Abstract: Besides the established procedures, a multitude of environmental organic compounds can be mineralized or at least degraded to species like acetate by irradiating iron(III) complexes adsorbed to certain broad-gap semiconductors by visible light. Quantum yields are increased considerably by adsorption with respect to LMCT photochemistry in homogeneous solution, and the semiconductor acts as a electron- (rather, valence band hole) transfer agent which conserves the oxidizing properties of the ligand radical originally produced for longer periods of time (although modulated down to $\varepsilon_{vb}$). The SC colloid particle, not excited itself, transports the hole, then allowing to oxidize co-adsorbed species present in small concentrations but also accumulated by adsorption. Water purification from various kinds of pollutants is feasible, and the reaction which is photocatalytic at turnovers $\geq 100$ referring to Fe complex can be kept up by air input into the suspension also tolerating repeated inputs of compounds to be removed. Except for some acetate formed, mineralization of substrates is complete.

Keywords: photooxidation, semiconductor, iron complex, water purification, heterogeneous catalysis, methods of enhanced surface activation

Introduction

The principal end of environmental chemistry is to design or understand chemical reactions which are relevant to the status of our environment or suited to improve it, ie to remove or convert chemical compounds before these get into contact with the environment and do harm to it. Like all other chemical reactions, these can occur in either a homogeneous or a heterogeneous setting, the latter eg involving heterogeneous catalysis.
like in the catalytic car exhaust converter [1]. Heterogeneous systems mainly draw upon adsorption (physi- and chemisorption) inducing polarization, cleavage and rearrangement of chemical bonds in the (potentially hazardous and thus to be removed) substrate.

Apart from eutrophicating pollutants (nitrate, phosphates) and certain toxic cations and anions (eg cyanide, nitrate(III)) most of the compounds which deteriorate the status of ambient and groundwaters are organic compounds, most of them (except for CCl₄, perfluorinated sulfonates and the like) being sensitive towards oxidation. However, most of these compounds are fairly stable even under Earth’s oxidizing atmosphere under ambient conditions, making them capable to pass through sewage treatment plants and persist in the environment for quite some period of time. Thus they can accumulate in both water and - if unpolar - biomagnify in aquatic organisms along the trophic chain. Besides organic compounds wilfully passed into the environment, eg as biocides, there are others with similar properties which get there after passing through and out of human or animal bodies after being applied as pharmaceuticals. Several of these compounds actually reach levels where adverse effects to fishes and other aquatic beings are noticeable, including 17α-ethynylestradiol (EE2, for oral anticonception) and diclofenac (2´,6´-dichloranilinophenylacetate-2, an analgetic agent, known as Voltaren®), both remaining essentially unchanged by classical procedure of sewage water treatment.

Although oxidation of most environmentally relevant organics is exothermic, it need not occur readily; rather, efficient and complete low-T oxidation of organics requires the use of platinum group metals (PGM) or complexes thereof as catalysts, like in fuel cells. One also has - apart for cost and large-scale availability - to be aware that eg a catalytic car exhaust converter best operates at some 400°C even though it contains both Pt and Rh. This T value of operation otherwise is rather typical for selective air or NOₓ oxidations of organics, such as production of nitriles or HCN from amines at Bi₂O₃, but anyway unsuited for water purification (“wet combustion”) essentially. Moreover, certain functional groups are able to produce highly toxic by-products, especially if combined with inorganic catalysts. A classical example is formation of chlorinated dioxines and dibenzofurans by partial air oxidation of halophenols or other haloorganics which occurs when Cu is present. Stepwise oxidation may (when caused by NO₂ and NO₃ radicals) or may not (by OH) decrease subsequent reactivity of intermediates towards mineralization, also [1]. Thus there apparently is a necessity either to achieve complete oxidation by appropriate, far more active catalysts of oxidation (eg enzymes) or to change reaction conditions at interfaces sufficiently. While it is hardly understood what really happens on heterogeneous catalyst interfaces except for direct view in some STM captures of simple cases, like CO oxidation on neat Pt [2], it is more feasible to increase activity by actively altering electronic (binding) conditions at the interface rather than simply looking for more active (and probably more “exotic” and expensive) catalyst formulations. Frankly speaking, even PGM interfaces (including Ru, Rh) will not accomplish organic oxidations near RT (room temperature). The reasons for this are related to the band model which applies to all solids, metals, insulators and semiconductors alike.

It takes additional activation of the interface by passing energy through it - be it electrical, electromagnetic (visible, UV, γ radiation) or even mechanical (tribochemistry) [3] - to achieve reasonable turnover rates near to room temperature, which is essential for water treatment in substantial amounts, like in sewage treatment. An energetized interface then becomes actually capable of complete mineralization of certain sorbates. Such
interfaces absorbing and transferring energy (and charge carriers) can be prepared from/on all of metals, semiconductors and isolators, be they solid or liquid (Hg, Ga, or liquid semiconductors as molten iodine or PAHs). The protocol (and reasoning) of stepwise activity increases from “mere” heterogeneous catalysis up to this novel method is outlined below.

All shape, population and energy levels of given bands may be changed, for example by exposure to UV/VIS radiation, inclusion of radionuclides, microwave impact or simply electric polarization. Except for formation of refractory, insoluble oxides with some valve metals (W, Nb, Ta, to some lesser extent Ti and Zr), stability of catalyst all of which will be influenced in both aqueous and other liquid media by such treatments, however. The same holds for semiconductors as the anionic partial lattice is composed of species which all are more reducing than valence band holes - which is inevitable given the origins of the valence band. Conversely, cations in p-type materials are more oxidizing than conduction band electrons. Hence the “normal” result of semiconductor excitation across the band gap will be corrosion of the support, unless coupled to protective redox systems such as polychalcogenides. Stability can be improved by either doing simple electrochemistry or “fixing” one kind of charge carrier to the site of its origins, to be cleaved sometime later by a thermochemical transformation.

**Catalytic oxidation**

Catalytic oxidation [4] - of all gases, fluids and supercritical fluids - is commonplace in environmental technology. As usual in environmental technology, the corresponding techniques and catalyst materials were not tailor-made for this purpose but taken from similar tasks in technical chemistry: eg the 5:1-Pt/Rh catalyst used in car exhaust converters for NO\textsubscript{x} redox treatment is simply the classical Ostwald catalyst originally taken for air oxidation of ammonia into NO, eventually producing nitric(V) acid. Likewise, Cu- or Bi oxides are used in similar functions like in technical catalysis [1]. Recently, this approach was extended to biological or biogenic catalysts, enzymes, for similar purposes (“biowashers”). Apart from heating (which is not feasible with enzymes), corresponding interfaces are not “energized”, however.

**Electrochemistry**

Of course, polarization during adsorption depends on relative polarities of sorbent and sorbate plus energy levels and topology of the Fermi surface of the solid and can be altered by “deforming” the latter. The classical way of doing this is by applying a stationary electrical potential, that is, by doing electrochemistry. After transfer of electrons to or from a sorbate, its internal bond energies will change allowing for cleavage of some chemical bonds (dismantling weaker ones, eg M-C bonds), often hitting critical functional groups, while charging of the sorbate (turning it into radical cations or anions) alters its sensitivity towards hydrolysis: eg, radical cations will readily react with and take up OH\textsuperscript{–} ions [5, 6].

In organic electrochemistry, the material of electrodes is of paramount importance for the product distribution obtained in both reductions (eg of CO\textsubscript{2}) and oxidation [5, 7]. Aqueous electrochemistry at metal interfaces actually is that of/at interfacial oxide films, except for gold electrodes. Unless these oxide films display metal conductivity, (eg RuO\textsubscript{2}, IrO\textsubscript{2}), there actually is a liquid-semiconductor interface, and polarization of the electrode
brings about deformation of the Fermi edge. Beneath this, there is another metal- 
semiconductor interface, acting like a Schottky diode unless the oxide layers are so thin  
-like on Pt, about 0.4 nm) that tunnelling is relevant. Certain “critical” functional groups are  
particularly sensitive towards anodic oxidation; eg organotin compounds are readily cleaved  
[8]. While electrooxidations of hazardous compounds like substituted phenols [9, 10],  
trialkyltin ions [8], or aromatic amines work well in aqueous media including mud, position  
and stability of corresponding electrodes remain an issue for often very high potentials are  
used. Electrochemical (anodic) processes require a sufficient electrical conductivity of the 
medium to be purified; as a rule, it should be liquid.

**Photoelectrochemistry**

In photoelectrochemistry, oxidation and reduction entities are produced side by side [1,  
2], although usually with either a poor photocatalyst stability (non-oxide semiconductors) or  
minimal response at most towards visible light irradiation (Ti, Sn, Nb… oxides and ternaries made thereof). On the other hand, a principal advantage of photoelectrochemistry with respect to classical electrochemistry is that there are no preconditions on the  
conductivity of the medium to be altered; in fact, not only liquids (organic or aqueous,  
containing salts or acids or not) and solids can be processed but also gases. There are  
applications of this latter in environmental chemistry, eg air purification removing all CO,  
VOCs and nitrogen oxides alongside heavy-traffic roads and -tunnels, usually using TiO₂  
(rutile, anatas or un-specified). So, given the interference of both CB electrons and catalyst  
lability, a method would be welcome for oxidation of sorbates (dissolved potential  
pollutants) which produces oxidation equivalents (valence band holes in semiconductors)  
selectively while the electrons moving at same time in “classical” PEC would get and  
remain confined to certain sites. In the optimum case, generation of mobile carriers, ie  
holes, and trapping of electrons should be directly combined, with holes in semiconductors  
maintaining rather high oxidation potentials until - the later, the better - recombination  
occurs or there is attack on some co-sorbent.

**Semiconductor-mediated photooxidation by metal complexes**

This aim was achieved in our laboratory using sorbate layers of (LMCT  
[Ligand-Metal-Charge-Transfer]-active) transition metal complexes on either n- or p-type  
semiconductors of sufficiently large bandgaps (BG ≥ 2.5 eV) [11-14], doing photo- rather  
than electrochemistry. Radiation absorption is due to these complexes only while the  
suspended semiconductor particles do just shuttle injected holes to the co-sorbates to be  
oxidized. The mechanism of selective hole injection was corroborated in subsequent studies  
[13, 15, 16].

Metal complexes containing oxidizing (redox-active) transition metal or f-group  
[Eu(III), Yb(III), U(VI), Ce(IV)] elements or Hg²⁺ can undergo photoinduced electron  
transfer (LMCT-type photochemistry [17, 18]) with appropriate ligands bound to them;  
however, unless for subsequent irreversible decay of oxidized ligands (azide, oxalate), the  
quantum yields Φ of such reactions are low as the lifetimes of corresponding excited states  
are very short (usually, << 1 ns) and hence ligand-based oxidants will hardly get into  
a position to react with any external substrates existing as cosolutes [13]. However,  
recombination (backward electron transfer) can be suppressed most simply by adsorbing the
complex (which is the only component to absorb light here) to some broad-gap semiconductor [12-14, 16]. Then, valence band holes are injected, reconstituting the ligand anion while the additional electron is “fixed” to the metal centre. Afterwards these valence band holes diffuse through the semiconductor particle, eventually oxidizing organic co-sorbates somewhere at its surface. This is why this reaction - which was discovered and developed by one of us [11] - can be employed for oxidizing water pollutants also. In other cases, fragments from functional groups or from the C backbone of molecules thus degraded are trapped by either the metal centre (CO, halides, SCN–) or transferred to the activating ligand, eg to glycinate or anions of other amino acids (see formation of morpholinone) which, however, occurs at small quantum yields and thus poses no problems.

Materials and methods

For the purpose of wastewater treatment, an environmentally acceptable (ie, non-toxic) system was developed which consists of amino acid iron(III) complexes as light absorbers and Bi or Nb oxide colloids (semiconductors; Bi oxides being the basis of versatile heterogeneous catalysts also, although at far more harsh conditions). Reoxidation of Fe after photocharge transfer - leaving behind an amino acid chloro complex of Fe(II) - is done by simply passing air through the illuminated (visible light) suspension; there is no photoreexcitation of the SCs themselves.

Except for bismuth oxide (Fluka) and niobia, Nb2O5 (Riedel-deHaen, 99.99%, metal-based), the compounds and solvents (THF, methyl acetate, ethyl acetate) were obtained from Sigma-Aldrich (p.a. grade or higher) and used as purchased. Deionized water was obtained from a Millipore system. Diclofenac Na salt, also from Sigma-Aldrich (98.5%) was dissolved in tetrahydrofuran (10 g/dm³) and kept as a stock solution of which corresponding amounts (3 cm³) were added to the aqueous suspension (1.5 dm³) to get a 20 mg/dm³ solution in water. Fe(III) compounds (10 mg Fe/dm³ = 180 µM) and amino acids (1 : 2 molar ratio) were mixed shortly before using in distilled water as stock solutions were not stable over long times but produced Fe oxide precipitates. The 1:2 ratio left a fifth and sixth coordination site “vacant” for either other ligands (chloride, water) or chemisorption to an oxide interface; however, the complexes could in fact be removed from either semiconductor by washing with methanol also. Respective stabilities of Fe(II) and Fe(III) glycinate complexes are given in Table 1, showing there should be only weak dissociation of Fe(II) photoreduction product complex before it gets reoxidized by air.

<table>
<thead>
<tr>
<th>Metal ion (oxidation state of Fe)</th>
<th>First association constant</th>
<th>Second association constant</th>
<th>Third association constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(II)</td>
<td>4.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(III)</td>
<td>10.0</td>
<td>18.3</td>
<td>26</td>
</tr>
</tbody>
</table>

Irradiation (Fig. 1) was done under permanent stirring with admission of air under pressure for periods of 30 min or one hour each; for compounds more refractory than diclofenac and diphenylamine this was extended until overnight periods. Experiments were done with multiple additions of organic pollutant also. Extraction of the suspension was done by ethyl acetate, concentrating the solution in a Turbovap. In addition, tests were run
whether hydrolysis of ethyl or methyl acetates might be catalyzed by the oxide semiconductor colloids. No hints for formation of acetate ions in this manner were found; accordingly, all the acetic acid detected can be taken as a metastable degradation product of this photoreaction.

The photoreactor (Fig. 1) is an all-glass airlift reactor, 2 dm$^3$ volume. Due to the large densities of the suspended oxides, magnetic bar stirring had to augment suspension by air bubbles. Illumination was done by three 15 W neon-discharge bars arranged vertically around the glass vessel (that is, parallel to its long axis). This glassware causes complete UV absorption, precluding direct excitation of either Bi or Nb oxides. The Fe complexes are brownish-coloured; their spectra were obtained by a Lambda 40 spectrophotometer.

Fig. 1. The airlift reactor filled with niobia (2 g/dm$^3$) and the Fe amino acid complex; suspension by air passage and stirring. Three neon discharge bulbs (15 W each, to the left) provide light. For better viewing, the device is partly opened; in the original system, the bulbs are fitted to the glass vessel directly by wire. Photograph taken by H. Silbernagel

Analysis was done mainly using a Varian GC/MS system, consisting of a GC-3800 gas chromatograph and a Saturn 2000 mass spectrometer fitted to it (El ionization at 70.1 eV electron energy). The GC device contained a DB-1701 semipolar GC column (30 m×0.25 mm×0.25 µm). Retention times of diclofenac, its proxy diphenylamine and
possible fragments or isomerisation products of either such as aniline, carbazol, phenylacetic and 2,6-dichlorophenylacetic acids (all from Sigma-Aldrich) were measured and compared with published mass spectra of these compounds. Among unknown fragmentation products, acetic acid and morpholinone were identified from their mass spectra, compared with retention behaviour of an authenticated CH$_3$COOH sample. The retrieved sorbent samples were washed with methanol to obtain adsorbed primaries or intermediates to distinguish either from results of “genuine” photodegradation.

**Results**

Complete removal of 10÷20 mg solute/dm$^3$ usually takes less than two hours in the irradiated suspension. Small amounts of acetic acid are formed from the degraded organics, besides mineralization products. There are no chloroorganics left over in the product mixture (MS isotopic patterns). The three amino acids combined with Fe(III) [glycine, alanine, tyrosine\(^1\)] in these experiments reacted similarly, bringing all about complete destruction of diclofenac (retention time: 14.78 min) within reasonable periods of time. The efficiency of diclofenac cleavage decreased according to tyr > gly > ala. The morpholinone by-product at 11.60 min retention time did appear with glycine only; with alanine, there was a novel peak at some 14 minutes, instead. Comparing the Fe(III) sources FeCl$_3$ hydrate and FeSO$_4$ + H$_2$O$_2$, the latter yielded more active photocatalyst systems after addition of amino acid (afterwards\(^2\)). Accordingly, the white-light irradiation activates aminocarboxylate chelate ligands rather than Cl or OH ligands, then injecting holes. There were no larger amounts of (unidentifiable) additional by-products when replacing glycine with the other amino acids.

There is some conspicuous by-product of this kind of photochemical degradation, namely morpholinone (3-aza-δ-valerolactone), presumably formed by transfer of one ethylene-like C$_2$ unit to a glycinate ligand subsequent to its photoexcitation. While this reaction is both observed with FeCl$_3$ hydrate and Fe(III)sulphate as iron reducts besides glycine, it does not occur without an external carbon source such as diclofenac or aniline, and, by replacing glycine with other amino acids [alanine, tyrosine], the corresponding signal also vanishes to be replaced by more complicated ones with longer column retention times. There is precedent for ligand exchange at the metal site in such photoreactions \([11-13]\), affording CO ligands and thus metal carbyls (M = Mo, Os, Ir, Cu) but hitherto not for alkylation of an organic ligand in this kind of photoreactions.

In the niobia system, it is seen that Fe complexes (brownish to orange) are deposited on the white sorbent directly, tanning it accordingly. This is no precipitate of Fe oxides although this sorption brings about a pH decrease (the opposite with Bi$_2$O$_3$) but just the adsorbed complex which, unlike Fe oxides, can be readily removed by washing with methanol. By this adsorption of complexes to semiconductors (SCs), quantum yields $\Phi$ of LMCT photoreactions increase vastly \([13]\). Successful degradations, including both removal

\[^1\] Tyrosine was selected for comparison due to its role in photosynthetic water oxidation which suggests that the tyrosinyl radical, once formed, can also transfer charges to other solid supports. Although the formal redox potential of the tyrosinyl phenoxy radical is but 0.93 V, it is involved in oxidation of water there. In our experiments, tyrosinoferrates(III) show an enhanced reactivity with respect to the more simple glycinate or alaninate complexes.

\[^2\] This is not a FENTON system; in the catalytic cycle, formation of ferryl Fe$^{IV}$O$_2^+$ species as (then likely more efficient) hole injectors is very unlikely.
of functional groups like –CHO, halide, and complete mineralization or degradation to acetate ion, were demonstrated with PAHs (naphthalene up to tetracyclic ones), hetero-PAHs (e.g., carbazol), aldehydes [11, 15], aliphatic and aromatic (this work) amines, carboxamides, phenols [14] and CH-acids, including pharmaceutical residues such as diclofenac and its environmental decay products which do harm eg, to fishes and vultures. While chlorinated compounds are entirely removed (diclofenac, 4-chlorophenol or 2,6-dichlorophenylacetic acid), carbazol remains stable, except for adsorption, probably because its 1e-oxidation potential is too high to undergo hole attack (Tab. 2).

Table 2

<table>
<thead>
<tr>
<th>Substance</th>
<th>E\textsubscript{cb} or 1e-reduction potential (V vs SCE)</th>
<th>E\textsubscript{vb} or 1e-oxidation potential (V vs SCE)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi\textsubscript{2}O\textsubscript{3}</td>
<td>About –1.5</td>
<td>About 1.4</td>
<td>E\textsubscript{cb} calculated from E\textsubscript{vb}, bandgap (2.9 eV); pH 7</td>
</tr>
<tr>
<td>Nb\textsubscript{2}O\textsubscript{5}</td>
<td>About –1.2</td>
<td>2.2</td>
<td>E\textsubscript{cb} calculated from E\textsubscript{vb}, bandgap (3.4 eV); pH 7</td>
</tr>
<tr>
<td>diphenylamine</td>
<td>0.83</td>
<td></td>
<td></td>
</tr>
<tr>
<td>carbazol</td>
<td>1.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>aniline</td>
<td>0.63</td>
<td>0.63</td>
<td>Solvent: 2-propanol</td>
</tr>
<tr>
<td>phenol</td>
<td>0.63</td>
<td>0.63</td>
<td>Solvent: 2-propanol or water</td>
</tr>
<tr>
<td>4-cresol</td>
<td>0.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-chlorophenol</td>
<td>0.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-nitrophenol</td>
<td>0.92</td>
<td></td>
<td></td>
</tr>
<tr>
<td>tyrosine</td>
<td>0.93</td>
<td></td>
<td>Forming phenoxy radical</td>
</tr>
<tr>
<td>naphthalene</td>
<td>1.31</td>
<td></td>
<td>Solvent: CH\textsubscript{3}CN</td>
</tr>
<tr>
<td>anthracene</td>
<td>0.84</td>
<td></td>
<td></td>
</tr>
<tr>
<td>phenanthrene</td>
<td>1.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pyrene</td>
<td>0.86; 1.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>biphenyl</td>
<td>1.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>glycinate</td>
<td>(1.32)</td>
<td></td>
<td>Refers to onset of oxidation at Pt anodes in a manner of bidentate adsorption</td>
</tr>
</tbody>
</table>

The turnover TON (oxidation yield with respect to Fe catalyst) can be estimated as follows, giving proof this is really a photocatalytic oxidation: [Fe] is 10 mg/dm\textsuperscript{3} (some 180 µM/dm\textsuperscript{3}), while during six repeated additions up to 120 mg (some 590 µM) of C\textsubscript{14} compound diclofenac are degraded down to CO\textsubscript{2}, some acetate plus Cl\textsuperscript{–}, NH\textsubsuperscript{3}…, that is, about 8.2 millimoles of carbon undergo oxidation (> 45 times the amount of Fe in the system). The Fe(III)-induced photooxidation is transferring one electron (or hole, respectively) each time, whereas oxidation of aromatic CH moieties to CO\textsubscript{2} will take three electrons per carbon. Although the yields of acetate by-product are not exactly known (yet small), and degradation of C-Cl sites and of the aliphatic side chains are to be treated differently, with diphenylamine nitrogen apparently undergoing release as NH\textsubscript{3} (pH increase during photoreaction) rather than any oxidation at N (N remaining NH\textsubscript{3} is common in “classical” photoelectrochemistry of organonitrogens also) taking place it is safe to conclude that every iron complex central ion present in the suspension will undergo the cycle of complex formation with amino acid excess, photodissociation, charge transfer and air reoxidation (Fig. 2 a-c) more than a hundred times. Thus it is a catalytic reaction indeed.
Some, thus small, part of glycinate or other amino acid ligand will become alkylated to yield (substituted) morpholinone.

While in removals of aromatic amines including diclofenac, phenols or aldehydes, both niobia and bismuth oxide are completely stable in aqueous suspension even though oxide partial lattices might undergo $h^+$-induced oxidation, there are problems with long-term stability in decomposing PAHs: while $h^+$ oxidation potential suffices to remove them all (including naphthalene and biphenyl) at $\text{Bi}_2\text{O}_3$, triplet states of some PAHs adsorbed can reduce bismuth oxide to elemental bismuth, causing it to turn first green, then dark-brown and finally black (colloidal Bi). Bleaching by hydration is also observed, forming white BiO(OH). Otherwise, only minute traces of dissolved Bi are passed into solution/suspension by these alterings.

**Discussion**

The reaction can be done with environmentally acceptable (non-toxic) sensitizer systems, concerning both metal complexes and semiconductors (which, however, was not the only criterion for selecting the two SCs used here); it is photocatalytic (TON > 100 with respect to Fe), allowing for multiple additions and removals of pollutant compound(s) and the by-products are not toxic either. Concerning the “optimum” extent of interaction between a possible catalyst and the substrate(s), consider Sabatier’s rule stating that “intermediate”ly strong binding is best. This also holds for biological catalysis [4, 21]. This is an appropriate description of the sorbent properties of both used oxides also.

It is better suited for combination with sewage water treatment than cleaning up an already polluted open water as the product mixture from ambient photolysis contains substantial amounts of carboxylics (more persistent than the original diclofenac and thus piling up eg in Lake Zurich) formed by photochemical closure of a third ring in the same manner as diphenylmethanes and diaryl ethers, diaryl sulfides convert into fluorennes, dibenzofuranes or dibenzothiophenes, respectively [22], under UV irradiation. As carboxylics readily adsorb to the semiconductors but do not undergo oxidation owing to their high-lying oxidation potentials there, they cannot be removed in a catalytic fashion by this procedure, at least when using these semiconductors and sensitizers.

All the experiments showed that diclofenac was more reactive (degraded faster) than either simple diphenylamine or phenylacetic acid (hypothesized product of aniline group cleavage). Accordingly, oxidations of aryamines or aromatic carboxylic acids conform to the expectation that kinetics are controlled by the Hammett equation [23] with a positive $\rho$ value like is commonly observed in oxidations of benzenoid aromatics, be they induced by free radicals like OH or electrophilic agents such as $\text{NO}_3^-$, $\text{SO}_3^-$ or by simple oxidants (eg, bromine in glacial acetic acid, $\text{Hg}^{2+}$ in water [which latter causes aryl anion transfer from $\text{EAr}_4$, $\text{E} = \text{Si}$ to Pb, according to $\text{Hg}^{2+} + \text{EAr}_4 \rightarrow \text{EAr}_3^+ + \text{ArHg}^+$].) The same trend of liability towards this kind of photooxidation vs $\sigma_p$ was observed with a series of para-substituted phenols (and some others, including thymol and salicylic acid) earlier [14]; however, the inertness of 4-nitrophenol here might also be attributed to the fact that its anodic oxidation potential of 0.924 V (in both 2-propanol [24] and neutral water [our measurements by CV; [14]) is very close to $\varepsilon_{\text{ox}}$ for $\alpha\text{-Bi}_2\text{O}_3$. Also see Table 2.
There is a relationship among all $\sigma_p$, the 1e-oxidation potential of aromatic organics and $k_{OH}$ (both in air and aqueous; Fränzle 2000, unpublished) while reactions with common 1e-oxidants like Ce(IV), $\text{^3O}_2$ [25], follow Hammett-type kinetics also. The same apparently is observed here in photovoltaic chemistry, when “blurring” of the data by electron transfer from conduction band is suppressed.

The key mechanism is hole injection to the valence band of the sorbent by photoproduced (LMCT transition) ligand radicals (Figs. 2a-c) [11, 15] and subsequent oxidative quenching of the holes by organic pollutant co-adsorbed to the semiconductor particles, with air reoxidation (Fig. 2c) of Fe(III) and amino acid excess in solution effecting reconstitution of the photosensitizing Fe complex.
When there is no semiconductor around, Fe(III)-α-amino acid complexes undergo photooxidation readily producing CO$_2$ and aldehydes (or glyoxylic acid) besides NH$_4^+$ [17, 26], starting in the visible wavelength region at $\lambda \approx 450$ nm. Adsorption to (either n- or p-type) semiconductors obviously suppresses this reaction in favour of hole transfer.

The Kolbe electro- and Photo-Kolbe photoelectrooxidations of carboxylate ions from acetate onwards take potentials much above +2 V vs SCE, on Pt or semiconductors, respectively. Subjecting glycinate to Kolbe electrooxidation conditions does not yield ethylene diamine [7], but trimethylamine [27] as principal product; PEC produces traces of oligopeptides. While photodecarboxylation may take place in presence of diverse oxidizing ions causing formation of some organometal species [28], the oxidation potential of amino acid ligands still remains unknown whereas that of R-COO radical is estimated to be $\approx 2.0$ V (also see, photooxidations with NO$_2^+$ [11]), with just psec lifetimes against CO$_2$ cleavage which still is sufficient for hole injection. Thus glycinate “survives”, except for small extents of ring-closing alkylation or apparently of oligopeptide formation (which latter [glycine oligomers] was noticed earlier in classical PEC setups [29]).

References

HETEROGENNA KATALIZA ŚRODOWISKOWA.
OCZYSZCZANIE WODY PRZEZ AKTYWOWANE INTERFEJSY -
NOWE PROCEDURY AKTYWACJI POWIERZCHNI

Abstrakt: Poza ustalonymi procedurami wiele związków organicznych występujących w środowisku może być mineralizowanych lub co najmniej degradowanych do np. octanów przez naświetlanie światłem widzialnym kompleksów z żelazem(II), zaadsorbowanych na niektórych szerokopasmowych półprzewodnikach. Wydajność kwantowa znacznie wzrasta dzięki adsorpcji ze względu na fotochemię LMCT (Ligand-to-Metal Charge Transfer) w jednorodnym roztworze. Półprzewodnik działa jak przekaźnik elektronu (lub raczej dziury w półprzewodniku), który utwala utleniające właściwości rodników ligandu, pierwotnie wytwarzanych w dłuższych okresach czasu. Koloidalna cząsteczka półprzewodnika, sama niewzbudzona, jest nośnikiem dziury i umożliwia utlenianie współadsorbowanych związków występujących w niewielkich stężeniach, a także zgromadzonych w wyniku adsorpcji. Oczyszczanie wody z różnego rodzaju zanieczyszczeń jest możliwe, a reakcja fotokatalityczna o wydajności ≥100 w odniesieniu do kompleksu Fe może zachodzić z udziałem powietrza wprowadzanego do zawiesiny, tolerując ponowne wprowadzanie związków, które mają być usunięte. Z wyjątkiem niektórych octanów mineralizacja substratu zachodzi całkowicie.

Słowa kluczowe: fotoutlenianie, półprzewodniki, kompleks żelaza, uzdatnianie wody, kataliza heterogenna, metoda zwiększonej aktywacji powierzchni