

Photocatalytic degradation of 3,4-xylyl *N*-methylcarbamate (MPMC) and other carbamate pesticides in aqueous TiO₂ suspensions

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Abstract

Five carbamate pesticides were degraded photocatalytically on TiO₂. The comparison of their disappearance rates showed that the degradation rate is governed predominantly by their adsorbability to TiO₂, and followed Hammett's law in a different manner from ordinary electrophilic reaction. As a degradation pathway of 3,4-xylyl *N*-methylcarbamate (MPMC) successive hydroxylation of aromatic ring was suggested, and polyhydroxylation is considered to lead to the opening of the aromatic ring to form oxygenated aliphatic intermediates. It was indicated in this process that the formation of acetic acid, one of the major aliphatic intermediates, mainly originates from methyl substituents on the aromatic ring. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Photocatalysis provides a new method for water decontamination. Recent intensive study showed that it can be applied to the degradation of many pollutants [1]. Among them, pesticides have been considered to be one of the major pollutants to which it is promising to apply photocatalysis [2,3]. Many pesticides cannot be

degraded by conventional biological methods [4,5], whereas complete mineralization can be achieved by photocatalysis [6,7]. In this work the photocatalytic degradation of several carbamate pesticides were studied in regard to degradation rate, degradation process and intermediate compounds, and the degradation rate was correlated to the chemical structure of the pesticides to investigate the factors influencing the photocatalytic reaction.

Carbamates are an important group of insecticides which are widely used throughout the world. Contamination of surface and underground waters by these pesticides have been

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reported in different parts of the world [8–11]. Because of their toxicity and that of their degradation intermediates [12], their complete degradation is of great environmental concern.

2. Experimental

The TiO_2 used throughout the experiment is TP-2 (anatase) supplied by Fujititan. Its specific surface area is $17.3 \text{ m}^2/\text{g}$ [13].

Carbamate pesticides used in this study are of analytical grade and their chemical structures are shown in Fig. 1.

For degradation experiment 75 mg of TiO_2 powder was suspended in 25 ml of $10^{-4} \text{ mol l}^{-1}$ solution of pesticide in a Pyrex glass bottle by stirring magnetically. The bottle was illuminated by a 500 W super-high-pressure mercury lamp through a water filter. After illumination for a given time, the sample was filtered through a Millipore membrane filter of $0.2\text{-}\mu\text{m}$ pore size and the filtrate was subjected to analyses.

Degradation was monitored by a JASCO 880-PU with a multiwavelength UV–VIS detector JASCO MD-90. The aromatic intermediate was identified by the same instrument. Organic acid intermediate was analyzed by an ionchromatograph Yokogawa IC 7000.

NO_3^- , NO_2^- and NH_4^+ were detected by an ionchromatograph consisting of a JASCO 880-PU pump and Shodex CD-4 conductometer. Total organic carbon (TOC) was measured by a Shimadzu TOC-500.

Aldehyde and ketone were determined following the method described in the literature [14,15]. Solubilities of pesticides were measured as follows [16]. An adequate amount of pesticide was dissolved in water at room temperature by stirring for 1 week, and then left standing for 1 day at 25°C . After filtration the filtrate was analyzed.

3. Results and discussion

3.1. Degradation rate

Degradation rate of MPMC increased with pH, while TOC removal rate was constant from pH 4.0 to 8.8 and significantly smaller at pH 2.5 (Fig. 2). The time required for 90% of pesticide ($t_{0.9}$) to disappear was plotted against pH for five pesticides in Fig. 3. The common trend among these pesticides is that the rate decreases with decreasing pH up to pH 6.0. The effect of pH may be explained by the increase in positive charges of both TiO_2 particle and pesticide (its amide group) with lowering pH, which result in their electrostatic repulsion. On the other hand, pH dependency of TOC removal rate is more complicated. For MPMC, XMC and MIPC the rate was smallest at pH 2.5 (Fig. 4), while for MTMC and MCC the rate was nearly independent of pH from pH 2.5 to 8.6.

The photocatalytic degradation rate of many compounds is determined by their affinity with

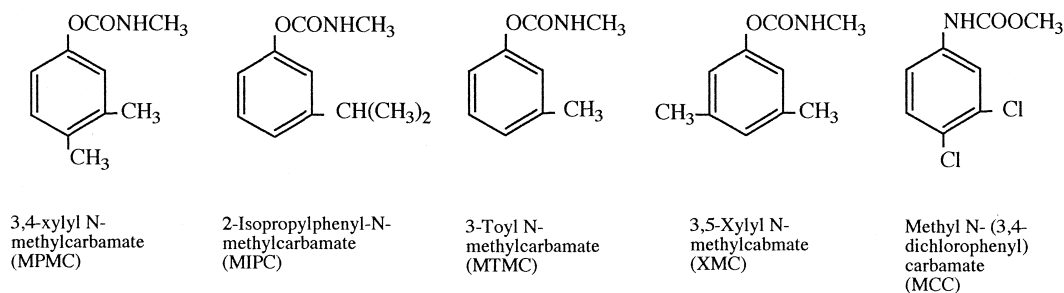


Fig. 1. Chemical structures of five carbamate pesticides.

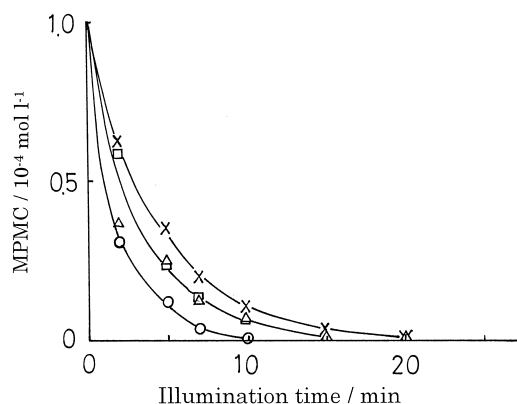


Fig. 2. Photocatalytic disappearance of MPMC at different pH's. ○ pH 8.8, △ pH 6.1, □ pH 4.0, × pH 2.5.

electrophilic OH group and adsorbability to TiO_2 . D'Oliveira et al. [17] proposed the following simple equation to formulate this relation and showed that the degradation of chlorophenolic compounds fit this equation.

$$k = A\sigma + B \log K_{ow} + C \quad (1)$$

where k is apparent rate constant, σ is Hammett's constant, K_{ow} is a partition constant between 1-octanol and water, and A , B and C are constants. In this equation K_{ow} is assumed to be applicable to the partition between TiO_2 surface and water. Since Hammett's law is rep-

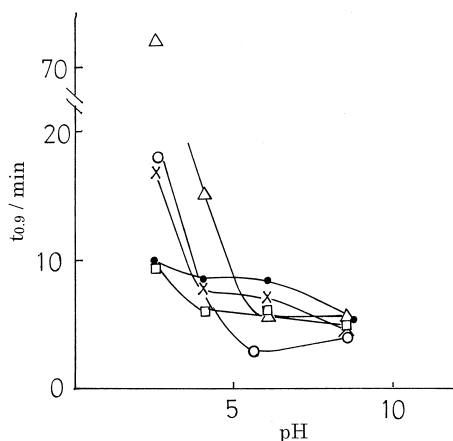


Fig. 3. Effect of pH on the photocatalytic disappearance rates of five pesticides. $t_{0.9}$: time for 90% disappearance. ● MPMC, △ MIPC, □ MTMC, × XMC, ○ MCC.

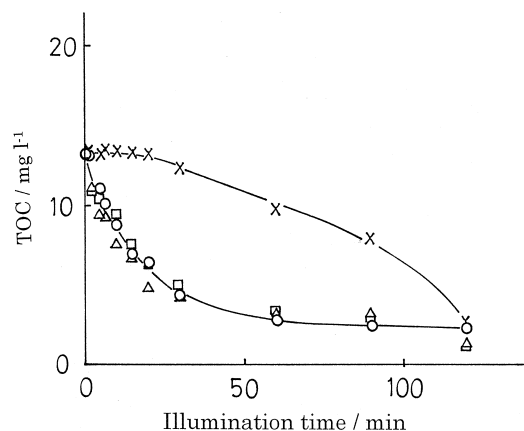


Fig. 4. Photocatalytic TOC eliminations of MPMC at different pH's. ○ pH 8.7, △ pH 6.1, □ pH 4.0, × pH 2.5.

resented by $\log k/k_0 = \rho\sigma$ and ρ (constant) < 0 in electrophilic reaction [18,19], the following equation is more likely for this relation.

$$\log k = -\rho\sigma + B \log K_{ow} + C \quad (2)$$

Since $\log k_{\text{int}}/k_0 = -\rho\sigma$ (where k_{int} is the intrinsic rate constant), Eq. (2) expresses that the degradation takes place for pollutant adsorbed to TiO_2 in the equilibrium between TiO_2 surface and water, although K_{ow} may not represent adsorption quantitatively. The values for K_{ow} are not available for the present compounds. However, K_{ow} can be derived from the solubility in water by the relation proposed by Mackay et al. [20]:

$$\log K_{ow} = D - \log s \quad (3)$$

where s is solubility in water and D is constant. From Eqs. (2) and (3), Eq. (4) is obtained:

$$\log k = -\rho\sigma - B \log s + E \quad (4)$$

where $E = BD + C$. The solubilities of these pesticides are not available in literature, hence approximate values were determined by the procedure described in Section 2. These values and those for σ are listed in Table 1. In the calculation of collective value for σ , the value of each functional group with regard to the carbamate group was employed [21], and the contributions

Table 1
Hammett constants, solubilities and pseudo-first-order kinetic constants for photocatalytic degradation of carbamate pesticides

	$\Sigma\sigma$	$s/10^{-3}$ mol l^{-1}	$\log s$	k/min^{-1a}	$\log k^a$
MPMC	-0.24	6.4	-2.19	0.081	-1.09
MIPC	-0.15	2.6	-2.59	0.083	-1.08
MTMC	-0.07	6.2	-2.21	0.093	-1.03
XMC	-0.14	2.3	-2.64	0.093	-1.03
MCC	0.6	0.19	-3.72	0.125	-0.90

^aThe intensity of the light source was reduced by applying 10% neutral filter.

of the carbamate group were assumed to be the same for five pesticides, neglecting possible little difference of MCC from other pesticides (Fig. 1). Generally the σ value is not available for *o*-position, and therefore the same value as that for *p*-position was employed according to the discussion in the literature [17,22]. It was found that the solubility is approximately proportional to Hammett's constant (Fig. 5). This relation is expressed by Eq. (5).

$$\log s = F - G\sigma \quad (5)$$

By inserting Eq. (5), Eq. (4) is simplified to Eq. (6).

$$\log k = (H - \rho)\sigma + I \quad (6)$$

where $H = BG$, $I = -BF + E$. Eq. (6) indicates that the degradation rate is proportional to Ham-

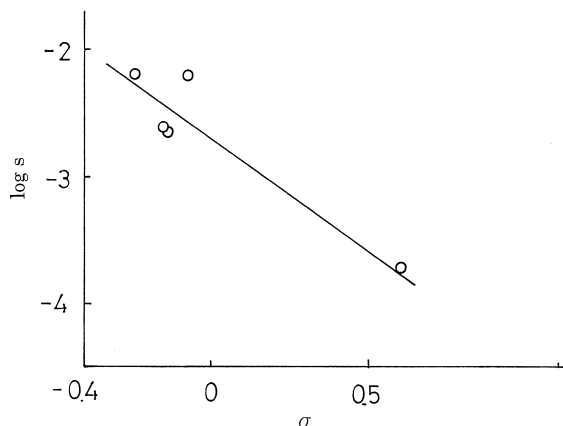


Fig. 5. Relation between solubility and Hammett constant for carbamate pesticides.

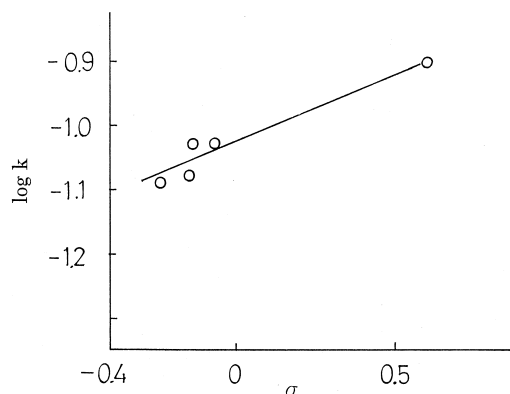


Fig. 6. Relation between apparent kinetic constant for photocatalytic disappearance and Hammett constant.

mett's constant. To evaluate this relation, k was obtained from separate degradation experiments in which a 10% neutral filter was applied to the light source to slow down the degradation (Table 1). A proportional relation between $\log k$ and σ is shown in Fig. 6, from which $H > \rho$ was obtained. Since H and ρ represent the contributions of the adsorbability and electron density on the aromatic ring, respectively, it can be concluded that the former is more important in determining the degradation rate. The positive value of the slope for this proportionality is peculiar for electrophilic reaction [18,19].

3.2. Intermediate compounds

Three aromatic intermediates were identified in MPMC degradation: 3,4-xyleneol, methylhydroquinone and hydroxyhydroquinone. They were formed quickly and disappeared within 20 min. The formation of these compounds may suggest the following degradation pathway of MPMC (Fig. 7). The first step of the degradation may be the replacement of the carbamate group by the OH group to form 3,4-xyleneol (I). OH group thus derived makes *p*-position susceptible to the attack of electrophilic OH radical [19], which leads to the production of methylhydroquinone (II). In the same manner the CH_3

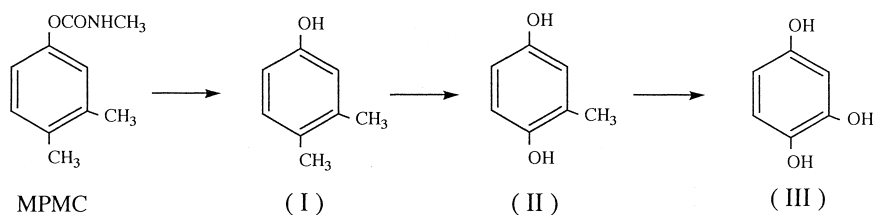


Fig. 7. Possible degradation pathway of MPMC.

group at *o*-position with regard to the OH group in methylhydroquinone is replaced by OH to form hydroxyhydroquinone (III). The formation of these compounds demonstrates successive hydroxylation of aromatic ring. Polyhydroxylation may eventually lead to the opening of aromatic ring to form aliphatic compounds.

Several oxygenated aliphatic compounds such as organic acid, formaldehyde [$(2\text{--}2.6) \times 10^{-4}$ mol l $^{-1}$] and acetone [$(2.9\text{--}3.6) \times 10^{-6}$ mol l $^{-1}$] were detected from MPMC degradation. The formation curves of several organic acids are shown in Fig. 8. Nearly the same organic acid intermediates were observed with other pesticides. Acetic acid, formic acid and formaldehyde were formed in the largest quantities for all the pesticides. The maximum concentration of acetic acid formed from five pesticides were in the order: XMC > MPMC > MTMC >

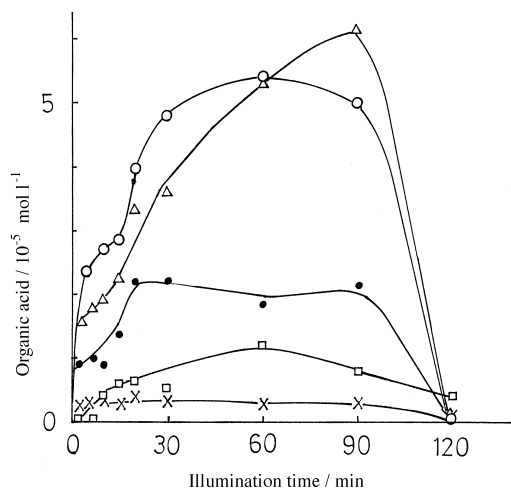


Fig. 8. Formations of organic acid intermediates from MPMC degradation. ○ Formic acid, △ acetic acid, □ glyoxylic acid, ● glycolic acid, × propionic acid.

MIPC > MCC. This order reflects the number of methyl substituents, and hence suggests that methyl substituent contributes to the formation of acetic acid. On the other hand the maximum concentrations of formic acid and formaldehyde were not related to the chemical structures of the pesticides. The maximum formation of organic acid intermediate was observed at pH 2.5. This may be attributed to its low degradation rate, due to its small adsorbability to TiO $_2$ at this pH.

3.3. Final degradation product of MPMC

NH $_4^+$ and NO $_3^-$ were formed as mineralization products, as well as CO $_2$ and H $_2$ O. Fig. 9 shows that nitrogen in MPMC was converted predominantly to NH $_4^+$, and NO $_3^-$ was less than 20% of NH $_4^+$ throughout the degradation reaction. The formations of both NH $_4^+$ and NO $_3^-$ were slow, and nearly stoichiometric nitrogen was recovered only after 3 h.

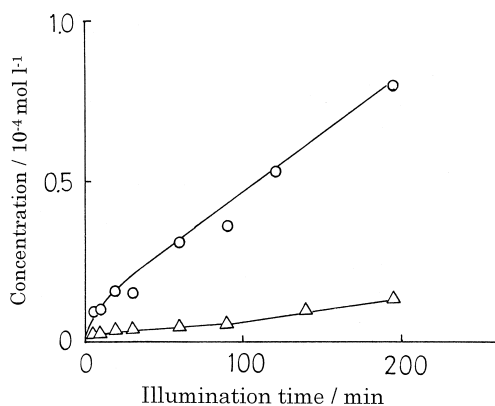


Fig. 9. Formations of NH $_4^+$ and NO $_3^-$ from MPMC degradation. ○ NH $_4^+$, △ NO $_3^-$.

4. Conclusion

Disappearance of the five carbamate pesticides were quick and the rates increased with pH. Their photocatalytic degradations are governed by their adsorbability to TiO_2 more than electron density on the aromatic ring and followed Hammett's law, but in a different manner from ordinary electrophilic reaction. The formation of acetic acid as major intermediate was attributed partly to methyl substituents on the aromatic ring. In the mineralization process nitrogen was converted predominantly to NH_4^+ .

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