

# Isotope Effects in Photocatalysis: An Underexplored Issue

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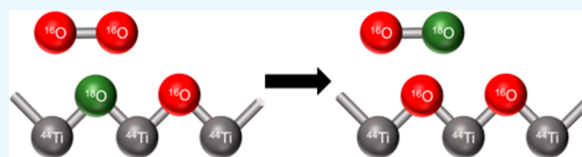


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**ABSTRACT:** In order to improve the performance of well-established photocatalysts and to develop new potential photocatalyst materials, an understanding of the underlying mechanisms of photocatalytic reactions is of the utmost importance. An often neglected method for studying the mechanism is the investigation of isotope effects. Although just a few studies related to isotope effects exist, it has been shown to be a powerful tool for exploring mechanisms of photocatalytic processes. Most of the reports are focused on  $\text{TiO}_2$ , which is the most studied photocatalyst, while there is a lack of data for other photocatalyst materials. This mini-review represents an overview of research utilizing isotope effects in the area of photocatalysis. The benefits and the importance of these studies will be highlighted, and the potential for these processes to be applied for the study of further photocatalytic reactions and different photocatalyst materials will be shown.



## INTRODUCTION

Semiconductor photocatalysis is a versatile technology that has been applied to a broad range of applications from treatment of contaminated water and air to energy conversion and storage.<sup>1a–e</sup> In designing and developing this process for practical commercial applications, it is critical to have a robust understanding of fundamental mechanistic processes that are occurring on the surface of the semiconductor material.<sup>1c–j</sup> A broad range of physical and chemical methods have been used in developing our understanding of these surface processes over the past four decades.<sup>1j–o</sup> One area that has not been applied to the same extent is the application of isotope effects to probe photocatalytic processes and mechanisms.

For this purpose, it is always necessary to perform two sets of experiments. In one experimental run one species (e.g., the photocatalyst) is labeled, and in a further run the same reaction is performed but with the same species unlabeled. This allows a comparison of both runs to make conclusions related to the mechanism of the investigated reaction.

The labeling of reactant molecules or the photocatalyst allows us to study the transfer of atoms between both species. For a correct interpretation of the obtained results, several points need to be considered. Besides a reaction during illumination, also a reaction in the dark needs to be performed since it might be possible that an exchange of atoms occurs spontaneously between the photocatalyst and the reactant molecules, which could lead to wrong conclusions for the reaction under illumination. Further, it is important to consider all possible reaction products that might be produced. For example, if  $\text{CO}_2$  is the reaction product and the incorporation of  $^{18}\text{O}$  is expected, it is necessary to detect  $\text{C}^{16}\text{O}_2$ ,  $\text{C}^{16}\text{O}^{18}\text{O}$ , and  $\text{C}^{18}\text{O}_2$ .

In the case of the investigation of solvent isotope effects, the effect of the exchange of  $\text{H}_2\text{O}$  by  $\text{D}_2\text{O}$  on the rate constant is investigated. It can be recommended not only to perform experiments in pure  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  but also to consider mixtures of both solvents.

This paper explores the areas in which these techniques have been used successfully to date and also looks at the scope for more extensive application of such methods to studying the photocatalytic process promoted by semiconductor materials. In this mini-review, works from our groups as well as works from other groups are considered.

## ISOTOPIC LABELING OF SEMICONDUCTOR PHOTOCATALYST MATERIALS AND TARGET MOLECULES FOR REACTION

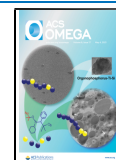
Isotopic labeling is a method to investigate the incorporation of atoms from reactant molecules into the surface of the photocatalyst and vice versa during a reaction, which allows the mechanism of chemical processes on surfaces to be followed. In the case of  $\text{TiO}_2$  as a photocatalyst, oxygen labeling (exchange of  $^{16}\text{O}$  by  $^{18}\text{O}$ ) is commonly used. For this, two different methods exist, since the reactant molecules can be either isotopically labeled or  $\text{TiO}_2$  itself.

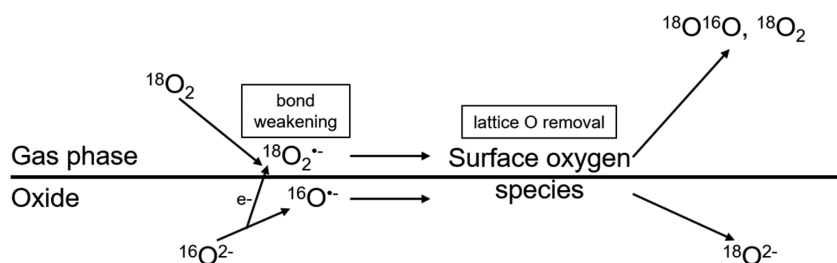
Courbon et al.<sup>2</sup> showed that after  $^{18}\text{O}_2$  adsorption on  $\text{Ti}^{16}\text{O}_2$  and following UV illumination  $^{16}\text{O}^{18}\text{O}$  and  $^{16}\text{O}_2$  can be detected in the gas phase, while the  $^{18}\text{O}_2$  content decreases,

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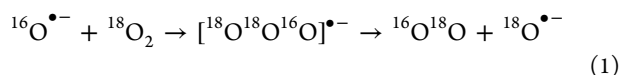




**Figure 1.** Proposed mechanism of oxygen isotopic exchange by Pichat et al.<sup>3</sup> Created in analogy to ref 3.

which proves the incorporation of  $^{18}\text{O}^{2-}$  into the surface of  $\text{TiO}_2$ . Furthermore, they were able to confirm that only one surface oxygen anion is involved in the exchange at a time. The proposed mechanism of the oxygen isotopic exchange (OIE), as described by Pichat et al.,<sup>3</sup> is depicted in Figure 1. After the excitation with light, with an energy equal to or higher than the band gap energy of  $\text{TiO}_2$ , electron–hole pairs are formed. The conduction band electrons are able to reduce  $^{18}\text{O}_2$ , which leads to the formation of superoxide radicals ( $^{18}\text{O}_2^{\bullet-}$ ). Since the additional electron is in an antibonding orbital, the O–O bond is weakened in the superoxide radical. In the lattice of the oxide, an  $^{16}\text{O}^{2-}$  anion transfers an electron to the conduction band, forming an  $^{16}\text{O}^{\bullet-}$  radical, which causes a weakened bond to the neighboring  $\text{Ti}^{4+}$  cations. Further, the generated species react with each other, leading to the incorporation of  $^{18}\text{O}^{2-}$  in the surface and the release of  $^{16}\text{O}^{18}\text{O}$  and  $^{16}\text{O}_2$  to the gas phase. However, Pichat et al.<sup>3</sup> pointed out that there is, to the best of their knowledge, no proof for the existence of a complex between  $^{18}\text{O}_2^{\bullet-}$  and  $^{16}\text{O}^{\bullet-}$ .

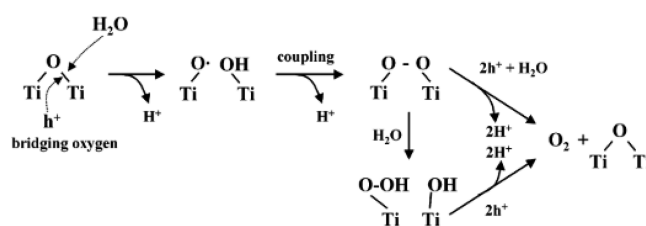
Tanaka<sup>4</sup> suggested that the OIE reaction proceeds via an  $\text{O}_3^{\bullet-}$  radical anion, while Murata et al.<sup>5</sup> were able to confirm the formation of this species. Equation 1 describes the reaction mechanism based on the formation of an  $\text{O}_3^{\bullet-}$  intermediate,<sup>6</sup> which thus rules out a direct involvement of a superoxide species as proposed by Pichat et al.<sup>3</sup> Courbon et al.<sup>2</sup> found that the activity for the photooxidation of isobutane correlates with the activity for the OIE and thus concluded that an  $\text{O}^{\bullet-}$  species is involved in both reactions, which supports the mechanism.



The isotopic-labeled oxygen can be used also simultaneously with other unlabeled molecules to investigate the effect of the OIE. For example, Liao et al.<sup>7</sup> reported that during UV illumination of a  $\text{TiO}_2$  surface no oxygen exchange between  $^{18}\text{O}_2$  and adsorbed CO occurs, while for adsorbed  $\text{CO}_2$ ,  $\text{CO}_3$ , and  $\text{HCOO}$  species an oxygen exchange was observed.

A further approach is to use directly isotopic-labeled reactant molecules instead of  $^{18}\text{O}_2$ . Isotopic-labeled water ( $\text{H}_2^{18}\text{O}$ ) was used by Nakamura et al.<sup>8</sup> to support their proposed mechanism (Figure 2) for the oxygen evolution of rutile in contact with aqueous solutions during illumination, with  $\text{Ti}-\text{O}-\text{O}-\text{OH}$  and  $\text{Ti}-\text{O}-\text{O}-\text{Ti}$  as intermediates. Zhang et al.<sup>9</sup> showed that  $^{18}\text{O}$ -enriched cyclohexanol and benzyl alcohol form in the presence of  $\text{TiO}_2$  and  $^{16}\text{O}_2$  during illumination in benzotri-fluoride cyclohexanone and benzaldehyde that contain approximately 100%  $^{16}\text{O}$ . Further, they were able to exclude the possibility of oxygen transfer from the  $\text{TiO}_2$  to the molecule.

Besides isotopic labeling of the reactant molecules, a further method is to label the photocatalyst.  $^{18}\text{O}$ -enriched surfaces can



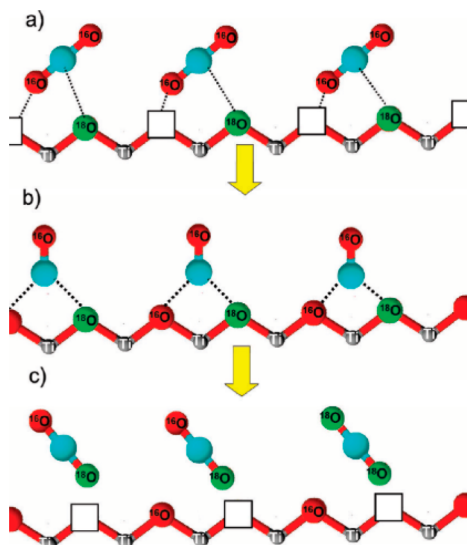
**Figure 2.** Mechanism for the oxygen evolution of  $\text{TiO}_2$  (rutile) in aqueous solutions with a pH between 1 and 12 during illumination. Reprinted with permission from ref 8. Copyright 2004 American Chemical Society.

be prepared via different approaches. The surface of  $\text{Ti}^{16}\text{O}_2$  can be  $^{18}\text{O}$ -enriched in contact with  $^{18}\text{O}_2$  at 750 K,<sup>10</sup> under UV irradiation in  $\text{H}_2^{18}\text{O}$  for 12 h,<sup>9</sup> or by applying a potential of 1 V in an  $^{18}\text{O}$ -containing electrolyte during illumination.<sup>11</sup> It needs to be taken into account that the  $^{18}\text{O}$ -enrichment is limited to the surface of  $\text{TiO}_2$ .<sup>12</sup> Kavan et al.<sup>13</sup> reported the synthesis of isotopically pure  $\text{Ti}^{18}\text{O}_2$  by the hydrolysis of  $\text{TiCl}_4$  in  $\text{H}_2^{18}\text{O}$ , yielding anatase, which can be transformed to rutile by heating to 1000 °C in a vacuum.

Henderson<sup>10</sup> investigated the formic acid decomposition at an  $^{18}\text{O}$ -enriched (100)  $\text{TiO}_2$  crystal without illumination. It was demonstrated that  $^{18}\text{O}$ -containing products are released during the decomposition ( $\text{H}_2\text{C}^{18}\text{O}$ ,  $\text{HC}^{16}\text{O}^{18}\text{OH}$ ,  $\text{HC}^{18}\text{O}^+$ , and  $\text{H}_2^{18}\text{O}$ ), which confirms the incorporation of lattice oxygen into the products. Henderson<sup>14</sup> also investigated the same reaction at an  $^{18}\text{O}$ -enriched (110)  $\text{TiO}_2$  crystal in the dark. Similar as for the (100) crystal, the transfer of lattice oxygen to the product molecules was observed. Bogdanoff and Alonso-Vante<sup>11</sup> studied the photoelectrooxidation of formic acid in the presence of  $^{18}\text{O}$ -enriched  $\text{TiO}_2$ , but no incorporation of  $^{18}\text{O}$  was observed in the detected  $\text{CO}_2$  molecules. Civiš et al.<sup>15</sup> reported for formic acid in contact with isotopically pure  $\text{Ti}^{18}\text{O}_2$  during illumination that no oxygen exchange occurs between the oxygen atoms of  $\text{Ti}^{18}\text{O}_2$  and the formic acid during adsorption and decomposition since strongly bonded formate species inhibit the exchange. Although no exchange takes place,  $\text{C}^{16}\text{O}^{18}\text{O}$  and  $\text{C}^{18}\text{O}_2$  can be detected. These products are formed by the spontaneous exchange of oxygen between  $\text{C}^{16}\text{O}_2$  molecules and  $\text{Ti}^{18}\text{O}_2$ . The comparison of the studies shows that there is no direct agreement, if lattice oxygen can be incorporated in the products of the formic acid decomposition or if products containing  $^{18}\text{O}$  can be detected at all. It needs to be noted that only Civiš et al.<sup>15</sup> used isotopically pure  $\text{Ti}^{18}\text{O}_2$ , while in the other reports  $^{18}\text{O}$ -enriched surfaces were investigated.

Kavan et al.<sup>13</sup> reported for the interface between isotopically pure anatase  $\text{Ti}^{18}\text{O}_2$  and  $\text{C}^{16}\text{O}_2$  that without illumination an OIE reaction occurs, while both  $\text{C}^{18}\text{O}_2$  and  $\text{C}^{16}\text{O}^{18}\text{O}$  were detected in the gas phase. If the surface of anatase is covered

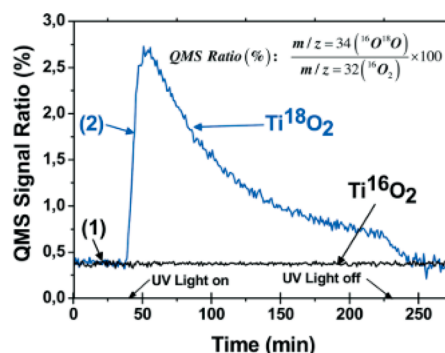
with adsorbed HCl and water, no OIE was observed. Civiš et al.<sup>12</sup> investigated the same interface in the dark and during illumination. As shown in Figure 3, an involvement of oxygen



**Figure 3.** Mechanism of the spontaneous isotopic exchange between C<sup>16</sup>O<sub>2</sub> and Ti<sup>18</sup>O<sub>2</sub> with the involvement of oxygen vacancies. (a) Adsorption of C<sup>16</sup>O<sub>2</sub> to the surface of Ti<sup>18</sup>O<sub>2</sub>. (b) Formation of a CO<sub>3</sub> bidentate species. (c) Release of a C<sup>16</sup>O<sup>18</sup>O molecule. Reprinted with permission from ref 12. Copyright 2011 American Chemical Society.

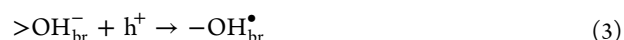
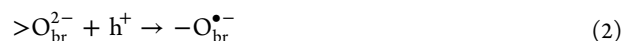
vacancies in the OIE reaction in the dark was found, while the whole process was found to be very fast. One oxygen atom of each C<sup>16</sup>O<sub>2</sub> molecule coordinates to a vacancy, while the carbon atoms coordinate to lattice oxygen (Figure 3a). A CO<sub>3</sub> bidentate species is formed with one oxygen atom from the C<sup>16</sup>O<sub>2</sub> molecule being incorporated into the TiO<sub>2</sub> lattice (Figure 3b). Afterward a C<sup>16</sup>O<sup>18</sup>O molecule is released from the surface, recreating an oxygen vacancy (Figure 3c). The major product of the OIE is C<sup>18</sup>O<sub>2</sub> with a minor content of C<sup>16</sup>O<sup>18</sup>O. The adsorption of water on the surface did not suppress the OIE, and thus the water is not competing with CO<sub>2</sub> for adsorption sites. By laser irradiation of the H<sub>2</sub><sup>16</sup>O-treated Ti<sup>18</sup>O<sub>2</sub>, it was possible to enhance the OIE reaction with C<sup>16</sup>O<sub>2</sub>. Further, as products of the photocatalytic reduction of C<sup>16</sup>O<sub>2</sub>, methane and C<sup>16</sup>O were detected.

Montoya et al.<sup>16</sup> investigated the H<sub>2</sub><sup>16</sup>O photooxidation in the presence of Ti<sup>18</sup>O<sub>2</sub> and Ag<sup>+</sup> ions as electron scavengers. During illumination, a higher <sup>16</sup>O<sup>18</sup>O/<sup>16</sup>O<sub>2</sub> quadrupole mass spectrometry (QMS) signal ratio as compared to the dark could be detected, which turned back to the initial value after switching off the light (Figure 4). In contrast, by applying Ti<sup>16</sup>O<sub>2</sub> instead, independent from the illumination, no change in the QMS signal ratio appeared. Since in the case of Ti<sup>18</sup>O<sub>2</sub> <sup>16</sup>O<sup>18</sup>O was evolved, it could be concluded that the photooxidation of water proceeds via a bridging oxygen from the lattice of TiO<sub>2</sub>, which is incorporated in the oxygen molecules. In the initial step, a 2-fold-coordinated (symbol: >) bridging oxygen (>O<sub>br</sub><sup>2-</sup>) (eq 2) or a 2-fold-coordinated protonated bridging oxygen (>OH<sub>br</sub>) (eq 3) reacts with a photogenerated hole, leading to the formation of a 1-fold coordinated (symbol: -) bridging oxygen radical (-O<sub>br</sub><sup>•</sup>) and a 1-fold coordinated bridging hydroxyl radical (-OH<sub>br</sub><sup>•</sup>), respectively. The further steps yielding molecular oxygen



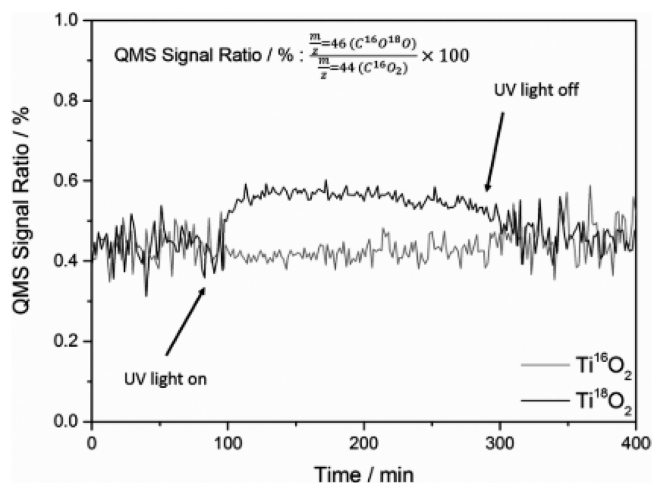
**Figure 4.** <sup>16</sup>O<sup>18</sup>O/<sup>16</sup>O<sub>2</sub> QMS signal ratio from the photooxidation of H<sub>2</sub><sup>16</sup>O in the presence of Ag<sup>+</sup> ions with Ti<sup>16</sup>O<sub>2</sub> and Ti<sup>18</sup>O<sub>2</sub>. Reproduced from ref 16 with permission from The Royal Society of Chemistry.

according to the water redox photooxidation (WRP) mechanism are described elsewhere.<sup>17</sup>

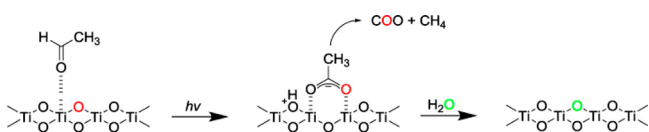


Melchers et al.<sup>18</sup> employed Ti<sup>18</sup>O<sub>2</sub> to analyze the mechanism of the anaerobic acetaldehyde degradation during illumination. In a previous study of the same authors, the incorporation of lattice oxygen into acetate after the adsorption of acetaldehyde was proposed, which resulted in the formation of CO<sub>2</sub> and CH<sub>4</sub>.<sup>19</sup> The comparison of the C<sup>16</sup>O<sup>18</sup>O/C<sup>16</sup>O<sub>2</sub> QMS signal ratio of Ti<sup>16</sup>O<sub>2</sub> and Ti<sup>18</sup>O<sub>2</sub> showed that during illumination no change for Ti<sup>16</sup>O<sub>2</sub> occurs, while for Ti<sup>18</sup>O<sub>2</sub> the ratio increases (Figure 5). Consequently, the incorporation of lattice oxygen into the product molecules, and thus the proposed mechanism (Figure 6), could be proven.

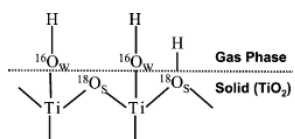
Montoya et al.<sup>20</sup> studied the anaerobic oxidation of benzene in aqueous solutions in the presence of Ti<sup>18</sup>O<sub>2</sub> and Ag<sup>+</sup> as electron scavenger. Ti<sup>18</sup>O<sub>2</sub> with an unlabeled hydrated surface (Figure 7), employing H<sub>2</sub><sup>16</sup>O, was used to distinguish between two possible reaction pathways. Either hydroxyl radicals are generated from adsorbed water species (<sup>16</sup>OH<sub>ads</sub><sup>•</sup>) or lattice



**Figure 5.** C<sup>16</sup>O<sup>18</sup>O/C<sup>16</sup>O<sub>2</sub> QMS signal ratio from the aerobic degradation of acetaldehyde in the presence of Ti<sup>16</sup>O<sub>2</sub> and Ti<sup>18</sup>O<sub>2</sub> under illumination. Reprinted from ref 18. Copyright 2020, with permission from Elsevier.



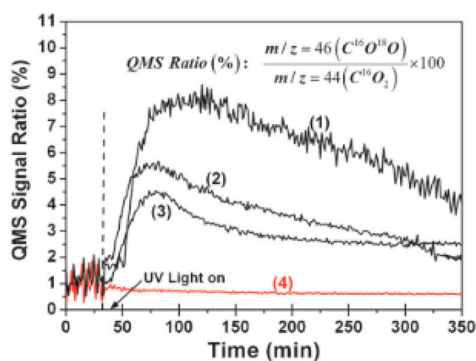
**Figure 6.** Reaction mechanism of the anaerobic degradation of acetaldehyde in the presence of  $\text{TiO}_2$  under illumination. Adapted from ref 18. Copyright 2020, with permission from Elsevier.



**Figure 7.**  $\text{Ti}^{18}\text{O}_2$  surface with labeled bridging oxygens ( $^{18}\text{O}$ ) and unlabeled chemisorbed water species ( $^{16}\text{OH}$ ). Reprinted with permission from ref 20. Copyright 2013 American Chemical Society.

oxygen is involved in the generation of radicals ( $^{-18}\text{O}_{\text{br}}^{\bullet-}/^{-18}\text{OH}_{\text{br}}^{\bullet}$ ) and thus the oxidation of benzene. The  $\text{C}^{16}\text{O}^{18}\text{O}/\text{C}^{16}\text{O}_2$  QMS signal ratio of  $\text{Ti}^{18}\text{O}_2$  was during illumination higher compared to unlabeled  $\text{Ti}^{16}\text{O}_2$ , which indeed confirmed the involvement of bridging oxygens in the mineralization of benzene and the incorporation of these species into the product molecules.

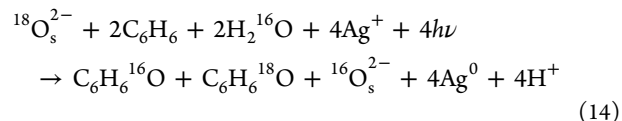
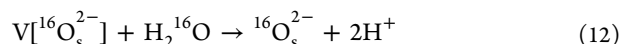
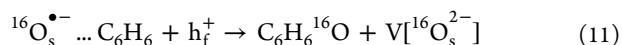
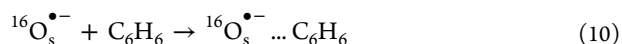
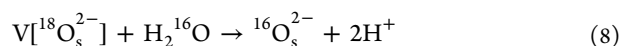
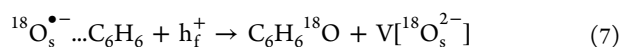
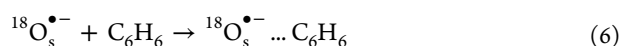
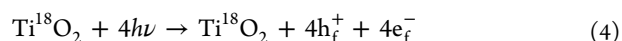
Montoya et al.<sup>21</sup> investigated also the oxidation of benzene in acetonitrile with  $\text{Ti}^{18}\text{O}_2$  in the presence of  $\text{Ag}^+$  as an electron scavenger to prove the incorporation of surface oxygen of  $\text{TiO}_2$  into the mineralization product  $\text{CO}_2$ . The  $\text{C}^{16}\text{O}^{18}\text{O}/\text{C}^{16}\text{O}_2$  QMS signal ratio of  $\text{Ti}^{18}\text{O}_2$  is dependent on the water concentration, while a lower concentration yields higher ratios (Figure 8). For  $\text{Ti}^{16}\text{O}_2$  the ratio under



**Figure 8.**  $\text{C}^{16}\text{O}^{18}\text{O}/\text{C}^{16}\text{O}_2$  QMS signal ratio from the anaerobic mineralization of benzene in acetonitrile in the presence of  $\text{Ti}^{18}\text{O}_2$  (1–3) and  $\text{Ti}^{16}\text{O}_2$  (4) under illumination. The following water concentrations were employed: (1)  $c(\text{H}_2\text{O}) = 0.560 \text{ mmol L}^{-1}$ , (2)  $c(\text{H}_2\text{O}) = 10 \text{ mmol L}^{-1}$ , (3)  $c(\text{H}_2\text{O}) = 24 \text{ mmol L}^{-1}$ , and (4)  $c(\text{H}_2\text{O}) = 24 \text{ mmol L}^{-1}$ . Copyright 2014 Wiley. Used with permission from ref 21.

illumination does not increase, which confirms the incorporation of surface oxygen into the  $\text{CO}_2$  product molecules. Based additionally on their further findings (participation of  $\text{TiO}_2$  terminal oxygen atoms as hole traps and the dissociative adsorption of  $\text{H}_2\text{O}$  into terminal oxygen vacancies), the authors were able to propose a terminal-oxygen indirect electron-transfer (TOIET) mechanism. The excitation of the labeled  $\text{Ti}^{18}\text{O}_2$  leads to the formation of free photogenerated electrons ( $e_f^-$ ) and holes ( $h_f^+$ ) (eq 4). A surface oxygen anion ( $^{18}\text{O}_s^{2-}$ ) is able to react with a free photogenerated hole, which

causes the formation of a terminal radical ( $^{18}\text{O}_s^{\bullet-}$ ) (eq 5). A physisorbed benzene molecule ( $\text{C}_6\text{H}_6$ ) coordinates to a terminal radical, and an incipient covalent bond is formed (eq 6). The reaction with a further free photogenerated hole causes the formation of a phenol molecule ( $\text{C}_6\text{H}_6^{18}\text{O}$ ), which contains an  $^{18}\text{O}$  atom that originates from the surface of  $\text{Ti}^{18}\text{O}_2$  and an oxygen vacancy ( $\text{V}[^{18}\text{O}_s^{2-}]$ ) (eq 7). The vacancy can be healed by the dissociative adsorption of a  $\text{H}_2^{16}\text{O}$  molecule, whereby an  $^{16}\text{O}_s^{2-}$  anion is incorporated into the surface of  $\text{Ti}^{18}\text{O}_2$  (eq 8). As shown in eqs 9–11, the incorporated  $^{16}\text{O}_s^{2-}$  anion can also act as a hole scavenger, which finally results in the formation of a phenol molecule that contains an  $^{16}\text{O}$  atom ( $\text{C}_6\text{H}_6^{16}\text{O}$ ). The resulting vacancy  $\text{V}[^{16}\text{O}_s^{2-}]$  is healed by the dissociative adsorption of a further  $\text{H}_2^{16}\text{O}$  molecule (eq 12).  $\text{Ag}^+$  ions are able to react with the free photogenerated electrons, which leads to the formation of metallic silver (eq 13). In eq 14, the complete process is summarized, which shows the exchange of an  $^{18}\text{O}_s^{2-}$  anion with an  $^{16}\text{O}_s^{2-}$  anion at the surface of  $\text{Ti}^{18}\text{O}_2$ .



## ■ SOLVENT ISOTOPE EFFECTS IN PHOTOCATALYSIS

Solvent isotope studies have been used extensively by organic chemists for decades. In this process, the relative rates of a reaction are compared, when they are carried out in normal water and deuterated water or “heavy” water. The solvent isotope effect (SIE) is the ratio of the rate constant in the “heavy” water ( $k_D$ ) to that observed in normal water ( $k_H$ ):

$$\text{SIE} = k_H/k_D \quad (15)$$

Typically the reactions in the heavy water solvent are significantly slower, and hence the rate constants are lower than those observed in normal water. The slower reaction rate in the deuterated solvent is due to the fact that the deuterated solvent has a lower vibrational zero-point energy, and hence a greater activation energy is required to dissociate the OD bond

compared to OH bonds. Consequently, the rates are slower in deuterated solvents, which are involved in reactions.

Cunningham and Srijaranai were the first to report the use of this technique for a semiconductor photocatalytic process in 1988.<sup>22</sup> In their investigation of the photocatalytic degradation of isopropanol (IPA) using TiO<sub>2</sub>, they observed a primary solvent isotope effect of 3. It was proposed that the reduced rate of IPA destruction in D<sub>2</sub>O was a result of the lower quantum efficiency for the formation of OD• radicals on the TiO<sub>2</sub> surface in the heavy water solvent. As a result of this, there would be a lower number of OD• radicals on the TiO<sub>2</sub> surface, which would be available to attack the isopropanol. On the basis of this proposal, they suggested that the photo-generation of hydroxyl radicals was the rate-determining step for the photocatalytic process.

Robertson et al. also observed a solvent isotope effect of 3 for the photocatalytic destruction of the cyanobacterial toxin microcystin-LR using a P25 TiO<sub>2</sub> photocatalyst.<sup>23a</sup> The solvent isotope effect observed by Cunningham for the decomposition of IPA was the same as that reported by Robertson for the cyanotoxin, considering the substantial difference in structure and the molecular mass of the two substrates. Robertson suggested that this was also a confirmation of Cunningham and Srijaranai's proposal that the hydroxyl radical generation on the photocatalyst surface was also the rate-determining step for the photocatalytic reaction.

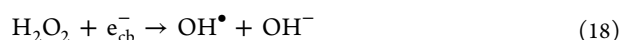
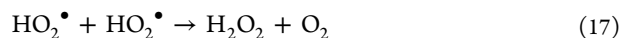
In a subsequent study, Robertson and co-workers investigated the solvent isotope effect on the degradation of microcystin-LR (MC-LR) and another cyanobacterial chemical metabolite, geosmin (GSM), using a Hombikat K01/C TiO<sub>2</sub> photocatalyst.<sup>23b</sup> In this case a solvent isotope effect of 1.5 was observed for microcystin and geosmin,<sup>23b</sup> which was approximately 50% lower than that found in the previous studies by Robertson et al. and Cunningham and Srijaranai (Table 1).

**Table 1. Kinetic Isotope Effect Based on the Photocatalytic Destruction of GSM and MC-LR in Normal and Heavy Water with Hombikat K01/C TiO<sub>2</sub> as a Photocatalyst<sup>a</sup>**

solvent	GSM		MC-LR	
	<i>k</i> (μM min <sup>-1</sup> )	relative rate	<i>k</i> (μM min <sup>-1</sup> )	relative rate
H <sub>2</sub> O	1.56	1.0	8.55	1.0
D <sub>2</sub> O	0.97	0.62	5.44	0.64

<sup>a</sup>Reprinted from ref 23b. Copyright 2011, with permission from Elsevier.

In this study, Robertson et al. proposed that the solvent isotope effect observed for both molecules was mediated via hydroxyl radicals, generated from the subsequent reduction of the superoxide radical anion, produced at the conduction band. After being generated, the superoxide would be hydrated or deuterated by the solvent to form a hydroperoxide ion (eq 16). The hydroperoxide ions may then interact to form hydrogen peroxide, which would then generate OH• (or OD•) radicals following an electron transfer from the conduction band again. This may be rate determining since O<sub>2</sub> has to be generated at the conduction band prior to the interaction with the solvent and the subsequent formation of OD• or OH• species (eqs 17 and 18).

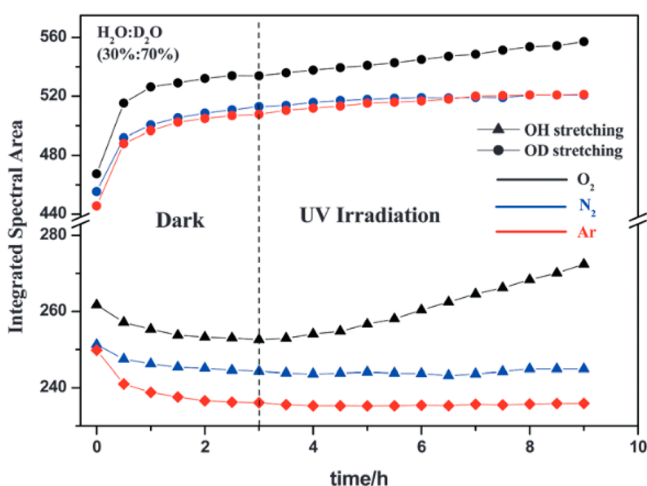


It was suggested that the observed solvent isotope effect could be a result of the rate of the reaction of the solvent with superoxide species rather than by the rate of reaction of OH• (or OD•) on the microcystin or geosmin. If the isotope reaction depended on this latter reaction, one would expect it to be the same no matter what photocatalyst or species being oxidized was utilized.

An interesting observation is the fact that the solvent isotope effect is approximately 3 for P-25 and approximately 1.5 for K01/C. They also suggested that since similar kinetic solvent isotope effects were observed for different substrate molecules on the same photocatalyst materials the interaction of the solvent with the photocatalyst and the rate of oxidation of the solvent were probably the rate-determining steps for the photocatalytic reaction, as opposed to conduction band reduction of oxygen as previously proposed by Gerischer and Heller.<sup>24</sup> Furthermore, Robertson et al. proposed that the reason the kinetic solvent isotope effect observed in this subsequent work was smaller than that in their previous study and Cunningham's work was due to the fact that different photocatalyst materials were employed,<sup>23b</sup> and hence the effect was likely to be dependent on the photocatalyst material.

Belhadj et al. used solvent isotope effects to study the adsorption of water and deuterium oxide on TiO<sub>2</sub> surfaces in the dark and under UV(A) irradiation using in situ ATR-FTIR spectroscopy under aerobic and anaerobic conditions.<sup>25a</sup> Under dark conditions in a mixture of H<sub>2</sub>O and D<sub>2</sub>O solvents, an isotopic exchange was found to occur on the surface of the TiO<sub>2</sub> material. Following irradiation with UV(A) light, the quantity of both OH and OD groups was found to be increasing in the presence of molecular oxygen. Additionally, hydroperoxide was generated through a photocatalytic process under aerobic conditions, which was believed to be produced as a result of the reduction of molecular oxygen adsorbed at the TiO<sub>2</sub> surface by the photogenerated conduction band electrons, as opposed to being generated via water oxidation from valence band holes. It was also demonstrated from the spectroscopic studies that under conditions where the percentage of H<sub>2</sub>O was significantly less than that of D<sub>2</sub>O there was an exchange of solvent groups on the TiO<sub>2</sub> surface with the OD<sup>-</sup> ions, having a stronger adsorption affinity to the photocatalyst compared to the OH<sup>-</sup> ions. Following illumination with UV light, both OH and OD groups were generated on the photocatalyst surface in the presence of oxygen. The generation of these groups also increased the hydrophilicity of the TiO<sub>2</sub> surface. If the experiment was conducted under either a nitrogen or argon atmosphere, there was no evidence of the formation of OH and OD groups, and the hydrophilicity was inhibited (Figure 9). This result indicated that under UV irradiation oxygen played a critical role in both the photocatalytic response and the photoinduced hydrophilicity.

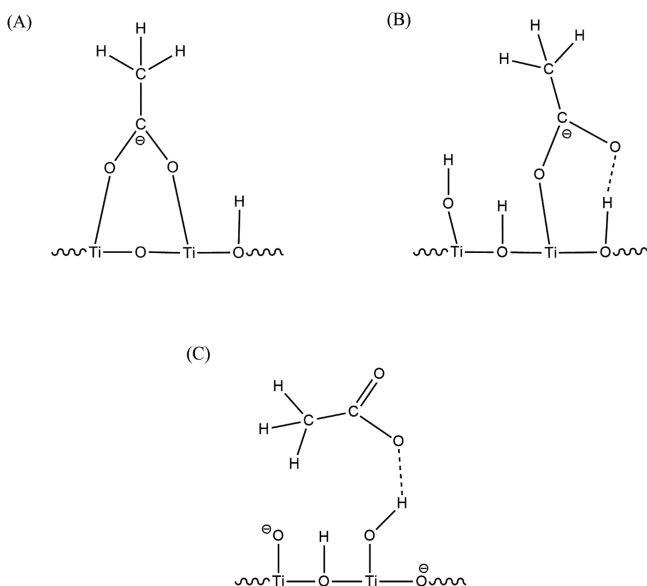
In a subsequent study, the adsorption and photocatalytic degradation of acetate on TiO<sub>2</sub> surfaces was investigated in H<sub>2</sub>O and D<sub>2</sub>O by both attenuated total reflection Fourier transformed infrared spectroscopy (ATR-FTIR) and EPR spectroscopy.<sup>25b</sup> Different interactions between the adsorbed acetate and OD groups resulted from the isotopic exchange on the TiO<sub>2</sub> surface following adsorption of D<sub>2</sub>O. The interaction



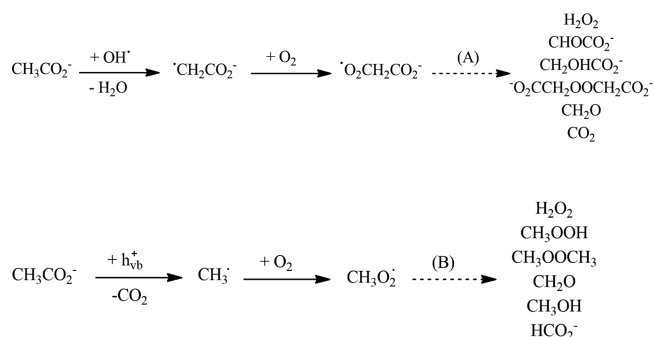
**Figure 9.** Evolution of the intensity of the integrated spectral areas of OH and OD stretching groups before and after UV irradiation: effect of dissolved O<sub>2</sub>, N<sub>2</sub>, and Ar on the adsorption of H<sub>2</sub>O–D<sub>2</sub>O on the TiO<sub>2</sub> surface. Reprinted from ref 25a. Published by the PCCP Owner Societies.

of the acetate with the TiO<sub>2</sub> surface was found to be strongly influenced by the pH, and a range of surface complexes with the acetate were observed to form. Under acidic conditions, the formation of a bidentate structure involving two distinct Ti atoms appeared to be the preferred complex structure. At pH values close to the point of zero charge for the TiO<sub>2</sub>, the acetate favored a monodentate complex, formatted through adsorption to the positively charged TiO<sub>2</sub> anatase material (Figure 10).

Following irradiation with UV(A) light, hydroxyl radicals were observed under alkaline conditions, while methoxy radicals were generated under acidic conditions. Two different degradation pathways were proposed for the acetate under acidic and alkaline conditions (Figure 11), which were



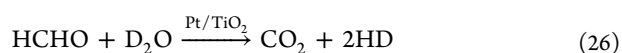
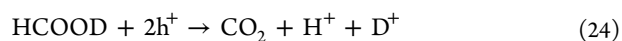
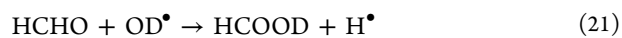
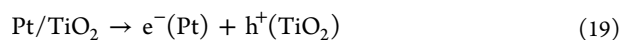
**Figure 10.** Schematic representation for the adsorption of acetate on the anatase surface (UV100) in the dark at pH < pHzpc (A), pH ≈ pHzpc (B), pH > pHzpc (C). Reprinted from ref 25b. Copyright 2016, with permission from Elsevier.



**Figure 11.** Proposed mechanism for the photocatalytic reaction of acetate at pH 9 (A) and pH 3 (B). Reprinted from ref 25b. Copyright 2016, with permission from Elsevier.

supported by the experimental studies performed using ATR-FTIR and EPR spectroscopy. Overall, the results of the EPR study suggested that under alkaline conditions acetate degradation was mainly promoted by attack by valence band generated hydroxyl radicals. Under acidic conditions, the degradation appeared to occur via direct oxidation via photogenerated valence band holes.

Solvent isotope studies were also used for the investigation of the simultaneous photocatalytic degradation of formaldehyde and hydrogen evolution on a platinumized TiO<sub>2</sub> material under an oxygen-free atmosphere.<sup>25c</sup> Using QMS and ATR-FTIR spectroscopy for analysis, the main reaction products obtained from the photocatalytic degradation of 20% formaldehyde were hydrogen and carbon dioxide in a ratio of 2 to 1. From the solvent isotope study, it was found that the rate of mineralization of formaldehyde to CO<sub>2</sub> is significantly reduced with increasing concentration of D<sub>2</sub>O. Following the investigation of the solvent isotope effect on the system using ATR-FTIR analysis, it was proposed that the formaldehyde oxidation was promoted by attack by OD<sup>•</sup> radicals, formed from the reaction with the photogenerated valence band hole. This reaction generated a surface-adsorbed deuterated formic acid (HCOOD), which subsequently underwent further oxidation by valence band holes in a photo-Kolbe-type reaction. The photogenerated conduction band electrons were proposed to simultaneously reduce H<sup>+</sup> and D<sup>+</sup>, originating from both formaldehyde and D<sub>2</sub>O, to form molecular HD. The yield of the HD gas was found to be strongly influenced by the solvent and was maximized when the ratio of H<sub>2</sub>O:D<sub>2</sub>O was 20%:80%. The proposed mechanism for the simultaneous hydrogen production and formaldehyde oxidation in the presence of D<sub>2</sub>O is summarized in eqs 19–26 below:<sup>25c</sup>



## ■ SCOPE FOR RESEARCH DEVELOPMENT AND FOCUS

Each of the studies considered in this paper related to the labeling of photocatalyst materials and target molecules have utilized  $\text{TiO}_2$  as the photocatalyst. This is also the case for the studies dealing with solvent isotope effects. Although  $\text{TiO}_2$  is the most studied photocatalyst material, there has only been a relatively small number of reports related to isotope effects. As has been detailed above, the use of these isotope studies has enabled important insights to be gained for photocatalytic reactions on  $\text{TiO}_2$ , but there is still significant scope for further studies using these techniques.

For future research, while also investigating the isotope effects of the photocatalytic decomposition of other substrates on  $\text{TiO}_2$  materials, it would be important to extend the studies to other photocatalyst materials as well. For example,  $\text{Fe}_2\text{O}_3$ ,  $\text{WO}_3$ ,  $\text{CdS}$ ,  $\text{C}_3\text{N}_4$ , and  $\text{SrTiO}_3$  are known as photocatalytically active materials, while the labeling of the catalyst or reactant molecules would allow us to get deeper insights into the corresponding mechanisms using these materials.

With respect to  $\text{TiO}_2$  itself, there are many more reaction mechanisms that should be investigated based on solvent isotope effects. In particular, the involvement of terminal hydroxyl or oxygen radicals in the photocatalytic mechanism, as one of the initial steps, might be either established or refuted.

The technique could also be used for kinetic studies, particularly in the case of rapidly decomposing intermediates, which may be more easily followed in the heavy water solvent.

## ■ CONCLUSION

The investigation of isotope effects represents a powerful tool in the area of photocatalysis to study the mechanisms of the reactions occurring on the surface of photocatalyst materials. Using this technique, it is possible to elucidate whether photocatalyst surface atoms are transferred into product molecules, while also the incorporation of atoms from reactant molecules into the surface of the photocatalyst can be observed. Furthermore, by exchanging  $\text{H}_2\text{O}$  by  $\text{D}_2\text{O}$ , the ratio of the rate constants between both solvents can be followed to investigate whether the generation of hydroxyl radicals is the rate-determining step of a reaction. Using  $\text{D}_2\text{O}$  as a solvent has a further advantage since it allows the determination of whether hydrogen atoms in product molecules originate from reactant molecules or from the solvent. Consequently, it is important to perform such studies to allow the determination of the mechanistic pathway of the photocatalytic process. It should be noted that isotope effect studies are, however, not enough as the sole process to provide such detail, but in combination with other tools, they can provide important information on such processes.

In conclusion, it is clear that the application of isotope studies is a versatile and useful tool for studying photocatalytic reactions; however, the technique has been only applied in a relatively small number of investigations. There is therefore great scope for the further application of this technique in the field of semiconductor photocatalysis, and it is anticipated that this will be an area of growing interest within the photocatalytic research community over the next few years.

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### Notes

The authors declare no competing financial interest.

### Biographies



Carsten Günemann received his M.Sc. degree in 2017 from the Gottfried Wilhelm Leibniz Universität Hannover under the supervision of Prof. Dr. Detlef W. Bahnemann, and he is currently a Ph.D. student in the same group. His research interests include transient absorption spectroscopy, (photo)electrochemistry,  $\text{TiO}_2$  films, and halide perovskites.



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