

Semiconductor-sensitized photodegradation of pesticides in water: the case of carbetamide

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Abstract

The kinetics of disappearance of carbetamide in water suspensions of TiO_2 , on illumination at $\lambda \geq 310$ nm (to avoid direct photolysis), were determined. The photocatalytic reaction was studied by measurement of the initial rate of degradation and the effects of the mass of catalyst and radiant flux were determined. The value of the quantum yield is approximately 0.01. A Langmuir-type relationship between the initial rate and the initial concentration indicates that reaction occurs with the adsorbed substrate.

The main intermediates in the degradation are of two types: (a) hydroxylated products and derivatives; (b) products of cyclization of the side chain. The structure of carbetamide allows the formation of these two types of compound, which are explained by the reaction with two different oxidant species: hydroxyl radicals and holes.

Keywords: Degradation; Kinetics; Metal oxides; Photocatalysis; Pesticide

1. Introduction

For several years, light has been used in the chemical treatment of water. In all cases, the direct action of light is limited due to the absorption spectra of the pollutants to be eliminated. Thus direct photochemical reaction has given way to a sensitized photochemical or photoassisted reaction via the introduction of compounds such as H_2O_2 [1–4] or ozone [5–7], which allow the formation of oxidizing species such as OH^\cdot . Following the same type of action, photocatalytic experiments aided by semiconductors, such as TiO_2 , have been undertaken and have begun to show promising results. This study is designed to improve the fundamental understanding of this type of process for water purification.

Of the chemicals likely to be found in groundwater, pesticides have a non-negligible presence and their elimination is necessary, especially if the water is to be used for household consumption. We are therefore working on this class of pollutants, and the present study concerns one pesticide in particular: carbetamide. This molecule exhibits the peculiarity of being relatively unaffected by the direct action of light; in addition, its

structure, containing both an aromatic ring and an aliphatic chain, is particularly interesting as it allows two different types of photoreaction to take place, as shown later.

A comparison of the rates of reaction assisted by two photocatalysts (TiO_2 and ZnO) is performed, and the influence of various parameters, such as the power of the light irradiation source, the mass of the catalyst and the concentration of the pollutant, is examined. The nature of the photochemical intermediates is also studied. Finally, using these results, a mechanism is proposed.

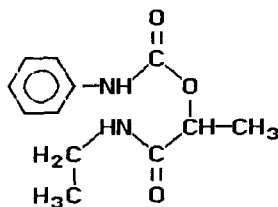
2. Experimental section

2.1. Materials

TiO_2 was “Degussa P 25” grade (non-porous anatase; surface area, $50 \text{ m}^2 \text{ g}^{-1}$; mean diameter, approximately 30 nm). ZnO was “Les mines de la Vieille Montagne neige A” grade (surface area, $9.5 \text{ m}^2 \text{ g}^{-1}$; mean diameter, approximately 110 nm). O_2 , N_2 and N_2O were “Air Liquide high purity” grade. All solutions were prepared with doubly distilled water.

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Finally, carbetamide (see below) is a pesticide from Rhône-Poulenc (CA number 16118-45-0); its solubility in water is 3.5 g l^{-1} at 25°C .



The radiolysis experiments were carried out using γ rays from a cobalt irradiator (Institut de Recherche sur la Catalyse, CNRS, Lyon).

2.2. Photoreactor and light source

The batch photoreactor was a cylindrical flask of approximately 60 ml, open to the air, with an optical Pyrex window (at the bottom) of about 3 cm in diameter and a water circulating jacket of about 6 cm in diameter (allowing temperature regulation to $298 \pm 2 \text{ K}$). It was mounted at a distance of 6 cm from the top of the lamp assembly, which consisted of a horizontal HPK 125 W mercury lamp supplied by Philips, fixed at the middle of a vertical metallic cylinder which allowed natural ventilation of the lamp.

Filters were selected to obtain the desired wavelengths and calibrated metallic grids were used to attenuate the incident light.

The incident radiant flux was centred at 365 nm and represented about $10^{16} \text{ photons cm}^{-2} \text{ s}^{-1}$, measured by chemical actinometry and a radiometer.

2.3. Procedures

The suspension was prepared by adding 30 cm^3 of a solution containing the desired concentration of carbetamide at natural pH to the photoreactor containing 30 cm^3 of an aqueous suspension of powder catalyst (TiO_2 or ZnO). The sample was sonicated for 30 min to obtain a good dispersion of the photocatalyst. After bubbling for 30 min with the appropriate gas (O_2 , N_2 , N_2O), the mixture was magnetically stirred in the dark for 10 min prior to illumination.

2.4. Analysis

Quantitative and qualitative analysis of the organic compounds in the samples was carried out by high performance liquid chromatography (HPLC). The HPLC apparatus consisted of a pump (Waters 510), fitted with a guard column, and a Hypersil C_{18} ($10 \mu\text{m}$; length, 25 cm; inside diameter, 4.6 mm) analytical column associated with an integrator (Waters 740 type). The wavelength of detection was 254 nm (UV III LDC

detector). Good separation of the reactant and products was achieved within 15 min by the mobile phase: 60% methanol, 40% water (v/v). To remove particles before HPLC analysis, the samples were centrifuged and, if necessary, filtered through $0.40 \mu\text{m}$ Millipore discs.

3. Results and discussion

3.1. Kinetics of carbetamide disappearance

3.1.1. Nature of semiconductor (TiO_2 , ZnO)

- Fig. 1 shows the kinetics of disappearance of carbetamide (initial concentration $C_0 = 100 \text{ mg l}^{-1}$ ($4.23 \times 10^{-4} \text{ M}$)) under the four following conditions:
- (1) without semiconductor at $\lambda \geq 250 \text{ nm}$ (i.e. within the absorption band of carbetamide); the pollutant is progressively destroyed (4.5% at 3 h illumination);
 - (2) at $\lambda \geq 310 \text{ nm}$ (i.e. outside the absorption region of carbetamide); no change in concentration is detected after illumination for 24 h;
 - (3) in the presence of TiO_2 (400 mg l^{-1}) at $\lambda \geq 310 \text{ nm}$; rapid degradation occurs; the pollutant becomes undetectable within an illumination time of 90 min;
 - (4) in the presence of ZnO (400 mg l^{-1}) at $\lambda \geq 310 \text{ nm}$; the disappearance of the pollutant is faster than with TiO_2 ; no carbetamide is present after 60 min of illumination.

These experiments show that the photocatalytic degradation in the presence of the semiconductors (TiO_2 , ZnO) is more efficient than direct photolysis. On illumination at $\lambda \geq 310 \text{ nm}$, only photocatalytic degradation occurs without photochemical interference.

Moreover, the photocatalytic degradation with the ZnO sample is faster than that with TiO_2 in spite of

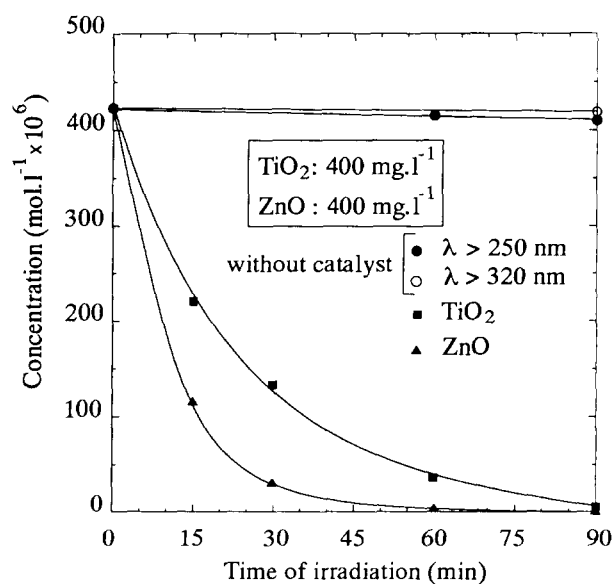


Fig. 1. Kinetics of disappearance of carbetamide in water (initial concentration, 100 mg l^{-1} ($4.23 \times 10^{-4} \text{ M}$)).

the larger surface area of the latter photocatalyst (approximately five times the ZnO surface area). Degussa P25 type TiO_2 is the most efficient type of TiO_2 . Nevertheless, it seems that ZnO is more efficient than TiO_2 in this type of reaction.

All of these studies were performed with the photoreactor described in Section 2.2. The effects of various parameters on the initial rate of disappearance of carbetamide have been determined. These effects allow relevant information to be obtained in order to optimize the degradation of carbetamide photocatalytically.

3.1.2. Effect of the mass of TiO_2

The initial rate r_0 increases linearly with an increase in the amount of catalyst up to a level corresponding to the complete absorption of incident light by TiO_2 . Fig. 2 represents such a variation, as expected for a catalytic reaction. The amount of 100 mg l^{-1} at the beginning of the plateau was chosen to study the effect of other parameters.

3.1.3. Effect of the initial concentration C_0

Fig. 3 shows that the initial rate r_0 increases with increasing C_0 , up to $4.2 \times 10^{-3} \text{ mol l}^{-1}$ (980 mg l^{-1}). This variation has been treated according to a Langmuir–Hinshelwood-type relationship [8–11]

$$r_0 = kKC_0/(1 + KC_0) \quad (1)$$

where k and K are the rate and adsorption constants respectively. The linear transformation of the data according to

$$\frac{1}{r_0} = \frac{1}{k} + \frac{1}{kKC_0} \quad (2)$$

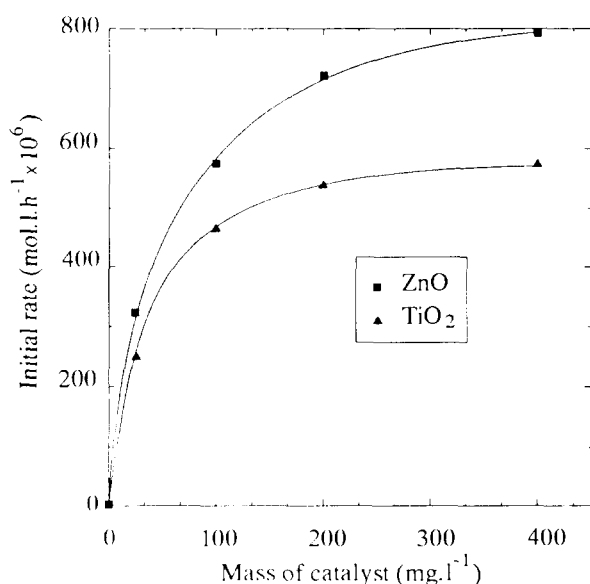


Fig. 2. Initial rate of degradation vs. mass of catalyst. Initial concentration of carbetamide, 100 mg l^{-1} .

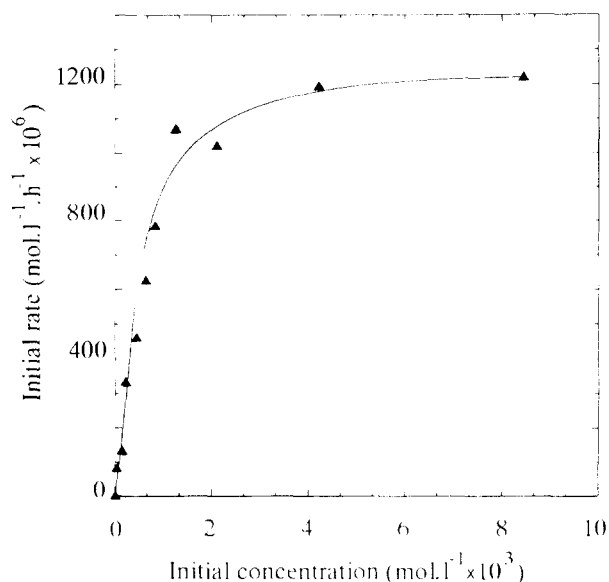


Fig. 3. Initial rate of disappearance vs. initial concentration. TiO_2 , 100 mg l^{-1} .

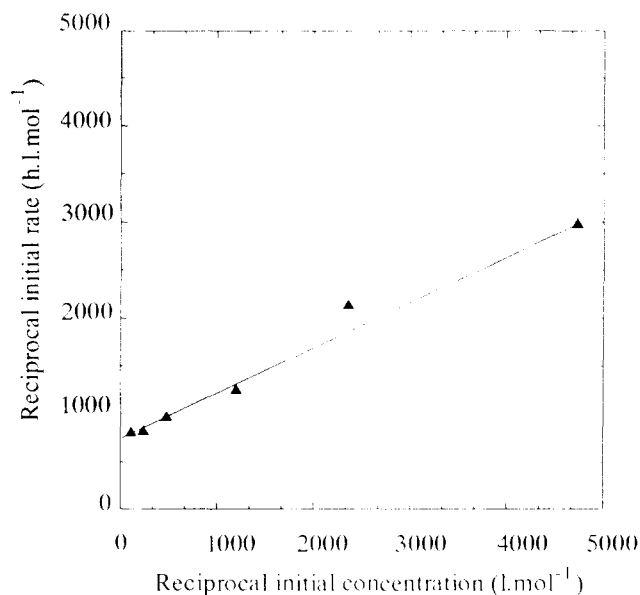


Fig. 4. Relationship between reciprocal initial rate and reciprocal concentration

allows the plot in Fig. 4 to be drawn, whose intercept and slope give the values $k = 1.3 \times 10^{-7} \text{ mol l}^{-1} \text{ s}^{-1}$ and $K = 1700 \text{ l mol}^{-1}$ respectively.

The value of k has no absolute meaning because it depends on the experimental conditions. The value of the adsorption constant K is very low in comparison with other aromatic compounds [8].

Nevertheless, the degradation seems to be a first-order reaction at low concentrations of carbetamide, but a zero-order reaction at high concentrations.

3.1.4. Effect of radiant flux

The total incident power ($\lambda \geq 310$ nm) varies between 30 and 250 mW (Fig. 5). For high flux, a plot of r_0 vs. the square root of P_0 produces straight lines. This type of relation indicates the predominance of the recombination of photoproducted charges over the oxidation of carbetamide at high flux [12]. It would be interesting to control and minimize this recombination.

3.1.5. Quantum yield

Because of the presence of a Pyrex filter ($\lambda > 310$ nm) and titanium dioxide absorption ($\lambda < 400$ nm), the quasi-monochromatic beam of actinic light was centred on the 365.4 nm mercury line of the source. To calculate the quantum yield, the mass of TiO_2 must be large enough to absorb totally the incident light over a path length of 6 cm.

The radiant flux was measured in two ways.

- (1) With a radiometer detector "Photodyne" 88 XL which gives the flux; in this case, the response bandwidth of the radiometer was centred on 360 nm. The result gives approximately 8×10^{-7} einstein s^{-1} potentially absorbable by TiO_2 .
- (2) With a chemical actinometer using uranyl oxalate. The UO_2^{2+} solutions were such that the absorption of the radiant flux was total between 310 and 400 nm through a 6 cm depth. In this case, the absorption was close to that of TiO_2 , and the UO_2^{2+} concentration was approximately $5 \times 10^{-3} \text{ mol l}^{-1}$. Taking into account the quantum yield of the actinometer, i.e. 0.5, the photon flux is near 9×10^{-7} einstein s^{-1} . This value is practically the same as that of the radiometer, but the precision is probably

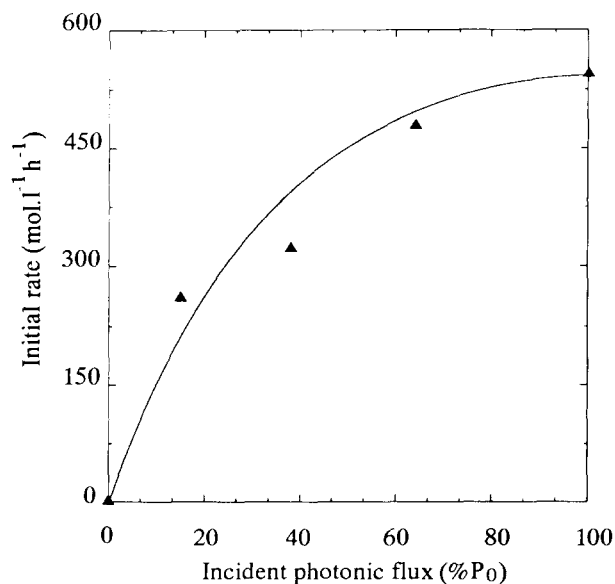


Fig. 5. Relationship between the incident photon flux and the initial rate. $P_0 = 4.8 \times 10^{17}$ photons s^{-1} ; TiO_2 , 200 mg l^{-1} ; carbetamide concentration, 100 mg l^{-1} .

better because of the non-homogeneity of the incident beam.

As the kinetic study of the disappearance of carbetamide shows an initial rate equal to $r_0 = 7.76 \times 10^{-9} \text{ mol l}^{-1} \text{ s}^{-1}$, the calculated quantum yield is near 8.6×10^{-3} . This value seems low, but the light scattering by the solid particles is large, so that this quantum yield can be considered as a lower limit.

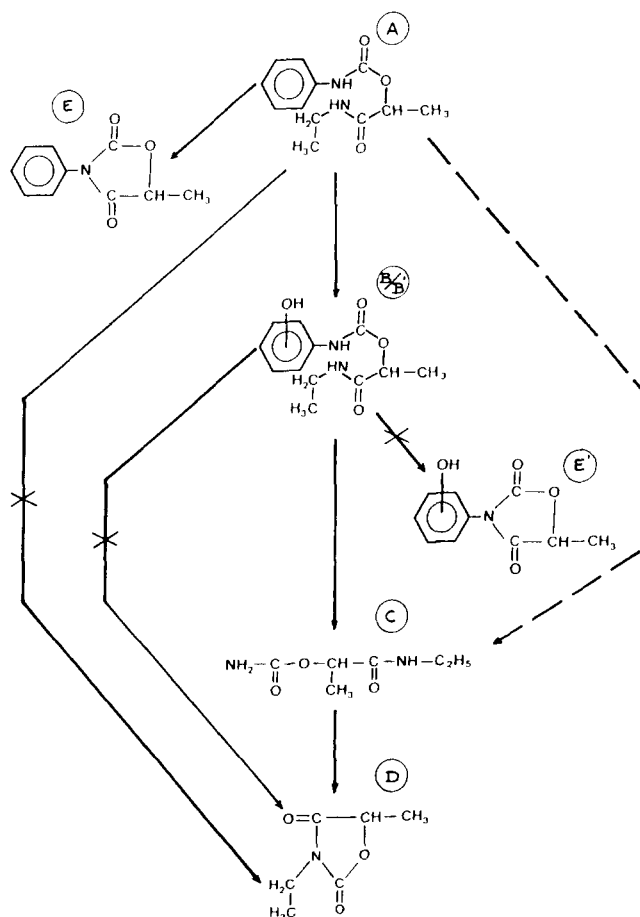
3.2. Products of carbetamide photocatalytic degradation

3.2.1. Long-time irradiation: mineralization

If the irradiation time is long enough, no trace of organic matter can be detected in the solution. A good mass balance was found between the quantities of carbetamide consumed and the CO_2 evolved. These measurements demonstrate that carbetamide and the intermediate products are completely mineralized.

3.2.2. Reaction intermediates (Scheme 1)

When the irradiation time was short, seven primary intermediates were detected by HPLC under the indicated conditions. Five of these intermediates were identified by HPLC and liquid chromatography-mass spectrometry (LC-MS). These five products can be classified into three groups:



Scheme 1.

- (1) compounds corresponding to the hydroxylation of the aromatic ring of carbetamide or derivatives (B, B'); they are the first to appear;
- (2) compounds which result from the cleavage of the side chain (C);
- (3) compounds which show cyclization of the side chain (E, D).

The two other intermediates were not identified, due to their low concentration in the solution.

The concentrations of the five main intermediates were in the order: [B], [B'] \gg [C] \gg [E], [D].

It was not possible to detect aniline, aminophenols or products such as E', corresponding to both the hydroxylation of the ring and the cyclization of the side chain.

No attempt was made to identify the secondary intermediates en route to total mineralization. However, it seems reasonable to assume that aliphatic compounds, more or less oxidized (aldehydes, acids, etc) are formed, as proposed in the case of phenol photocatalytic degradation [13].

3.3. Mechanism of carbetamide photocatalytic degradation

Many reports on the photocatalytic degradation of organic compounds in aqueous solutions have suggested the action of OH \cdot radicals [14–19]. These radicals can be produced by the surface reaction of the photo-produced holes with adsorbed OH $^-$ ions or adsorbed water. The corresponding electron reaction would be the formation of superoxide ions (O $_2^{\cdot-}$) from dioxygen present in the solution and would generate H $_2$ O $_2$ [20]. H $_2$ O $_2$ is very unstable over UV-illuminated TiO $_2$, also giving OH \cdot radicals. These mechanisms have already been proposed by many workers.

Therefore the presence of hydroxylated compounds is not surprising. The cleavage of the side chain seems to be promoted by hydroxylation of the ring; direct cleavage from carbetamide is probably a minor process.

Cyclization of the side chain gives very low concentrations of D and E.

In radiolysis experiments with γ rays, well known to give OH \cdot radicals [21], the same hydroxylated compounds (B, B') are found as well as compounds due to cleavage of the side chain (C). No cyclic compounds were detected.

The quenching of OH \cdot radicals by alcohols or benzene was studied. By increasing the concentration of these quenchers a limit is obtained. This indicates that another mechanism is also responsible for the disappearance of carbetamide: it represents approximately 8% of the total reaction. The most probable mechanism is the capture of a hole by adsorbed carbetamide [22,23]: this reaction is thermodynamically possible. Nevertheless, this phenomenon is less probable than the formation

of OH \cdot radicals, because of the presence of OH $^-$ ions at the surface of TiO $_2$. The radical cation formed in this way can give a cyclic product via a reaction of the same type as the cyclization of α,ω -diamines [24].

4. Conclusions

The photocatalytic degradation of organic pollutants in aqueous solutions was studied using two semiconductors with different efficiencies; it appears that titanium dioxide (TiO $_2$) is the best photocatalyst taking into account its good activity and non-toxicity.

For the chosen pollutant, carbetamide, two methods of oxidation were observed: oxidation by OH \cdot radicals originating on the surface of the photocatalyst; direct oxidation by holes created by the action of light on the semiconductor.

These two reactions are not of the same importance and give different intermediates. Nevertheless, after a long irradiation time, all compounds are mineralized. This result is important in the field of water decontamination: the elimination of intermediates, possibly more toxic than the starting pollutant, is achieved.

This photocatalytic method has good potential for application on a large scale. For this, it will be necessary to decrease the electron–hole recombination to increase the quantum yield of the photocatalytic reaction. Moreover, the problem of photocatalyst recovery remains. The solution to this problem will probably be achieved by the use of a supported or immobilized semiconductor [25–30].

Acknowledgment

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