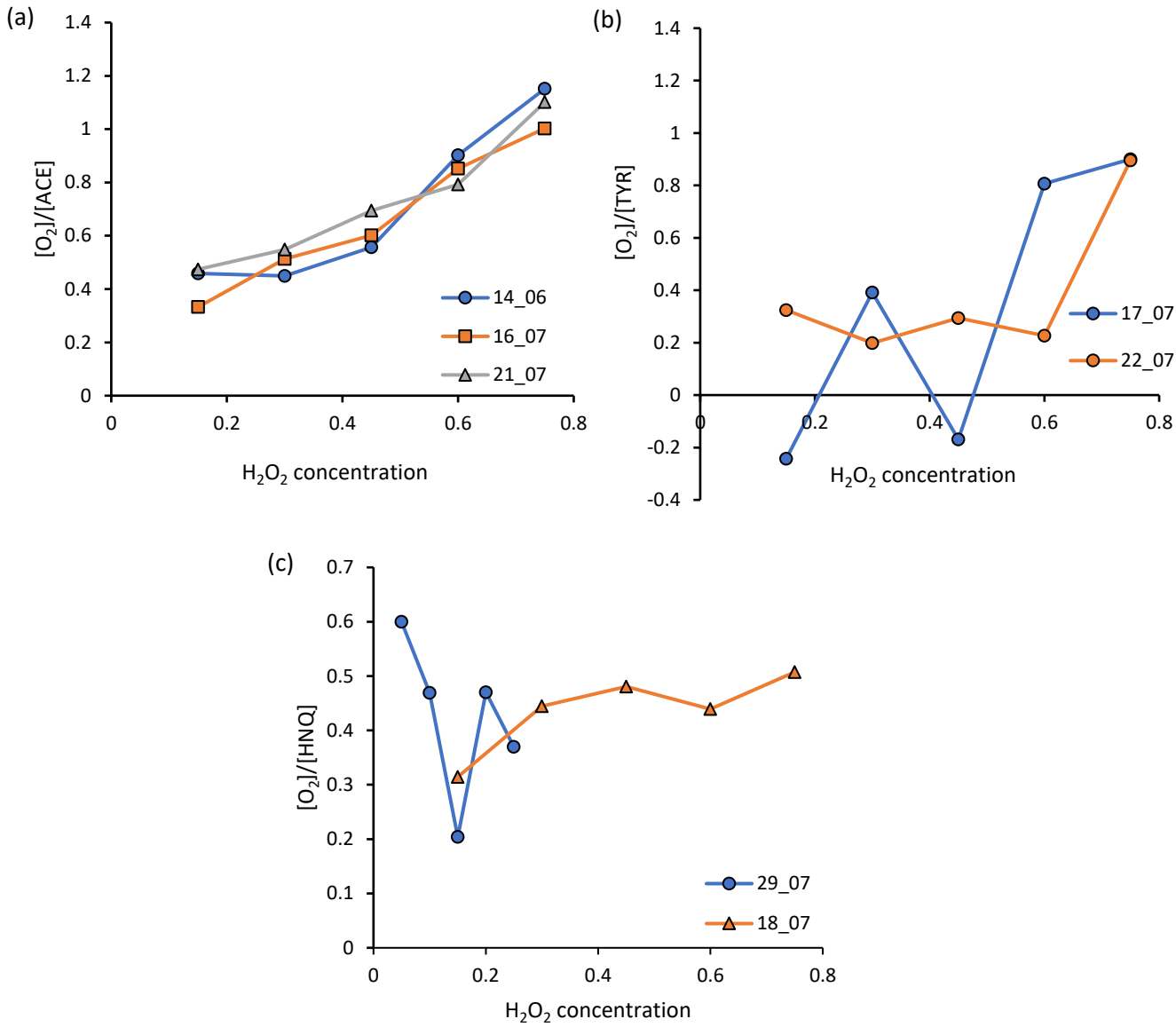

***Figure 6**: Ratios of dissolved oxygen concentration and acetaminophen (a), tyrosine (b), and HNQ (c) with the increase in H_2O_2 concentration.*

6 Conclusion and outlook

The objective of this thesis is to quantify the co-consumption of dissolved oxygen during the photochemical transformation of three phenols (acetaminophen, L-tyrosine, and HNQ) when reacting with two key reactive oxygen species. Thus, the primary aim was to determine the ratios of dissolved oxygen and phenol consumption in experiments with singlet oxygen and hydroxyl radicals, providing insight into how important dissolved oxygen is in photochemical research on phenols.

The hypothesis that the ratio of consumed dissolved oxygen to phenol (O_2:phenol ratio) approaches 1 during photochemical transformation of phenols by singlet oxygen or hydroxyl radical is partially supported, as O_2:phenol ratios close to 1 were only observed in the hydroxyl radical experiments with acetaminophen and tyrosine. In singlet oxygen experiments, all three phenolic compounds underwent oxidation. The observed O_2:phenol ratios were significantly larger than 1, and this indicates that singlet oxygen reacts not only with the parent phenols but also with their transformation products. This was particularly evidenced for tyrosine at pH 7.0, where O_2:phenol-ratios approached 4. These values show that secondary reactions, such as intermediates or products, are very important in total dissolved oxygen consumption. Notably, although acetaminophen and HNQ both experienced higher second-order rate constants with singlet oxygen at pH 8.4, tyrosine experiments showed more total dissolved oxygen consumption at this pH. Additionally, it is indicated that interactions with products become more important as time progresses.

In experiments with hydroxyl radicals, all three phenolic compounds underwent degradation. Acetaminophen exhibited a consistent increase in the O_2:phenol-ratios with increasing H_2O_2 concentrations, reaching approximately a 1:1 ratio. In contrast, the O_2:phenol ratios for tyrosine and HNQ showed scattering across replicates and experimental conditions. HNQ was nearly completely degraded at lower H_2O_2 concentrations compared to acetaminophen and tyrosine.

O_2:phenol-ratios , on average, were 3.4, 4, and 3.75 times lower than the corresponding ratios in singlet oxygen reactions with acetaminophen, tyrosine, and HNQ. It can be explained by the much higher reactivity of hydroxyl radicals compared to singlet oxygen [39, 41, 42]. Hydroxyl radicals rapidly react with phenols to yield aryloxy radicals, which are not necessarily dependent upon dissolved oxygen to proceed to final products. Therefore, phenol degradation may occur independently of O_2 consumption.

The hypothesis that the consumption rates of dissolved oxygen and phenols in experiments with singlet oxygen and acetaminophen or tyrosine increase with pH, while the rates in

experiments with HNQ do not, is supported. This observation can be explained by looking at pK_a values of acetaminophen, tyrosine, and HNQ (9.5, 10, and 3.98, respectively) [26, 29, 32]. As pH increases, a greater amount of acetaminophen and tyrosine exists in their deprotonated forms, leading to higher consumption rates of both dissolved oxygen and phenols. In contrast, HNQ has a pK_a lower than two selected pH levels for the experiments, indicating that further increase in pH does not result in additional deprotonated species. Therefore, the consumption rates of dissolved oxygen remain the same after increasing the pH conditions. Furthermore, O_2:phenol-ratios are unaffected by pH, as expected, but with only one exception from tyrosine experiments. The ratios from these experiments were observed to change with different pH levels, where they increased significantly at pH 7.0 compared to pH 8.4. This suggests that the products of tyrosine have greater reactivity toward singlet oxygen at pH 8.4.

Future research should prioritize repeating experiments with hydroxyl radical, especially for the case of tyrosine and HNQ, to improve reproducibility and to clarify the variability observed in dissolved oxygen to tyrosine/HNQ stoichiometric ratios. In addition, investigate a more diverse set of phenols with different structural features to better understand how they affect the reactivity with singlet oxygen and hydroxyl radical. Beyond phenols research, future studies should investigate the role of phenol's phototransformation products, and their interaction with reactive oxygen species at different pH conditions.

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