

Mechanisms of catalyst action in the TiO₂-mediated photocatalytic degradation and *cis–trans* isomerization of maleic and fumaric acid

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Abstract

The partial photocatalytic degradation of maleic acid has been investigated with the purpose of elucidating the mechanism of catalyst action for some of the early transformations. In particular, it is proposed that the photocatalytically induced *cis–trans* isomerization of maleic acid and fumaric acid is initiated by adsorption-dependent reductive electron transfer. An investigation into the involvement of superoxide in the oxygenation reactions observed near neutral and higher pH clearly demonstrates that superoxide does not initiate the chemistry.

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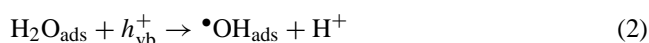
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1. Introduction

Semiconductor-mediated photocatalytic degradation of organic pollutants in water is a well-documented phenomenon that has found extreme generality with regard to substrate, particularly with TiO₂ photocatalysts [1–9]. Among the most important classes of compounds from both chemical and environmental perspectives is the group containing aromatic rings, including various phenolic pollutants, PCBs, and many herbicides and pesticides. Over the last few years, areas that have received much greater attention in the study of these pollutants are the array of chemical pathways by which compounds are degraded and the related issue of the mechanisms by which the chemical transformations take place.

It is widely understood that the great majority of chemical steps are oxidative in nature, usually involving hydroxyl radical-like chemistry or oxidative electron transfer. Though photocatalytic degradation results in the oxidation of organic carbon to CO₂, there are a few instances in which reductive steps (Eq. (8)) are known, such as in the reduction of azo dyes [10–15], electron poor aromatics [16–18], or quinones [19–25]. However, in many mechanistic discussions of degradations of large organic molecules, a key

issue is not whether reduction of the organic occurs, but rather over the competition between processes represented in Eqs. (2)–(4), i.e., whether oxidation occurs by way of hydroxyl type chemistry or direct oxidative electron transfer.



In this paper, we examine the early transformations related to the degradation of maleic and fumaric acid under conditions of TiO₂-mediated photocatalytic degradation. These compounds are ubiquitous intermediates in the degradation of aromatic compounds [24–32]; their degradation is thus important in the mineralization of a wide variety of pollutants.

Among the earliest photocatalytic studies on carboxylic acids is Bard's report on the degradation of benzoic acid in

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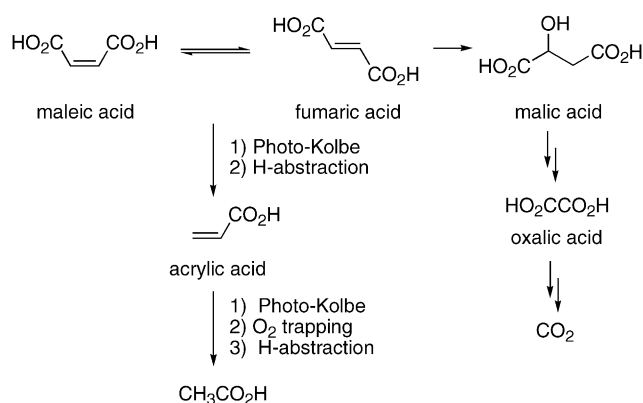
aqueous media using platinumized TiO₂ [33]. Hydroxylation of the aromatic ring to give salicylic acid and decarboxylation with oxidation to give phenol (presumably after secondary reaction of Ph• with O₂) were the initial transformations. Subsequent studies focused on the regiochemistry of hydroxylation of benzoic acid and various halogenated derivatives [34,35]. It was reported that hydroxylation of monochlorophenols was not competitive with decarboxylation [35], but hydroxylation and decarboxylation were both reported as primary reactions of polychlorophenols [36]. With aromatic polycarboxylic acids, both hydroxylation and decarboxylation are reported as primary reaction pathways [37].

There are also several publications reporting the degradation of various simple alkyl carboxylic acids. Again following early work by the Bard group, subsequent investigators reported that there is a significant pH dependence on the balance between H₂ and CH₄ evolution from acetic acid and that longer chain acids (e.g., butyric acid) gave evidence for non-Kolbe pathways apparently initiated by hydrogen abstraction from the alkyl groups [38,39]. Production of chloride was also noted from chloroacetic acid derivatives [39].

Facts directly relevant to the present investigation emerge from a recent study of the degradation of butyric acid [40]. The equilibrium concentration of butyric acid in aqueous solution is higher at pH values above the acid dissociation constant, implying that adsorption is stronger for the protonated acid. Nonetheless, the observed rate of degradation was higher at pH 6.9 than that at pH 3.6. Product distributions varied, but this was attributed mainly to the different distributions of species available to react after radical formation. The interpretation was based on a competition between hole oxidation to give the decarboxylation and chemistry initiated by hydrogen abstraction. Similar competitive chemistry was observed for the more functionalized hydroxybutanedioic acid (malic acid) [41].

2,4-Dichlorophenoxyacetic acid (also known as the herbicide 2,4-D) and closely related compounds have received special attention because of their direct environmental relevance [42–46]. Following the pattern outlined above, the main initial product (2,4-dichlorophenol) derives from decarboxylation, but studies also report competitive arene hydroxylation under some conditions. The most detailed mechanistic work of these was again interpreted in terms of a competition between direct hole oxidation and hydroxyl radical chemistry. At low pH (where we may infer that the equilibrium adsorption constant is higher), it is asserted that direct oxidation by holes predominates, whereas hydroxyl-type chemistry predominates in neutral and basic solution. A purely radical mechanism based on competition between surface-bound and bulk solution chemistry was rejected on the basis of experiments using solution-phase hydroxyl radical scavengers [42].

The most relevant study to the present work is a paper by Franch et al. in which the degradation of oxalic, fumaric, and maleic acids is reported [47]. Adsorption isotherms indi-



Scheme 1. Summary of pathways proposed by Franch et al. for photocatalytic degradation of maleic or fumaric acid at pH 3 in TiO₂ slurries [47].

cate that approximately three times more maleic or fumaric acid is bound to TiO₂ at pH 3 than at pH 9. Like the butyric acid case, the initial degradation rate is modestly higher at the higher pH, despite the poorer adsorption. These authors conclude that degradation occurs in the homogeneous phase at high pH by means of solvated hydroxyl radicals. Franch et al. also report a change in product distribution with pH. At pH 3, the fastest process is *cis–trans* isomerization, which is attributed to interaction between the acids and photogenerated holes. Aside from this, the major product is reported to be acrylic acid (CH₂=CH–CO₂H), attributed to photo-Kolbe chemistry. A small amount of photohydration to malic acid is reported as well. Downstream intermediates include acetic, oxalic, and formic acids. This is summarized in Scheme 1. At pH 9, very little intermediate build-up is reported aside from oxalic acid, implying that the first chemical step is slower than subsequent oxidations. In a related study of the degradation of malic acid [41], maleic and fumaric acid are reported as observed intermediates, implying that photoinduced dehydration may occur, as well as photoinduced hydration.

In this paper, we report an investigation of the degradation of maleic and fumaric acids that begins in a manner parallel to the work of Franch et al. [47]. Most of our product observations are in agreement with the previous work. We report a series of experiments designed to elucidate more clearly the mode of molecule-catalyst interaction that leads to various processes, including especially tartaric acid formation and the *cis–trans* isomerization.

2. Experimental

2.1. Materials

All reagents were purchased from Aldrich and used without further purification unless otherwise indicated. Tartaric acid and Superoxide dismutase (SOD, from bovine erythrocytes, 3000 units in 0.8 mg) were purchased from Sigma.

Water was purified with a Milli-Q UV plus system (Millipore, resulting in a resistivity more than $18 \text{ M}\Omega \text{ cm}^{-1}$). TiO_2 was Degussa P-25. The epoxides of sodium fumarate and sodium maleate were prepared [48] by stereospecific epoxidation by the method of Payne and Williams [49]. Dihydroxyfumaric acid dimethyl ester was prepared by a reported method [50].

2.2. Standard degradation conditions

Except as noted, degradations were carried out under these standard conditions. A 100 mL aqueous sample containing 2.0 mM maleic acid (unless other concentration or substrates, e.g., fumaric acid, are specified) and 50 mg suspended TiO_2 was prepared. The pH of suspension was adjusted using HCl (pH 2), phosphate buffer (10 mM, pH 7.0), or NaOH (pH 12). The mixture was treated in an ultrasonic bath for 5 min to disperse larger TiO_2 aggregates and purged with O_2 for 20 min in the dark before the irradiation was started. The mixture was continuously purged with O_2 throughout irradiation. Irradiations were carried out with magnetic stirring and a fan that kept the temperature at ambient levels in a Rayonet mini-photochemical reactor equipped with eight 4 W “black light” fluorescent lamps which have a broad emission spectrum centered at 360 nm. A few experiments were carried out with similar low-pressure fluorescent tubes with emission centered at 300 nm, as noted. Both sets of tubes were those sold by Southern New England Ultraviolet Company for use with the Rayonet reactors. After reaction, the mixtures were acidified, centrifuged, and passed through 0.2 μm Whatman filters to remove TiO_2 . Water was removed by freeze-drying. Small, calibrated quantities of adipic acid were added after the photoreaction when an internal standard was required for quantification.

2.3. General analytical methods

Following the removal of water, the intermediate degradation products were identified and quantified as their trimethylsilyl (TMS) derivatives, using GC-MS procedures reported in our earlier work [24]. For analyses concerned with product identification, parallel workups in which a reduction step (NaBH_4 or NaBD_4) was inserted before the silylation were also carried out [24]. The GC-MS instrument was a Varian 3400CX GC equipped with a 30 m DB-5 column, coupled to a Finnigan Magnum ion trap mass spectrometer. The temperature program was 120°C for 4 min, followed by a ramp to 200°C at $5^\circ\text{C}/\text{min}$, then ramp at $15^\circ\text{C}/\text{min}$ to 280°C . An HP 5890 gas chromatograph with FID detection was also used for routine quantification.

2.4. Additional experimental conditions

2.4.1. Superoxide experiments

Potassium superoxide (KO_2) is slightly soluble in dry dimethyl sulfoxide (DMSO). Using the method of Valentine

[51], 0.15 M solutions of KO_2 were prepared in the presence of 0.30 M 18-crown-6 [52]. Maintenance of the characteristic pale yellow color of these solutions was taken as evidence that the superoxide remained. Reactions using either pyridine or DMSO as the solvent for maleic acid were carried out with KO_2 :maleic acid molar ratios of 1:1, 5:1, 1000:1, and 5:1 in the presence of 1% added water. The following example is representative of the reaction conditions. To a solution of maleic acid (100 mL, 2 mM in DMSO), the KO_2 solution (50 mL) was added dropwise over the course of 1 h. The solvent was evaporated under vacuum and the residual material was silylated as usual and analyzed by GC-MS. Neither degradation of maleic acid nor any new organic compounds were observed.

2.4.2. Superoxide dismutase (SOD) experiments

The method of Pichat and co-workers [27,53–55] was closely followed, and some of his experiments were duplicated as positive controls, as our results were universally negative, i.e., there was little or no effect of adding SOD. In the relevant experiments, maleic acid (39 mmol) and TiO_2 (25 mg) were dispersed in 50 mL water, buffered at pH 7 with the buffer supplied with the enzyme by Sigma. After ultrasonic treatment and O_2 purging as usual, 1500 units of SOD were introduced. The mixture was irradiated for 40 min, and then worked up and analyzed in the usual fashion. Control experiments using identical conditions, save that the SOD enzyme was not added, produced identical results.

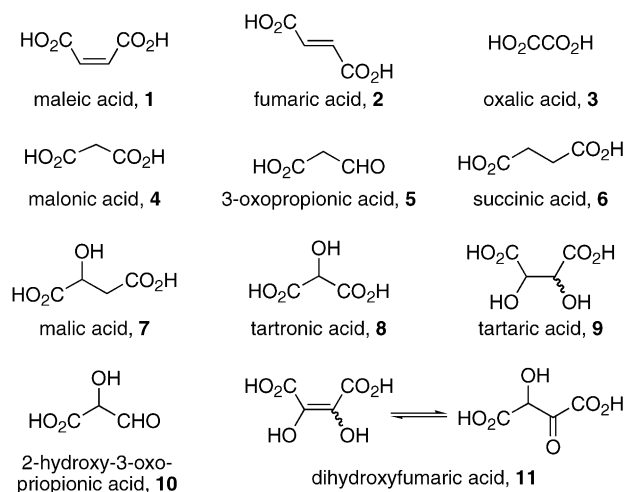
2.4.3. Fluoride experiments

These degradation reactions, workup, and analyses were carried out in the standard fashion, with the following exceptions: sufficient NaF was added to raise the concentration of the solution to 20 mM before addition of the TiO_2 . The pH of the slurry was adjusted to 3 to maximize surface coverage by fluoride ions [56,57]. As noted in the text, experiments were carried out both under conditions of constant O_2 purging and Ar purging. A merry-go-round apparatus, which accommodated 10 mL, rather than 100 mL, samples, was used to allow simultaneous photolyses of the O_2 - and Ar-purged samples.

3. Results and discussion

3.1. Product mixtures and exploratory degradations

Photocatalytic degradations of maleic acid (**1**) were carried out at pH 2, 7, and 12 using the light from broadly emitting fluorescent tubes centered at 360 nm. The solutions initially contained 2.0 mM maleic acid and 50 mg TiO_2 in 100 mL O_2 -saturated water, unless otherwise noted. Separate control experiments showed that no degradation occurred in the absence of TiO_2 or irradiation. Experiments carried out in the absence of O_2 are described in more detail below, but oxidative transformations were curtailed, compared to



Scheme 2. Starting materials and observed products.

the ordinary conditions. We did not repeat the more extensive kinetic experiments of Franch, et al. but observed that the degradations were faster at high pH, in line with their reports [47].

We observed many of the same degradation intermediates as Franch, and a few more. This is probably reasonable, given that we used GC-MS detection, and they used HPLC with UV detection. However, we did not observe any acrylic acid, nor did Herrmann et al. in their study of malic acid, which generated fumaric/maleic acid [41]. The four-carbon intermediates we observed included fumaric acid, malic acid, tartaric acid, dihydroxyfumaric acid, and succinic acid as shown in Scheme 2. The presence of dihydroxyfumaric acid (**11**) was deduced in the degradations at neutral pH from reductive workups using NaBD₄, which yield deuterated tartaric acid before silylation. The ratio of mass intensities showed that slightly more than half of the tartaric acid peak represented **11**. Control experiments showed that none of the reported compounds decomposed under the experimental conditions (in the dark) throughout the pH range used on the time-scale of our workups and analyses.

Downstream degradation products were also observed. The three-carbon intermediates included 3-oxopropionic acid, malonic acid, tartronic acid and 2-hydroxy-3-oxopropionic acid. The only identified 2-carbon product was oxalic acid. We did not assay for either acetic or formic acid. Small quantities of very high molecular weight compounds (i.e., long GC retention times) were sometimes observed.

As previously noted [47], there is a distinct dependence of the product mixtures on pH. The observed mixtures obtained after a fixed irradiation period of one hour and silylative workup are shown in Table 1 and Scheme 2. A representative time-trace of intermediates of partial degradation at pH 12 is given as Fig. 1.

Control experiments, consisting of partial degradations using 30 mM H₂O₂, in lieu of TiO₂, and irradiation centered

Table 1

Product distributions (mM) after 1 h irradiation for degradations of 2.0 mM maleic acid (**1**) at pH 2, 7, and 12.

Compound	pH 2	pH 7	pH 12
1	1.43	1.34	0.66
2	0.20	0.01	0.019
3	0.011	0.19	0.21
4	0.036	0.015	0
5	0.058	0.09	0
6	0.012	0.008	0
7	0.005	0.004	0.004
8	0	0.029	0.25
9	0	0.029	0.369
10	0	0.09	0.006

at 300 nm, were carried out. These reactions produce free hydroxyl and hydroperoxyl radicals. The observed early intermediates were very similar to those reported for the pH 7 TiO₂ experiments (Table 1), regardless of the pH of the H₂O₂ experiments. Tartaric acid was the largest component of the product mixture and fumaric acid was not observed. Along with the dark controls, these experiments show that the variation of products with pH shown in Table 1 is not due to selective secondary degradation of intermediates, but rather to differential rates of formation.

3.2. Isomerization mechanisms and the question of bulk water versus surface-bound mechanisms

One of the most fundamental questions regarding the nature of the substrate-catalyst interaction in photocatalytic degradation is whether reactions occur in the homogeneous bulk phase or at the surface of the catalyst. It is not a question that can be easily settled with steady-state kinetics experiments: every plausible kinetic model based on surface-bound or homogeneous reactive intermediates reacting with

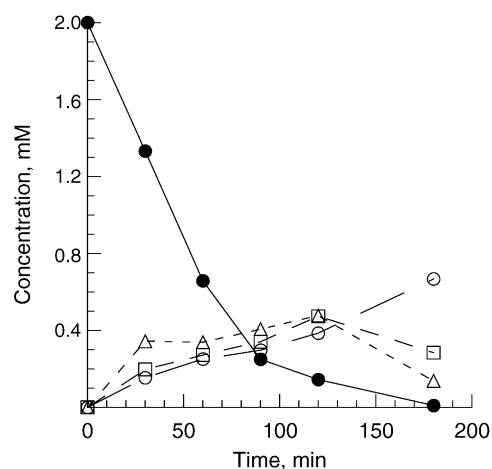


Fig. 1. The variation of the relative concentration of maleic acid (filled circles) and oxalic acid (open circles), tartronic acid (squares) and tartaric acid (triangles) at pH 12. The initial concentration of maleic acid was 2.0 mM.

substrate yields kinetic information of the same form [58]. Thus, this is still a question of some dispute, though the more conventional position at this point is that most reactions occur at the surface [59]. Nonetheless, previous investigators argued that degradation at higher initial pH occurs in the bulk water [47] because of the inverse relationship between the degradation rate and adsorbed material. Additionally, methanol, a known scavenger of HO^\bullet , was lowered the rate of degradation by a factor of 2 at pH 9, but not at all at pH 3.

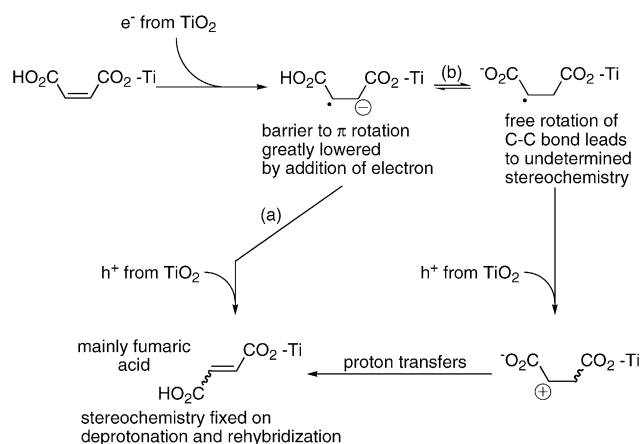
In other publications, we have suggested that hydroxyl-like chemistry may occur at or near the surface of the catalyst, but may have less rigorous requirements for specific adsorption modes or sites of adsorption than direct electron transfer reactions between the substrate and the photoactivated TiO_2 particle [24,29]. For example, surface-bound hydroxyl radicals may be formed and remain stable until diffusion either from bulk or through multilayer adsorption brings an appropriate substrate in contact with the reactive species. On the other hand, it is unlikely that a valence-band hole will “wait around” for an organic substrate, rather than finding a surface trap to make a surface-bound hydroxyl radical.

The formation of fumaric acid from maleic acid at low pH struck us as a reasonable case to test for surface-bound versus bulk mechanisms. Also, the preliminary product study data and H_2O_2 photolyses suggested the possibility of an electron transfer mediated reaction of a carboxylic acid that did not lead to Kolbe chemistry, an unusual result.

Having established that HO^\bullet from H_2O_2 photolysis does not cause substantial *cis-trans* isomerization of maleic acid, we investigated whether maleic acid acts as the electron acceptor or donor with activated TiO_2 . The first set of experiments compared normal O_2 -saturated suspensions to otherwise identical Ar-purged suspensions, i.e., those without O_2 . This technique usually [60] results in the almost complete shutdown of degradative processes [24,25,29,61]; this is universally attributed to efficient e^-/h^+ recombination because there is no O_2 available to act as an electron sink. Inhibition occurs even when reactions are postulated to occur by oxidative electron transfer. However, if an alternative electron acceptor is available, then reactivity can continue.

Standard maleic acid degradation suspensions, adjusted to pH 2, were prepared such that half were O_2 -purged as usual, and half were Ar-purged, and they were simultaneously photolyzed. After 1 h of photolysis, the O_2 -purged solutions had a total conversion of 24%. This could be fully accounted for by the appearance of fumaric acid (19%), malonic acid (1.4%), succinic acid (2.7%), and malic acid (0.9%). The Ar-purged solutions had a remarkable 83% conversion, of which 82.5% was fumaric acid, with the observable remainder being succinic acid.

This experiment clearly shows that O_2 in fact *inhibits* the *cis-trans* isomerization of maleic acid, providing strong evidence that maleic acid acts as an electron acceptor. The simplest explanation for the increased efficiency in the absence of oxygen is straightforward: under oxygenated conditions,



Scheme 3. A plausible schematic mechanism for *cis-trans* isomerization that begins with reductive electron transfer. The protonation states of the intermediates are speculative. (a) Rotation of the $3e^-$ p-system, probably in the μs time regime, assumed to be faster than proton transfer in the acidic aqueous regime. (b) Protonation by low pH water assumed to be faster than $\text{C}_2\text{-C}_3$ bond rotation.

O_2 acts as a competitor with maleic acid for accepting electrons from activated TiO_2 . This interpretation requires that superoxide not be an effective catalyst for *cis-trans* isomerization (as later shown, see below), that the radical anion can isomerize, and that the radical anion is able to return the electron to TiO_2 or another species [62]. An outline of a reasonable mechanism is given in Scheme 3.

It is well understood that the rotational barrier of p-systems is drastically lowered by the addition of an electron because it occupies a formally antibonding orbital and thus reduces the p bond order. We are unaware of definitive experiments that give the timescale of bond rotation near room temperature for appropriately close model systems, but reasonable estimates based on epr experiments put the *cis-trans* isomerization of some stilbene-like radical anions in the microsecond time regime [63–65]. If this is faster than protonation of the radical anion in aqueous acidic medium, then the isomerization is accomplished at this stage. Return of the electron to the TiO_2 particle re-sets the stereochemistry of the double bond, as shown in path (a). However, it is not immediately clear whether the bond rotation of the three-electron p-system is faster than the rate of protonation of the anion radical in acidic media. Even if protonation is fast, though, the essence of the mechanism is preserved, as shown in path (b), in that oxidation of the (protonated) radical will be quite facile.

These results led us to attempt to obtain a photocatalyzed photostationary state of the maleic/fumaric acid mixture at pH 2. These experiments were carried out under standard pH 2 conditions, save that they were Ar-purged and that experiments were carried out using both maleic and fumaric acids as starting materials. The results (Fig. 2) show that essentially identical product mixtures are obtained and that, as expected, fumaric acid is predominant. The final product mixtures were very close to 92% fumaric acid, 7% maleic

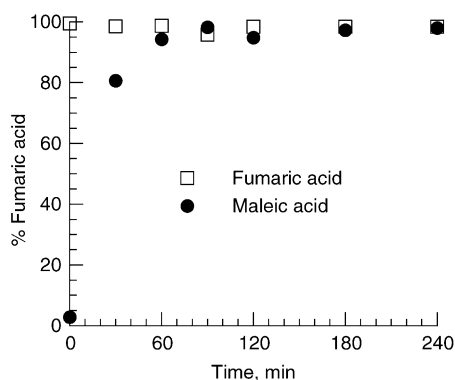


Fig. 2. A photostationary state arrived at by photocatalytic treatment of either maleic or fumaric acid in the absence of O_2 at pH 2. The final proportion of fumaric acid is approximately 94%.

acid and 1% succinic acid, relative to the initial 2.0 mM concentration. It is interesting to note that the sole new product observed is a reductive product from maleic/fumaric acid, consistent with reductive electron transfer.

The O_2 versus Ar experiment was repeated at pH 12, where the acids are completely dissociated when in the bulk phase. Under these conditions, after an hour, the oxygen-saturated sample had lost 85% of its initial maleic acid. Of that, only 2.5% was fumaric acid, with oxalic acid making the bulk of the remainder (78%) along with small quantities of the other usual materials, in agreement with Franch's reports. This latter result, along with the high conversion, obviously implies considerable downstream degradation. With Ar-purging, the total conversion was only 32%, of which only 2.2% was fumaric acid. (Of the rest, 29.5% was malic acid.) The most important result here is that Ar purging does not completely shut down the reaction. A possible interpretation is that maleic acid can act as an electron acceptor even at this high pH, but that in its deprotonated state it is not as reactive to isomerization, perhaps because it cannot undergo the necessary protonation for easy bond rotation before back electron transfer or other chemistry occurs (e.g., Scheme 3, path b). The binding isotherms of Franch et al. [47] clearly demonstrate that there is still adsorption between maleic or fumaric acid and TiO_2 even at high pH, which is at least consistent with this speculation.

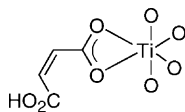
Another set of experiments was carried out in the presence of fluoride anion. The addition of fluoride anion to TiO_2 suspensions at low pH has been shown to produce homogenous hydroxyl radicals and dramatically reduce the surface-bound chemistry of phenol, a poorly adsorbing substrate [56,57]. Broadly speaking, this effect is attributed to displacement of the surface hydroxyls by fluoride (maximized at pH 3–4) and the concomitant change in surface properties. Water can be oxidized to form hydroxyl radicals that are not bound to the titania surface. For example, cyanuric acid, a compound that does not adsorb to TiO_2 in solution and is ordinarily completely resistive to photocatalytic degradation by TiO_2 slurries, is degraded by the TiO_2/F system [66]. Minero also

showed that TiO_2/F was able to degrade phenol in the absence of O_2 much more rapidly than does "naked" TiO_2 , though more slowly than in the presence of O_2 . Presumably, this derives from diffusing HO^\bullet effectively leading to more efficient charge separation than is possible with naked TiO_2 .

Degradations of maleic acid and fumaric acid were carried out at pH 3 in the absence of O_2 with fluoride added, and without fluoride (also without O_2) as a control. The addition of fluoride was shown to severely curtail *cis-trans* isomerism. After 1 h of simultaneous photolysis of four maleic acid samples, the product distribution for the control sample was fumaric acid 6.0%, succinic acid 1.0%, malic acid 2.0%, with a total conversion of 9.0% [67]. In the presence of fluoride, identical photolyses showed that the fumaric acid was reduced to 1.8%. Malic acid was observed at 4.7%, for a total conversion of 6.5%. The clear implication of these data is that inhibition of adsorption also inhibits *cis-trans* isomerization, again consistent with an electron transfer-mediated mechanism.

Separate degradations were also carried out at pH 3 with fluoride anion with O_2 present. The mass balance was poor, even at moderate conversion. At 31% conversion of maleic acid, 0.3% oxalic acid, 1.6% fumaric acid, 0.6% tartronic acid and 2.2% tartaric acid were detected. A similar result showing very little isomerization was observed using fumaric acid as the starting material. The poor mass balance again implies that further degradation of the early intermediates to CO_2 was probably faster than the initial step. While TOC experiments were not run to check this, the result is consistent with Minero's report of much greater mineralization with O_2 than without [56,57]. Again, the implication is that solution phase chemistry is not responsible for the isomerization reaction.

As a final control, the substrate was modified by using the methyl ester (i.e., dimethyl maleate), rather than the carboxylic acid. This would prevent a binding mode in which C–O–Ti linkages were made. Using otherwise standard degradation conditions, at neutral pH, the major observed products were the dimethyl ester analogs of tartaric acid, dihydroxyfumaric acid, and the monomethyl ester of oxalic acid. At pH 2, however, the major product was dihydroxyfumaric acid diester, with almost no dimethyl fumarate observed. We thus conclude that there is a quality about the carboxylic acid functionality itself—differentiated from the ester—that is required for efficient *cis-trans* isomerization. We postulate that this property is related to a C–O–Ti binding mode analogous to that which was proposed (for example) by Moser et al. for aromatic acid derivatives [68], or characterized by Martin et al. for 4-chlorocatechol [69]. The relevant bond lengths make it seem most likely that a single Ti atom is involved, but we cannot rule out a second one, nor can we be sure whether one or both of the carboxylic acids is adsorbed in this way. One might speculate that only a single carboxylic group is chemisorbed in order to account for the favoring of the *trans*-configured fumaric acid over maleic acid, but this is not a requirement.



With all these data in hand, the various mechanistic possibilities for *cis*–*trans* isomerization at low pH may be summarized:

- Direct photolysis might cause conventional photochemical *cis*–*trans* isomerization. This mechanism is eliminated by the control experiments in which the TiO₂ was not included and did not produce isomerization.
- Acid- or base-catalyzed dark reactions might cause isomerization. The dark control experiments eliminated this pathway.
- Superoxide and/or HOO• might reversibly add to the olefin, transiently eliminating the double bond and allowing isomerization. Experiments described in Section 3.3 eliminate this as a likely explanation.
- Maleic acid might serve as an electron *donor* to activated TiO₂, transiently causing formation of the maleic acid radical cation, which would have a considerably lower barrier to rotation. This is the most conventional explanation [47,70,71]. One problem with this explanation is that it is the same initial step invoked for the Kolbe-type decarboxylation, though it is possible that the same radical cation could lead to both reactions. However, it is difficult to rationalize why the isomerization would be more efficient in the absence of O₂ at low pH than it is in the presence of O₂ if this mechanism were operating.
- Maleic acid can serve as an electron *acceptor* from photoactivated TiO₂, transiently causing formation of the maleic acid radical anion, which would have a considerably lower barrier to rotation, with or without protonation, as illustrated in Scheme 3. This is the mechanism we favor.

A further comment on our interpretive framework, which varies slightly from that of Franch et al., is in order. The essential distinction is that while both they and we postulate two types of reactivity (of which one is electron transfer at the surface), we believe that there is no requirement for their assertion that the second type is reaction in the bulk phase of the water. The distinction in reactivity between methyl maleate and maleic acid, along with the TiO₂/F results support the idea that the predominant chemistry at low pH, i.e., *cis*–*trans* isomerization, requires surface adsorption, but does not speak to the higher pH results, where the product distributions are different.

We have reported analogous changes in chemistry from oxidative electron transfer chemistry to hydroxyl-like chemistry with the change of phenolic OH-groups to methoxy groups on benzene rings [29]. In those experiments [29], adsorption was modified by the capping of the phenols and its resulting prevention of C–O–Ti type adsorption, rather than by changing pH. We argued that the hydroxyl type chem-

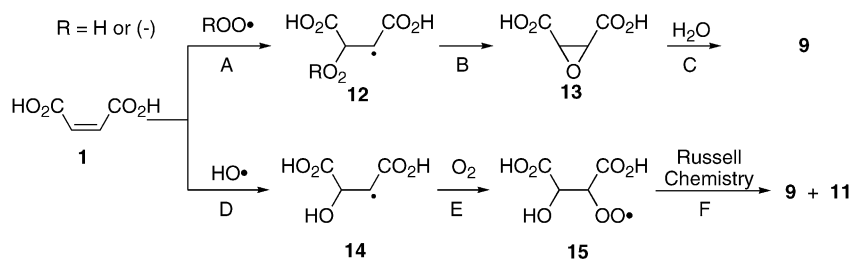
istry could be due to non-specific binding with the titania surface and/or reactions very near the surface. Alcohol additives were more effective in slowing down the hydroxyl-type chemistry than the electron transfer chemistry, but they were also shown to displace the poorly binding substrates; these were also the same ones that suffer the great proportion of hydroxyl-type chemistry. Very similar arguments can be used to explain the dependence of the products on pH for maleic acid. Thus, while the current data certainly do not eliminate the possibility of bulk phase TiO₂-mediated reactivity at neutral and basic pH, we find nothing compelling about either our data set or that of Franch et al. [47] to confirm it. However, we remain compelled by the experiments of Minero and co-workers (e.g., [56,57,59]), and feel that this should be the assumption in the absence of convincing evidence to the contrary in support for homogeneous-phase chemistry.

3.3. Mechanisms of oxygenation reactions

Given our interpretation that the *cis*–*trans* isomerization is best explained by reversible reductive electron transfer chemistry, we wished to explore the possibility that some of the oxidation (or, perhaps more properly, oxygenation) products might begin with a step that itself was formally reductive in nature. The most obvious candidate was reaction between maleic acid and superoxide near neutral pH, where the latter is largely deprotonated and nucleophilic. While the acids are also largely deprotonated in homogeneous solution, they might still be associated with the titania in such a way as to make them behave like the ester, rather than the anion or dianion, and thus act as good Michael acceptors. Though the adsorption coefficient is not as high at high pH as it is in acidic solution [47], we were intrigued with the possibility that a surface-bound tartaric acid might suffer from attack by nucleophilic hydroperoxyl/superoxide species, rather than electrophilic hydroxyl species, as outlined in Scheme 4.

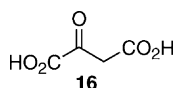
At pH 7 and 12, the HOO•/O₂^{•-} equilibrium lies far to the side of superoxide. It is obviously more nucleophilic than the conjugate acid, making step A more reasonable. Further, we hypothesize that the substrate is surface-bound to maintain its effectively “protonated” state with regard to Michael-type attack at the β-position, relative to the adsorbing acid group. Step B is thermodynamically downhill and related reactions are well known in the organic literature [72–78]. In aqueous solution, **13** is an obvious precursor to **9** by either acid or base catalyzed ring opening. The path shown by steps D–F is the more conventional mechanism for oxidative chemistry under these and similar conditions [79,80]. We thus sought tests to explore plausibility of the path beginning with step A. The first was to test for the intermediacy of **13**.

Compound **13**, the epoxide of maleic acid, was prepared as its sodium salt. It was hypothesized that a competition between hydrolysis and oxidation might lead to **9** and **11**. However, photocatalytic treatment of **13** did not produce

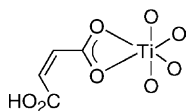
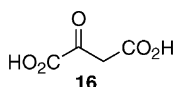


Scheme 4. Possible mechanisms for formation of **9** and **11**. For simplicity, free, rather than surface-bound compounds are shown. It is understood that protonation states will vary, though protons also stand in for potential Ti atoms in various potential bound states in the scheme.

detectable amounts of **11** when degradations were carried out to low conversion at pH 2, 7, and 12. The major product at pH 2 was oxalacetic acid (**16**), with some tartaric acid formed. At pH 7, these were observed in reverse order of importance. At pH 12, even at low conversion, more products were observed: $\mathbf{16} > \mathbf{3} > \mathbf{9} > \mathbf{8} > \mathbf{4}$.



A hypothesis that might have accounted for the lack of observation of **16** in the degradations of maleic acid is that **16** is particularly rapidly degraded. In fact, degradations beginning with **16** at 2 mM did produce intermediates that were observed in maleic acid degradations. At pH 2, tartaric acid and dihydroxyfumaric acid were the most predominant products. At pH 7, tartaric acid was predominant. At pH 12, compounds **4**, **8**, **3**, and **9** were observed, in that order of abundance, indicating that decarboxylation reactions had become competitive with initial hydroxylations. However, degradations of **16** were not significantly more rapid than those of any other substrate, and the very fact that it was so easily observed in the degradations of **13** casts doubt on the idea that its degradation is particularly rapid in other experiments.



It was also plausible that superoxide was involved in the reaction, but that the other details of the A–B–C pathway of Scheme 3 were incorrect, i.e., that **12** does not form an epoxide. Thus, we sought more direct evidence regarding superoxide itself.

Following the precedent of Pichat and coworkers [27,53–55], degradations were carried out in the presence of commercial samples of superoxide dismutase (SOD), an enzyme that catalyzes the disproportionation of superoxide to hydrogen peroxide and O_2 . As a first step, selected

results from the Pichat lab were reproduced. In these, addition of superoxide dismutase hindered the degradation of dimethoxy benzene and quinoline near neutral pH. With maleic acid at near-neutral pH (using the commercial buffer supplied with the enzyme), the presence of SOD did not qualitatively affect the rate of degradation. Neither did it suppress tartaric acid formation, which was still the major four-carbon intermediate. Small quantities of fumaric acid were also observed, consistent with ordinary degradations at this pH. This suggests that superoxide is not the primary reactant in formation of tartaric acid.

Finally, maleic acid was treated with superoxide solutions formed by dissolving commercially available KO_2 in dry DMSO containing 18-crown-6. Reactions were carried out in pyridine, anhydrous DMSO, and wet DMSO with superoxide: maleic acid ratios of 1:1, 5:1, and 1000:1. No maleic acid-derived products were observed at the lower ratios of KO_2 :1. A trace quantity of fumaric acid (and oxalic acid) was observed after an hour of treatment at the 1000:1 ratio. These conditions are at orders of magnitude higher concentrations of superoxide than is plausible under normal photocatalytic conditions, though the solvent differs and the TiO_2 surface does not serve to pre-organize the mixture. No tartaric acid, oxalacetic acid or any three-carbon compounds were observed in any of these experiments.

We thus conclude that superoxide is not an important initiating reactant in the formation of any of the four-carbon intermediates, including the *cis*–*trans* isomerization products under the TiO_2 -mediated conditions. In the absence of evidence to the contrary, we thus favor the conventional hydroxyl addition steps as the primary reaction mode to get to the oxygenated products. We also eliminate the reversible addition of superoxide as an important mechanism for *cis*–*trans* isomerization of maleic and fumaric acids.

4. Conclusions

Partial photocatalytic degradation of maleic acid gives rise to most of the plausible oxygenated compounds with four carbons or fewer. Our observations are generally in line with the recent report of Franch, et al. [47], save that we do not observe by GC-MS acrylic acid, which they report with HPLC and UV detection. The *cis*–*trans* isomerism of maleic

acid under acidic conditions is proposed to occur by way of reductive electron transfer to the adsorbed acid. The bases for this conclusion include the acid's superior adsorption at low pH [47], the near exclusivity of this process in the absence of O₂ (which usually acts as an electron acceptor), the increase in observed isomerization rate in the absence of O₂ (contrary to the great majority of photocatalytic degradation processes), and the suppression of isomerization with the addition of fluoride to the system.

An investigation into the possibility that other reactions begin with the reaction of maleic acid with superoxide in a similar electron/nucleophile-accepting mode produced results in clear contradiction with this idea. It is presumed that the formation of tartaric acid and dihydroxyfumaric acid—along with other smaller intermediates—occurs by conventional mechanisms beginning with hydroxyl attack on the substrate.

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