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Towards a better understanding of the initial steps in the photocatalyzed mineralization of amino acids at the titania/water interface. An experimental and theoretical examination of L-alanine, L-serine and L-phenylalanine

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Abstract

The pathway to the photomineralization of the three amino acids L-serine (L-Ser), L-phenylalanine (L-Phe) and L-α-alanine (L-Ala) is described experimentally on the basis of CO_2 evolution and conversion of the amino group to NH_4^+ and NO_3^- ions, and theoretically on the basis of molecular orbital calculations to define frontier electron densities and point charges on all the individual atoms. The relatively high negative point charges on the carboxylate oxygens are consistent with adsorption of the amino acids to the TiO_2 particle surface through the carboxylate function. Mineralization to carbon dioxide is complete for L-Ser (∼98%) and nearly so for L-Ala (∼90%), whereas for L-Phe the extent of mineralization is 59% corresponding to the total photooxidation of the phenyl ring carbons; for the amine function the extent of conversion is 87% for L-Ser, 97% for L-Ala and 91% for L-Phe. Relative formation yields of NH_4^+ and NO_3^- ions depend on the structural fragment R attached to the α-amino carboxylic acid functions, R-CH(NH_2)COOH. Primary attack of the amino acids by the $^{\bullet}OH$ radical is correlated with the frontier electron densities. Ammonia is formed through a photoreductive step by electron attachment onto the zwitterionic form of the amino acids, whereas nitrate is produced through a photooxidative step implicating a very tortuous series of events.

Keywords: Photooxidation; Photodegradation; Amino acid; Frontier electron density; Point charge; Titanium dioxide

1. Introduction

Damages caused to deoxyribonucleic acid (DNA) in vitro [1,2] and in human cells [1] by micronized TiO_2 particles, when incorporated as an active ingredient in sunscreen lotions to block the harmful sunlight UV-A and UV-B radiations, have recently been addressed. We have also reported on some initial studies on the photocatalyzed transformation of pyrimidine and purine bases alone and in DNA and RNA [3], and of *N*-containing compounds in aqueous TiO_2 dispersions illuminated by UV-B and UV-A components [4,5].

Amino acids are compounds that combine –COOH and –NH_2 functions and other moieties on the α-carbon. The rate of conversion of the amino function to NH_4^+ or NO_3^- ions is therefore expected to depend, to some extent, on the molecular structure of the amino acids as already shown for other *N*-containing systems by our coworkers [4,5]. In a preliminary study [3] we surveyed the photocatalyzed transformation of a large number of amino acids, aspartame, *N*-dodecanoylglutamate and *N*-dodecanoyl-β-alanine. A plausible pathway for this phototransformation was proposed, the details of which, however, necessitate further examination for the amino acids.

This paper reports the photocatalyzed conversion of the amino group to NH_4^+ and/or NO_3^- ions in UV-A/UV-B illuminated TiO_2 aqueous dispersions for the three amino acids L-serine (L-Ser), L-phenylalanine (L-Phe) and L-α-alanine (L-Ala). The temporal course of this conversion was followed by the evolution of CO_2, by the loss of the primary amine function, and by the formation of NH_4^+ and NO_3^- ions. Molecular orbital calculations have also been carried out for each atom of the amino acids to assess

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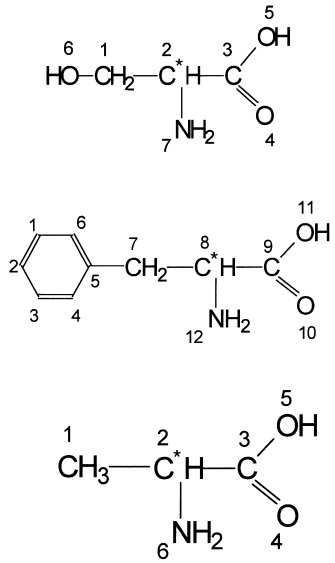
frontier electron densities and point charges in order to seek some correlations/clarifications between these properties and the experimental observations.

2. Experimental section

The amino acids L-α-alanine {CH_3–$C^*H(NH_2)COOH$}, L-serine {$HOCH_2$–$C^*H(NH_2)COOH$} and L-phenylalanine {C_6H_5–C^*H_2–$CH(NH_2)COOH$} were supplied by the Tokyo Kasei Co. and used as received; the TiO_2 photocatalyst was Degussa P-25, mostly of the anatase form (82.6% by X-ray diffraction) with a specific surface area of ~55 $m^2\ g^{-1}$ and particle size ca. 33 nm. Deionized and distilled water was used throughout, unless noted otherwise.



For the photocatalyzed conversion of the amino acids, an aqueous solution (0.1 mM; 50 ml) of the substrate and 100 mg of TiO_2 particulates (loading 2 g l^{-1}) were contained in a 124 ml pyrex reactor; the mixture was then dispersed by sonication for 5 min prior to illumination under continuous agitation with a 75 W Hg-lamp which provided three main irradiation wavelengths at 313 nm, 336 nm and 366 nm. The headspace volume in the pyrex reaction vessel was purged with excess oxygen gas for 15 min. Loss of the primary amine function was monitored by spectrofluorimetric analysis (JASTO FP-770 spectrofluorimeter) using the fluorescamine method [6,7]. At various intervals, the dispersion was sampled and filtered through a 0.22 μm membrane from which a small quantity of the amino acid solution (0.15 ml) was subsequently mixed with 0.15 ml of a borate buffer solution (pH 9) in a small test tube and then with 0.15 ml of a solution of fluorescamine (0.03%) dissolved in acetone.The concentration of ammonium and nitrate ions was assayed by high performance liquid chromatography (HPLC) employing a JASCO liquid chromatograph with a CD-5 conductivity detector, and either with a Y-521 cation column or an I-524 anion column. The temporal evolution of CO_2 was monitored by gas chromatography with an Ookura Riken chromatograph (model 802) with TCD detection using a Porapack Q column and helium as the carrier gas. Molecular orbinal calculations were performed using the CAChe system (by Sony/Tektronix Corporation) from the MOPAC version 6. These MO calculations were carried out to the single determinant (Hartree-Fock) level and optimal geometries of conformational minima were obtained at the AM1 level.

3. Results and discussion

The photocatalyst TiO_2 particles absorb UV-light at energies greater than threshold ~3.2 eV (i.e. at wavelengths below ~387 nm) to generate, ultimately, electrons and holes at the particle surface through a complex sequence of photophysical events in the bulk and on the surface [8]. The trapping of holes by OH^- groups and/or by H_2O molecules chemisorbed at the surface produce $^{\bullet}OH$ radicals, whereas electrons are trapped by the ubiquitous oxygen molecules to yield the superoxide radical anion of $O_2^{\bullet -}$, or the $^{\bullet}OOH$ radical on protonation, and by the surface Ti^{IV} ions to give the corresponding Ti^{III} states. Of relevance to the present study is predicting some further details of the photooxidative process through estimating the position of $^{\bullet}OH$ radical (or equivalent) attack on the amino acid structure and the mode of adsorption of the amino acid on the TiO_2 surface through appropriate molecular orbital calculations of electron densities and point charges of each atom of the substrate [4].

The evolution of CO_2 in the photodegradation of each amino acid is illustrated in Fig. 1, whereas the loss of the

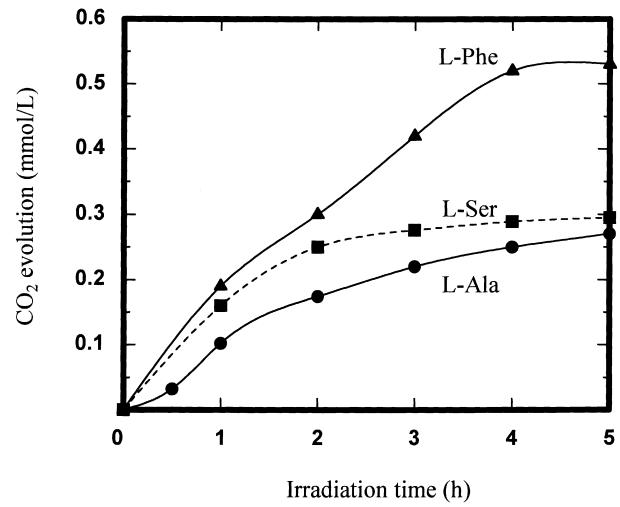


Fig. 1. Evolution of carbon dioxide from the TiO_2 photocatalyzed mineralization of the amino acids (0.1 mM; 50 ml dispersion; 124 ml pyrex reactor) L-phenylalanine (L-Phe), L-serine (L-Ser), and L-α-alanine (L-Ala) under illumination with UVA (313, 336 and 366 nm) wavelengths from a 75 W mercury lamp.

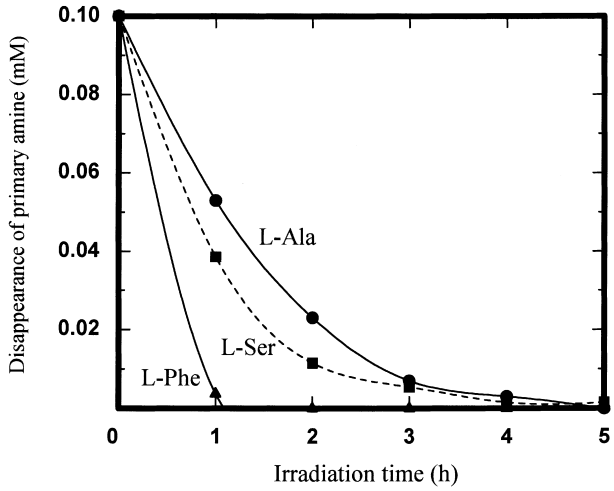


Fig. 2. Disappearance of the primary amine during the photodegradation of the amino acids L-phenylalanine (L-Phe), L-serine (L-Ser), and L-α-alanine (L-Ala). Other experimental details as in Fig. 1.

amine function is depicted in Fig. 2. Fig. 3 presents the evolution of ammonium and nitrate ions for all three amino acids. Kinetic data and yields of carbon dioxide, ammonia (as NH_4^+ ions) and nitrate ions after a 5 h illumination period are collected in Table 1.

Examination of the results of Table 1 and Figs. 1–3 produces some interesting observations:

1. Under the experimental conditions used (initial pH ~5.5) and with the dissociation and iso-electric/iso-ionic constants, amino acids exist in their zwitterionic form R–CH(NH_3^+)COO^- in solution.
2. The rates of mineralization of the amino acids, as evidenced by formation of carbon dioxide, vary in the order L-Ser (2.5)>L-Ala (1.1)>L-Phe (**1**) {values in parentheses are relative values}, and the mineralization yield (i.e. yield of CO_2 relative to the expected yield) varies as L-Ser (98%)≥L-Ala (90%)>L-Phe (59%).
3. The rate of loss of the amine changes as L-Phe (4.4)>>L-Ser (1.4)>L-Ala (**1**) similar to the rate of formation of NO_3^- ions, L-Phe >L-Ser >>> L-Ala, but different from the variation in the rates of formation of NH_4^+ ions, namely L-Ser (2.1)>L-Phe (1.5)>L-Ala (**1**).
4. The predominant product of the photoconversion of the primary amine function is NH_4^+ ions for all the amino acids (cf. Fig. 3), i.e. after the 5-hour irradiation period the yield of NH_4^+ varies as L-Ala (1.3)> L-Ser (1.05)=l-Phe (**1**) whereas for NO_3^- ions we have L-Phe (5.7) > L-Ser (3) >>>L-Ala (**1**), and the yield ratio NH_4^+/NO_3^- changes as L-Ala (7.2)>>>L-Ser (2.1)>L-Phe (**1**). For L-phenylalanine, the loss of the amine is 10-fold faster than evolution of carbon dioxide, five-fold faster than formation of ammonium ions, and two-fold faster than nitrate ion formation. By contrast, the rate of loss of the amine function in L-serine is slightly faster than CO_2 evolution and NO_3^- ion formation by a factor of ca. 1.3, and about the same as the rate of formation of NH_4^+ ions; for L-alanine, loss of amine takes place at a rate 2-fold faster than CO_2 evolution and NH_4^+ ion generation. However, formation of nitrate ions from the photoconversion of the L-alanine nitrogen is very slow, necessitating about 5 h of illumination before NO_3^- ions are detectable. The internal pressure in the reaction vessel increased on evolution

Table 1
Kinetic parameters and yields in the photomineralization of amino acids (0.1 mM; 50 mL) at the TiO_2/water interface

Parameters	L-α-alanine	L-serine	L-phenylalanine
pK'_1 (–COOH)[a]	2.34	2.21	1.83
pK'_2(–NH_3^+)[a]	9.69	9.15	9.13
$pI\{=(pK'_1+pK'_2)/2\}$[a]	6.00	5.68	5.48
CO_2 evolution			
10^{-2} k (min^{-1})	5.8±0.9	13.1±1.1	5.3±0.8
$t_{1/2}$ (min)	119	53	132
Yield (mM)[b]	0.27	0.29	0.53
Loss of –NH_2:			
10^{-2} k (min^{-1})	12.2±0.8	16.7±0.6	53.3±0.3
$t_{1/2}$ (min)	57	41.5	65
Formation of NH_4^+:			
10^{-2} k (min^{-1})	7.2±0.9	15.0±0.7	10.6±2.4
$t_{1/2}$ (min)	96	46	65
Yield (mM)[b]	0.094	0.078	0.074
Formation of NO_3^-			
10^{-2} k (min^{-1})	–	20.7±2.4	26.9±1.3[c]
$t_{1/2}$ (min)	–	33	26
Yield (mM)[b]	0.003	0.009	0.017
Ratio NH_4^+/NO_3^-[b]	31	9	4.3
Mineralization yield CO_2 (%)[b]	90	98	59
Total nitrogen converted (%)[b]	97	87	91

[a] [16].
[b] After a 5-h illumination period.
[c] After an induction period of ca. 30 min.

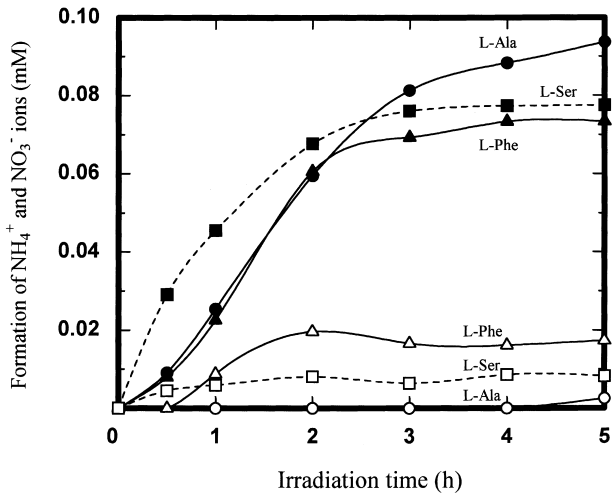
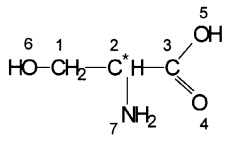


Fig. 3. Formation of ammonia (analyzed as NH_4^+) and NO_3^- ions during the course of the photomineralization of L-phenylalanine (L-Phe), L-serine (L-Ser), and L-α-alanine (L-Ala). Other experimental details as in Fig. 1.

Table 2
Frontier electron densities and point charge calculations of the L-serine (L-Ser) using the CACHe method from the MOPAC system



atom	Frontier electron density	Point charges
C1	0.135	−0.051
C2	0.087	−0.041
C3	0.634	0.389
O4	0.236	−0.490
O5	0.087	−0.333
O6	0.072	−0.407
N7	0.594	−0.384
H8	0.019	0.102
H9	0.046	0.106
H10	0.020	0.165
H11	0.004	0.303
H12	0.008	0.264
H13	0.030	0.181
H14	0.029	0.195

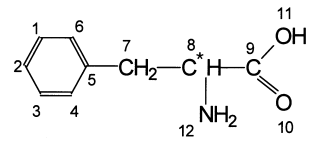
of CO_2; however, we did not take into account the possible removal of CO_2 by other pathways.

Frontier electron densities and point charges of all individual atoms in the amino acids L-serine, L-phenylalanine, and L-α-alanine were calculated using the CACHe system in the MOPAC program Version 6; the resulting values are summarised in Tables 2–4, respectively. We begin by noting that under the conditions used the charge of the TiO_2 particle surface is near-neutral at pH ca. 5.5; the iso-electric point of TiO_2 P-25 is in the range 5–6. We also show below that the amino acids chemisorb predominantly to the surface through the carboxylate oxygens as recently demonstrated for all-trans-retinoic acid [9].

Several points are worth noting in Tables 2–4. For L-serine the most negative point charges are located on the oxygen atoms O4, O5, and O6 and on the atom N7; however, because of the $–NH_3^+$ function under the prevailing conditions, the point charge is likely to be more positive than indicated (i.e.>-0.384). The same is also the case for N12 of L-phenylalanine (point charge >-0.391) and for N6 of L-alanine (point charge >-0.397). We expect therefore that the point of chemisorption of the amino acids be through the carboxylate oxygen (Scheme 1), although, we cannot entirely preclude partial adsorption of L-serine through its alcoholic oxygen O6; however, by analogy with alcohols adsorption through O6 must be minimal.

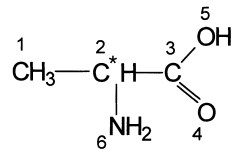
The magnitude of the negative point charges on the above oxygen and nitrogen atoms are not necessarily reflected by equivalent magnitudes of the frontier electron densities. For example, the highest electron density in L-serine is at the carboxylate C3 carbon and yet the point charge on this

Table 3
Frontier electron densities and point calculations of the L-phenylalanine (L-Phe) using the CACHe method from the MOPAC system

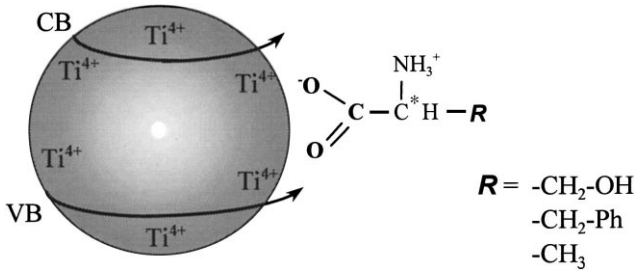


Atom	Frontier electron density	Point charges
C1	0.242	−0.154
C2	0.349	−0.151
C3	0.244	−0.152
C4	0.270	−0.150
C5	0.363	−0.096
C6	0.274	−0.143
C7	0.027	−0.169
C8	0.039	−0.028
C9	0.084	0.384
O10	0.032	−0.494
O11	0.012	−0.335
N12	0.041	−0.391
H13	0.000	0.161
H14	0.000	0.161
H15	0.000	0.161
H16	0.000	0.155
H17	0.000	0.159
H18	0.009	0.121
H19	0.005	0.126
H20	0.002	0.159
H21	0.001	0.305
H22	0.002	0.180
H23	0.002	0.190

Table 4
Frontier electron densities and point charge calculations of the L-α-alanine (L-Ala) using the CACHe method from the MOPAC system



Atom	Frontier electron density	Point charges
C1	0.140	−0.263
C2	0.090	−0.031
C3	0.643	0.382
O4	0.245	−0.500
05	0.085	−0.337
N6	0.673	−0.397
H7	0.005	0.098
H8	0.019	0.105
H9	0.006	0.111
H10	0.028	0.157
H11	0.003	0.302
H12	0.033	0.177
H13	0.029	0.195



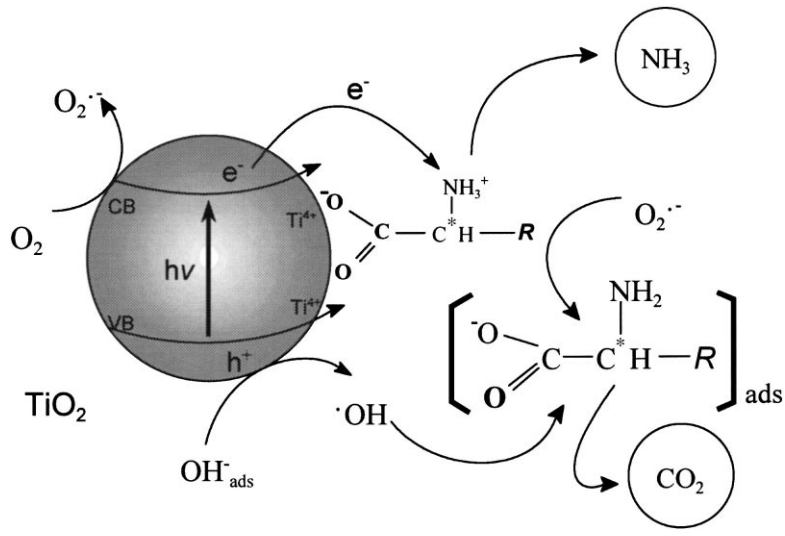
Scheme 1. View of adsorption of the three amino acids L-serine (R=-CH_2-OH), L-phenylalanine (R=-CH_2-Ph) and L-α-alanine (R=-CH_3).

carbon is +0.389 (Table 2); as well, the O6 oxygen atom in L-serine has a negative point charge of −0.407 and yet its electron density is very small, only 0.072. Similar inferences can be made for L-phenylalanine, where the carboxylate oxygens have very small electron densities (Table 3) and for L-alanine, where the O5 oxygen atom has a negative point charge of −0.337; the electron density is only 0.085 (Table 4).

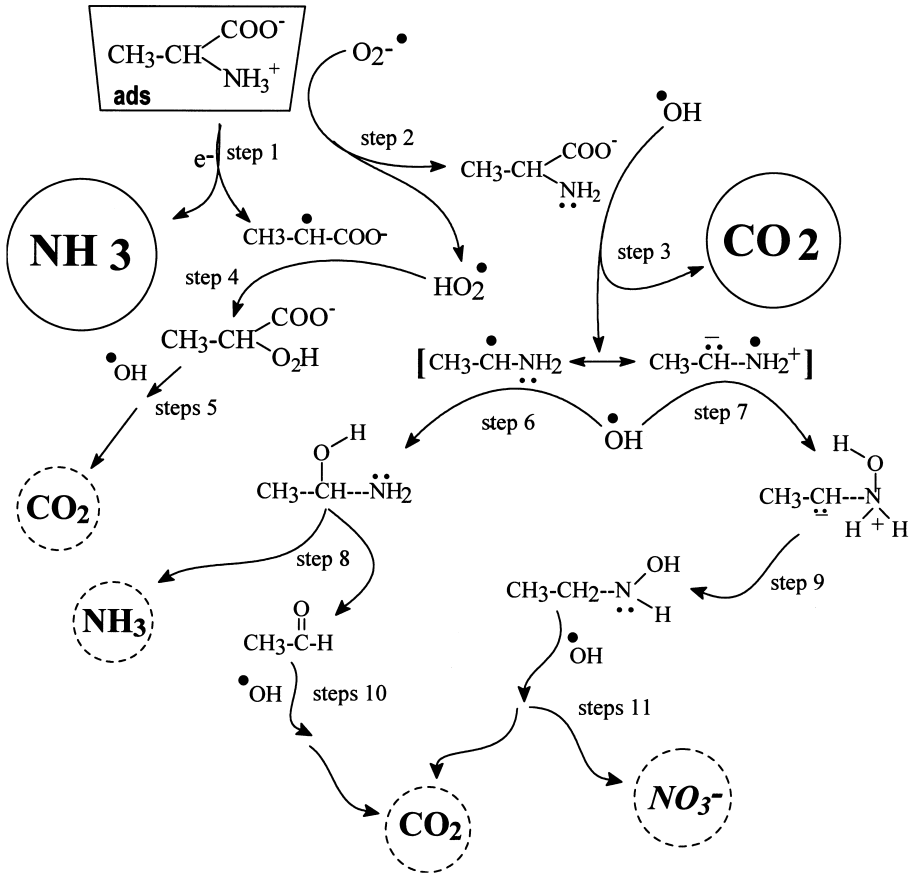
To the extent that the photooxidative mineralization is initiated by the surface-bound $^{\bullet}$OH radical species (or equivalent) [10] and that these species are highly electrophilic, we expect that the primary position(s) for $^{\bullet}$OH radical attack will be on those atoms with the largest electron density. For L-serine these atoms are the carboxylate C3 carbon and the amine N7 nitrogen. Primary $^{\bullet}$OH radical attack on C3 (see Table 2 for structure) should lead to prompt decarboxylation of the amino acid, whereas attack on the nitrogen will generate a hydroxylamine-type intermediate -NH×OH, which by analogy with *N*-hydroxysuccinimide [5] should be the major source of the NO_3^- ion (see below). However, unlike *N*-hydroxy-succinimide for which the nitrogen hetero atom was nearly quantitatively converted to nitrate, in the case of L-serine the relative quantity of nitrate is rather small (ca. 10%, and even smaller for L-alanine and L-phenylalanine) with 90% of the amine function converted predominantly to ammonium ions (cf. Fig. 3). This would be consistent with a smaller electron density on the N7 atom owing to the $-NH_3^+$ function which is more likely to be an electron acceptor on its way to ammonia [11]; Scheme 2 illustrates the major primary redox events of interest. Electron transfer from the TiO_2 particle to the chemisorbed amino acid should rapidly yield ammonia; as well, the surface adsorbed superoxide radical anion $O_2^{\bullet -}$ can extract a proton from the $-NH_3^+$ moiety to yield the $HOO^{\bullet}$ radical and the amino-carboxylate fragment which subsequent to attack by the $^{\bullet}$OH radical at the carboxylate carbon yields carbon dioxide. Consistent with this view, we note the similarity in the first-order rates of formation of NH_3 (1.5×10^{-2} min^{-1}) and evolution of CO_2 (1.3×10^{-2} min^{-1}) for L-serine which no doubt is the result of a concerted photoreductive and photooxidative reaction. Additional steps in the photomineralization of an amino acid are presented in Scheme 3, illustrated for L-alanine. Some of the steps were described earlier [3].

Suffice to note the tortuous road needed to produce the NO_3^- ions and the additional steps required to produce additional quantities of carbon dioxide and ammonia. Photomineralization of L-serine to carbon dioxide is, within experimental error, nearly complete (98%) by the end of the 5 h illumination period.

For the structurally equivalent L-alanine species, the largest negative point charges are also borne by the two carboxylate oxygens O4 and O5 and by the amine nitrogen N6 (Table 4). Thus, to the extent that the surface of the TiO_2 particles bears a positive potential under our experimental conditions, chemisorption of L-Ala onto the surface will also take place through the carboxylate function owing, at least in part, to coulombic forces (see above). Moreover, the analogous carboxylate carbon C3 and the amine nitrogen N6 have



Scheme 2. Initial redox events subsequent to hole and electron trapping (see text).



Scheme 3. View of some details in the photocatalyzed mineralization of amino acids; some of the radicals shown have been proposed from pulse radiolytic studies [12–15]. Adapted from ref. [3].

the highest electron density: 0.643 and 0.673, respectively. We deduce therefore that $^{\bullet}OH$ radical attack occurs on C3 and that electron transfer takes place at N6 of the $-NH_3^+$ moiety (see Scheme 2 and Table 2). In accordance with this, the rates of evolution of CO_2 and formation of NH_3 are again very similar within experimental error (Table 4; 5.8×10^{-3} min^{-1} and 7.2×10^{-3} min^{-1}). Nitrate ion formation in L-Ala through a hydroxylamine species is nearly non-existent until after ca. 5 h of illumination, by which time photomineralization of the amino acid to carbon dioxide is nearly quantitative (90%). Evidently, either $^{\bullet}OH$ radical attack on the amine nitrogen N6 is suppressed or the road to NO_3^- is some what impeded, if nitrate is formed by events depicted in Scheme 3.

L-Phenylalanine differs from the other two amino acids by having a phenyl group on the β-carbon; chemisorption also occurs through the $-COO^-$ oxygens O10 and O11 in agreement with the negative point charges on these atoms (Table 3). The presence of the phenyl group in L-Phe has a substantial influence on the values of the frontier electron densities, namely that the highest densities are located on the phenyl carbons and not on the carboxylate carbon C9 or the amine nitrogen N12 as noted for L-Ser and L-Ala. A glance at Scheme 2 reveals that the terminal aromatic ring in L-phenylalanine would be positioned away from the surface of the TiO_2 particles. According to frontier electron density calculations (Table 3), attack by $^{\bullet}OH$ radicals on L-Phe should be focused on the aromatic ring Cl-C6 carbons. The extent of CO_2 evolved after the 5-hour irradiation period must reflect, in a large part, the quantity of carbon dioxide originating from the photooxidation of the phenyl carbons (Table 1; yield ca. 59%; expected yield 60% from the ring). This accords with the notion that the carboxylate C9 carbon is not attacked by the $^{\bullet}OH$ radical owing to a very low electron density on C9 (0.084) compared to the equivalent carbons for L-Ser and L-Ala (0.634 and 0.543, respectively). Note that upon cleavage of the aromatic ring, the frontier electron densities given for L-Phe are likely to change for the carboxylate carbon C9 and for the amine nitrogen N12. Such changes might explain the greater nitrate yield for L-Phe compared to L-Ala and L-Ser (Table 1). The reaction kinetics mentioned above refer to the initial rate of photodecomposition of L-Phe having the higher frontier electron densities in the aromatic moiety. Since the subsequent photooxidative intermediate products are expected to have more complex structures and their identification may be difficult, some of the details of the photodegradation of L-Phe might be predicted through calculations.

Results of electron density calculations for the amine nitrogens reveal that the N12 atom of L-phenylalanine has the smallest electron density (0.041); by comparison, the electron densities for the nitrogens N7 of L-serine and N6 of L-alanine are 0.594 and 0.673, respectively (Tables 2–4). If these nitrogens are converted primarily to ammonia by the photoreductive step shown in Scheme 2 and Scheme 3, the L-Phe nitrogen will be the better electron acceptor, followed by the amine function of L-Ser and L-Ala. The positive charge on the amine functions should enhance electron transfer from TiO_2. Indeed, this expectation correlates well with the first-order rates of loss of the amine function (Fig. 2): 5.3×10^{-2} min^{-1} (L-Phe), 1.7×10^{-2} min^{-1} (L-Ser) and 1.2×10^{-2} min^{-1} for L-Ala (Table 1). However, there is no apparent correlation between the magnitude of the electron densities and the yields of NH_4^+ ions. Clearly, subsequent to $^{\bullet}OH$ radical attack and electron transfer as depicted in Scheme 2 and Scheme 3, there is a very complex sequence of events that takes place that ultimately leads to mineralization of the carbons to carbon dioxide and the nitrogens to ammonia (primarily) and to nitrate ions for L-Ser, L-Ala and L-Phe, specifically, and for other amino acids in general. We deduce therefore that frontier electron density calculations may be useful in predicting and rationalizing the predominant primary events (Scheme 2) in photocatalysis.

4. Conclusions

The photomineralization of three amino acids, L-serine (L-Ser), L-phenylalanine (L-Phe) and L-α-alanine (L-Ala) has been described on the basis of CO_2 evolution and conversion of the amine group to NH_4^+ and NO_3^- ions, and theoretically on the basis of molecular orbital calculations of frontier electron densities and point charges on all the individual atoms. The negative point charges on the carboxylate oxygens inferred adsorption of amino acids to the photocatalyst surface takes place through the carboxylate moiety. Mineralization to carbon dioxide is quantitative for L-Ser (∼98%), nearly so for L-Ala (∼90%), but much less for L-Phe (59%) for which carbon dioxide emanates mostly from the mineralization of the phenyl ring carbons. The amine function is almost completely converted {87% for L-Ser, 97% for L-Ala and 91% for L-Phe} predominantly to ammonia and to a smaller extent to nitrate ions. An attempt has been made to correlate the frontier electron densities with primary attack of the amino acids by the surface trapped charge carriers $^{\bullet}OH$ radical for the hole and $O_2^{\bullet-}$ and/or Ti^{III} states for the electron. Ammonia is formed through a photoreductive step; a photooxidative step has been inferred for production of nitrate ions through a hydroxylamine-type intermediate [5].

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