

# **Kinetic Modeling of TiO<sub>2</sub>-Catalysed Photodegradation of Trace Levels of Microcystin-LR**

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## **Supplementary Information**

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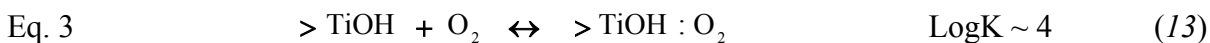
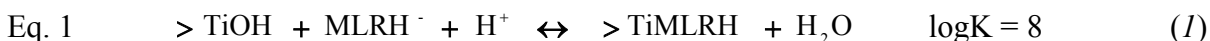
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## Modelling approach

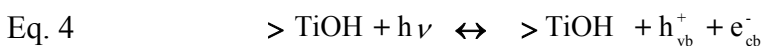
### Surface-mediated degradation (part A)

Microcystin-LR (MLRH<sup>-</sup>), the bulk organic (RR''CH<sub>2</sub><sup>-</sup>), and dissolved oxygen are firstly considered to sorb reversibly to TiO<sub>2</sub> surface hydroxy groups, i.e.



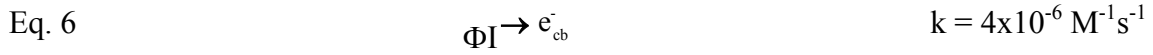
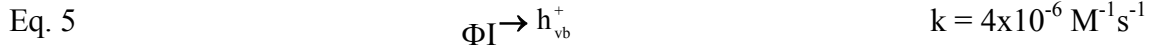
The logK for MLRH<sup>-</sup> adsorption is derived from surface complexation studies (1) and the conditional stability constant given for RR''CH<sub>2</sub><sup>-</sup> adsorption is based on adsorption fitting studies (5) and does not vary greatly with pH. Oxygen is assumed to form inner sphere complexes with the surface of TiO<sub>2</sub> (13-15).

Near UV light impinging on the TiO<sub>2</sub> surface leads to the formation of electron-hole pairs:

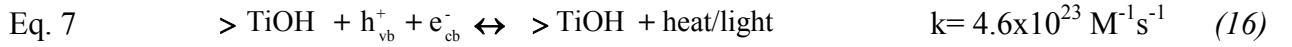


The number of holes arriving at the particle surface can be represented by  $\Phi I$  where  $I$  is a measure of the effective light intensity and  $\Phi$  is an efficiency factor. For a light flux of  $1600 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ , an illumination window approximately 3.5cm in diameter and 140mL reaction volume, the apparent light intensity is approximately  $10^{-5} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$ . Davis and Huang (16) used an efficiency factor of 0.4 to account for light reflection, variations in hole migration throughout different areas of single particles and recombination due to

traps in the bulk semiconductor particles. Similarly, given the need to maintain electroneutrality in the solid particle, the same factor may be used to describe electron arrival at the particle surface:



The photogenerated holes and electrons may migrate to the surface of the catalyst or recombine. Surface recombination can occur at a surface trap site:



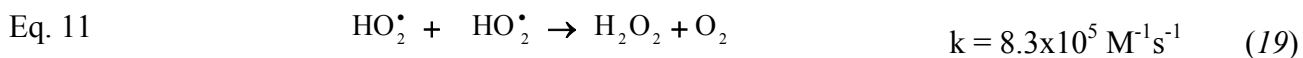
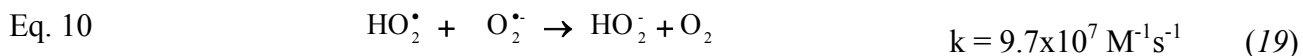
The recombination rate is considered to be a function of the number of trap sites available for recombination and is therefore dependent on the semiconductor purity and exact stoichiometry (16). Under oxygen rich conditions, adsorbed  $\text{O}_2$  is considered to be the primary electron acceptor and leads to the formation of surface  $\text{O}_2^{\bullet-}$ .



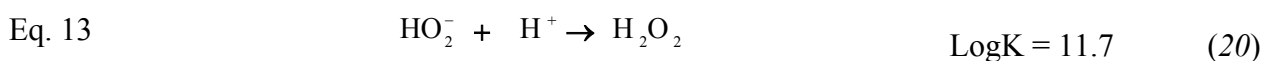
Recent studies have confirmed that the superoxide radical may desorb to solution (17, 18), i.e.



The complexation constant and desorption rate of surface trapped superoxide radicals is unknown and is one of the parameters used for fitting the model. The major pathway for termination of these radicals, in the absence of other scavengers, involves second-order pH dependent disproportionation to  $\text{H}_2\text{O}_2/\text{HO}_2^-$  and  $\text{O}_2$  (19).



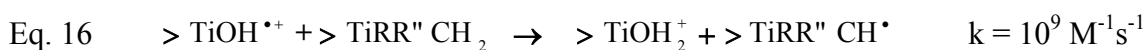
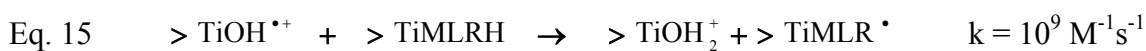
The dissociation constants for both  $\text{H}_2\text{O}_2$  and  $\text{HO}_2^\bullet$  ( $k_f = 5 \times 10^{10} \text{ s}^{-1}$ ) are given in eqs 12 and 13.



While debate still exists concerning the nature of the primary oxidizing species (13), surface oxidation is assumed to occur via the generation of hydroxyl radicals produced from photogenerated holes at the  $\text{TiO}_2$  surface. These radicals are trapped at the surface by titanol groups (13,21-23) and represented here as  $>\text{TiOH}^{\bullet+}$ , i.e.



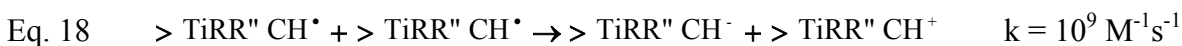
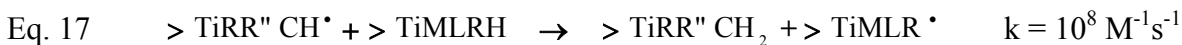
The rate of recombination of these surface hydroxyl radicals with conduction band electrons is expected to be relatively slow (13) enabling interaction with any other readily available (adsorbed) oxidisable species including  $\text{MLRH}^-$  and  $\text{RCH}_2\text{R}''$ : i.e.



Reaction of  $\bullet\text{OH}$  with peptides and proteins (eqs 15 and 16) invariably occurs as H abstraction reactions (24). Hydroxyl attack on peptides is faster than reactions with its individual amino acid components due to the deactivating influence of the protonated amine group (25). Fast and indiscriminate scavenging of surface hydroxyl radicals by the

MLRH<sup>-</sup> and RR''CH<sub>2</sub><sup>-</sup> is envisaged with very high forward rate constants. Solution phase reaction rates are on the order of 10<sup>9</sup>M<sup>-1</sup>s<sup>-1</sup> for the reaction of •OH with peptides and proteins (24).

The RR''CH<sup>•</sup> radicals generated at the semiconductor surface are expected to either react with other oxidizable species at the surface (such as adsorbed MLRH<sup>-</sup>) or other surface radical species; i.e.

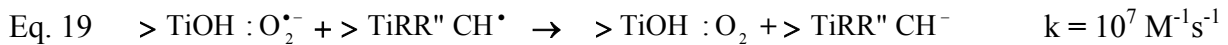


The RR''CH<sup>•</sup> radicals may react with other surface bound bulk organics leading to a cycling of RR''CH<sup>•</sup> radicals. As we are considering sensitised degradation over a relatively short time period (where relatively constant DOC concentrations suggest minimal mineralisation), the inclusion or omission of this pathway has very little effect on the degradation model.

The reaction rate between the newly formed organic alkyl radicals (eqs 17 and 18) and other organics (including MLRH<sup>-</sup>) in the solution phase is generally slightly slower than reactions with •OH radicals and range from 10<sup>7</sup> – 10<sup>9</sup>M<sup>-1</sup>s<sup>-1</sup>. It is estimated that the rates for these reactions is 10<sup>8</sup>M<sup>-1</sup>s<sup>-1</sup> based on data compiled by Neta et al. (12) for reactions between large alkyl radicals with peptides and proteins. Large organic alkyl radical-radical reactions are fast and consequently eq 18 has been assigned a homogeneous rate constant of 10<sup>9</sup>M<sup>-1</sup>s<sup>-1</sup>.

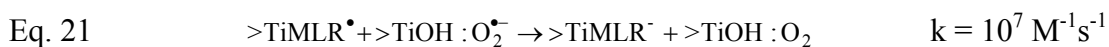
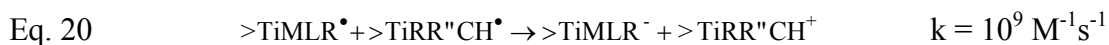
The surface superoxide radical may undergo possible H<sup>+</sup> mediated self termination (11) although this is expected to be relatively slow compared to the deactivation by

TiRR"CH• (eq 19). In the absence of surface radical scavengers, deactivation by surface trapped holes is considered the most likely decay process for surface generated superoxide (26) as the rate constant for this reaction is large ( $10^{10} \text{ s}^{-1}$  (11)) but, in the presence of adsorbed organics, the steady state concentration of surface trapped holes will be very low which effectively negates this deactivation pathway.



The rate constants for reactions between protonated and deprotonated superoxide species with peptides or proteins varies substantially but is generally within the  $10^2$  to  $10^6 \text{ M}^{-1}\text{s}^{-1}$  range (11). These rates are too slow compared to reactions with hydroxyl/peroxyl radicals to significantly impact the surface mediated degradation and are therefore omitted from the model.

The surface generated  $>\text{TiMLR}^{\bullet}$  radicals are assumed to be deactivated by surface alkyl radicals and superoxide as indicated in eqs 20 and 21 respectively.



The final breakdown product ( $>\text{TiMLR}^-$ ) is assumed to have no distinguishing features from the complex mixture of other cyanobacterial breakdown products. This follows experimental observations that the total organic carbon of the suspension does not decrease over the course of the 1h experiments, except for that which is attributed to

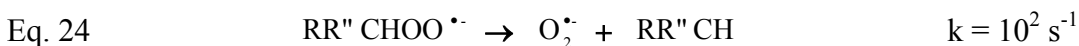
removal by adsorption. It is assumed that there is essentially no difference in the reactivity or adsorption properties of  $>\text{TiRR}''\text{CH}_2/ >\text{TiRR}''\text{CH}^-/ >\text{TiRR}''\text{CH}^+$ .

### Addition of solution phase toxin degradation (part B)

Desorption of surface-generated alkyl radicals may be represented as:



Due to the presence of high levels of  $\text{O}_2$  in solution ( $\sim 10^{-4}$  M),  $\text{RR}''\text{CH}^\bullet$  is likely to rapidly form peroxy radicals (eq 23) that may either undergo self-decomposition (eq 24) or propagation reactions with MLR (eq 25), bulk organic (eq 26) or  $\text{HO}_2^\bullet/\text{O}_2^\bullet$  (eq 27).



The rate of  $\text{O}_2$  addition to carbon-centred radicals is usually close to the diffusion controlled rate and irreversible. A typical rate constant of  $2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$  (10,26) is used for eq 23. The self-decomposition rates for biological-type peroxy radicals (eq 24) is typically  $10^2 - 10^3 \text{ s}^{-1}$  (10) and a value of  $10^2 \text{ s}^{-1}$  has been adopted in the model. The rate of reaction of peroxy radicals derived from biological-type molecules with other large molecules is generally in the order of  $10^7 - 10^8 \text{ M}^{-1}\text{s}^{-1}$ . Peroxy radicals from biological-type molecules include those derived from deoxyguanosine-OH adducts, thymidine-OH adducts, thymine-OH adducts or linoleate (10). Peroxy radicals from much larger molecules such as single or double-stranded DNA-OH adducts typically react more slowly with rate constants in the order of  $10^4 \text{ M}^{-1}\text{s}^{-1}$  (10). A rate constant of  $10^8 \text{ M}^{-1}\text{s}^{-1}$  has been used for the peroxy radical reaction with MLRH (eq 25). The organic peroxy

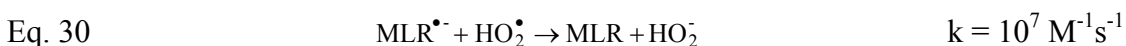
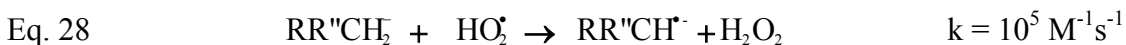
radicals will also react with the bulk organic and lead to the formation of new alkyl radicals (eq 26). This cycling of radicals will slightly decrease the overall degradation rate as less of the organic peroxy radicals terminate via eq 27. The peroxy radicals may also undergo a termination sequence involving the formation of *tert*-peroxy radicals, which would typically dissociate to molecular oxygen and two alkoxy radicals (19). While this sequence can be fast based on similar self-termination reactions for uracil-OH, thymine and linoleate derived peroxy radicals (10), it is not considered a primary termination sequence due to the much greater concentration of  $\text{HO}_2^\bullet$  available in solution with which the peroxy radicals would be expected to react with similar speed.

The formation of stable oxygenated intermediates has been observed in many detailed degradation studies although they are typically mineralised given sufficient exposure times. In order to simplify the modelling, we have assumed that slight oxygenation of large peptides and proteins will not significantly alter their adsorption properties or reactivity with radical species (ie. in eqs 25-27  $\text{RR}''\text{COOH}$  is equivalent to  $\text{RR}''\text{CH}_2$ ). While such an assumption would not be acceptable over a long reaction time (as the model would have no capacity to account for any mineralisation), it is acceptable if the degradation products are similar properties to the parent compounds and the reaction time is relatively short. To test this assumption, we have simulated the other extreme by not including slightly modified products in any further reactions, leading to an accumulation of the oxygenated products in the solution phase and an overall decrease in the reactivity of the solution. The greatest impact from this assumption is observed at low pH, high concentrations as given in Figure 4 (“Degradation model (parts A&B) &  $\text{RR}''\text{COOH}$ ”). The assumption shows only a minor deviation from the model (parts A&B) ( $\log\text{SSR} = -6.6$ ) and in fact slightly improves the fit to the degradation data at the tail end of the curve. At higher concentrations of organics (e.g. 420 nM MLR/ 14 mg/L bulk organic) it is predicted that some 80% of the bulk organic is converted to the slightly modified products within one hour. The effect is muted at higher pH due to the quenching of surface superoxide radicals by surface carbonate radicals (see discussion in the next



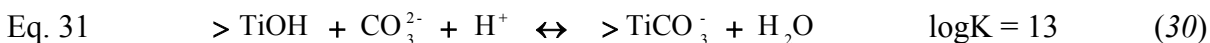
section) and only 30% of the bulk organic is converted to oxygenated products. Thus the assumption of assigning  $RR''COOH$  equivalent to  $RR''CH_2$  appears justified.

In part A of the model, we ignored the possibility that  $HO_2^\bullet/O_2^{\bullet-}$  may react with solution phase MLRH or the bulk organic. There is a wide variation in rate constants for  $HO_2^\bullet/O_2^{\bullet-}$  reactions with peptides and proteins. The typical range is  $10^2 - 10^6 \text{ M}^{-1}\text{s}^{-1}$ , which is considerably less than the rate constant for the reaction with organic peroxy radicals shown in eq 25. It is therefore unlikely that the primary solution phase degradation pathway for MLRH will be via superoxide (eq 29). An important potential pathway, however, is the production of peroxy radicals through reactions between the bulk organic and  $HO_2^\bullet/O_2^{\bullet-}$  as given in equation 28. Any alkyl radicals formed through interaction of the bulk organic with superoxide would be expected to rapidly react with dissolved  $O_2$  resulting in the formation of highly reactive organic peroxy radicals. Equations 28 and 29 are assumed to be moderately fast and the sensitivity of this assumption is discussed below. The primary termination pathway for solution phase microcystin radicals is considered to be with superoxide as given in eq 30.



### Addition of carbonate effects at high pH (part C)

Carbonate is considered to sorb reversibly to TiO<sub>2</sub> surface hydroxy groups, i.e.

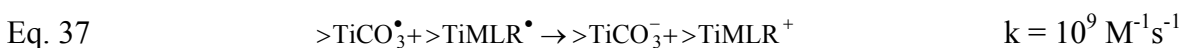
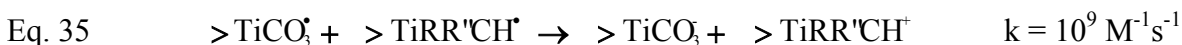
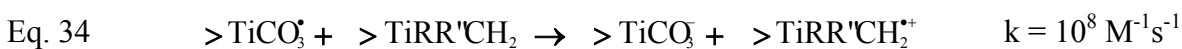
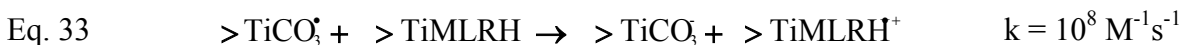


Once adsorbed to the particle surface, the carbonate complexes are expected to react with other radical species, particularly surface hydroxyl radicals:



Reaction of •OH with peptides and proteins (eqs 12 and 13) invariably occurs as H abstraction reactions (23) rather than electron transfer reactions that typically occur with smaller molecules such as carbonate (eq 32). The solution phase reaction rates are on the order of 10<sup>9</sup>M<sup>-1</sup>s<sup>-1</sup> for the reaction of •OH with peptides and proteins and approximately 10<sup>8</sup>M<sup>-1</sup>s<sup>-1</sup> for reactions with carbonate (23).

The carbonate radicals generated at the semiconductor surface are expected to either react with other oxidizable species at the surface (such as adsorbed MLRH<sup>•</sup>) or other surface radical species; i.e.



Reactions involving  $\text{CO}_3^{\bullet-}$  and peptides or proteins are typically fast and occur with rate constants in the order of  $10^8 \text{M}^{-1} \text{s}^{-1}$  (9). Little information is available on the reaction rate between carbonate radicals and organic radicals, although other carbonate radical-radical reactions (including reactions with anthrasemiquinone-sulfonate and –disulfonate) are typically very fast (9). Thus eqs 35 and 37 are considered to be very fast though and have been assigned homogeneous rate constants of  $10^9 \text{M}^{-1} \text{s}^{-1}$ . Reaction rate constants between surface superoxide species and the carbonate radicals has been obtained from Bielski et al (11).