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Dye-sensitized photodegradation of the fungicide carbendazim and related benzimidazoles

Juan P. Escalada [a], Adriana Pajares [a], José Gianotti [a], Walter A. Massad [b], Sonia Bertolotti [b], Francisco Amat-Guerri [c,*], Norman A. García [b,*]

[a] *UARG, Universidad Nacional de la Patagonia Austral, 9400 Río Gallegos, Argentine*
[b] *Departamento de Química, Universidad Nacional de Río Cuarto, Agencia Postal Nro. 3, 5800 Río Cuarto, Argentine*
[c] *Instituto de Química Orgánica, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain*

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Abstract

The present work studies the visible-light-promoted photodegradation of the colorless fungicide carbendazim (methyl 2-benzimidazolecarbamate) and several 2-substituted benzimidazoles (SBZ's), in water or water–methanol solution, in the presence of air and, as a photosensitizer, the synthetic xanthene dye Rose Bengal (RB) or the natural pigment riboflavin (Rf). The results indicate that the degradation of each particular SBZ depends on its chemical structure and on the sensitizer employed. In the presence of RB, the degradation always operates via a singlet molecular oxygen ($O_2(^1\Delta_g)$)-mediated mechanism, through a highly efficient process, as deduced from the comparison of the rate constants for physical and chemical quenching of $O_2(^1\Delta_g)$. In the presence of Rf, the visible-light irradiation of any of the studied SBZ's produces a series of competitive processes that depend on the relative concentrations of Rf and SBZ. These processes include the quenching of excited singlet and triplet Rf states by the SBZ and the generation of both $O_2(^1\Delta_g)$ and superoxide radical anion ($O_2^{\bullet -}$), the latter generated by electron transfer from excited Rf species to the dissolved oxygen. The overall result is the photodegradation of the SBZ and the photoprotection of the sensitizer.

Keywords: Carbendazim; Photodegradation; Photosensitization; Singlet molecular oxygen; Superoxide radical anion; Riboflavin

1. Introduction

Carbendazim (methyl 2-benzimidazolecarbamate, CBZ), a systemic fungicide of the benzimidazole (BZ) family, is widely used, generally in the form of an aqueous dispersion because its solubility in water is low (Tomlin, 1994). Under natural environmental conditions, CBZ is very stable, and it has been frequently detected in surface waters, with decomposition half-lives of two months under aerobic conditions, and 25 months in the absence of oxygen, giving rise mainly to its hydrolysis product 2-aminobenzimidazole (ABZ) (Tomlin, 1994). In the case of the photochemical decay of CBZ, the photodegradation products formed have been studied under different experimental conditions, irradiating both with sunlight and with UV light (Panadés et al., 2000). Under UV irradiation, quantum yields in the range $(1.1–4.8) \times 10^{-3}$ have been determined, depending on the oxygen concentration in the reaction medium (Mazellier et al., 2002a,b), and the photodegradation is more efficient than with sunlight (Boudina et al., 2003). Detected photoproducts were ABZ (major), hydroxylated BZ, 2-benzimidazole isocyanate, *N*-methoxycarbonylguanidine, guanine and *N*-methoxycarbonylurea

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* Corresponding authors. Fax: +34 91 564 4853 (F. Amat-Guerri), tel.: +54 358 46 76 439; fax: +54 358 467 6233 (N.A. García).
E-mail addresses: famat@iqog.csic.es (F. Amat-Guerri), ngarcia@exa.unrc.edu.ar (N.A. García).

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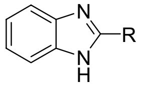
(Panadés et al., 2000; Mazellier et al., 2002a,b; Boudina et al., 2003).

The phototransformations induced on CBZ by OH radicals generated by the photolysis of hydrogen peroxide have been also studied, both in the absence and in the presence of hydrogenocarbonate ions (Mazellier et al., 2002a,b, 2003). In both cases, the observed photoproducts were explained as the result of two main degradation pathways: (1) benzene group oxidation, giving rise to hydroxylated benzimidazoles, and (2) change of the 2-$NHCO_2Me$ group to 2-$NHCO_2CO_2H$, and 2-$NHCO_2CHO$ (Mazellier et al., 2002a,b).

Few works have been devoted to the photosensitized irradiation of CBZ, and their main purpose was the identification of the photoproducts. Thus, the sunlight irradiation of aqueous solutions of CBZ produced greater loss of the substrate in the presence of Rf than in its absence (United Nations Environment Program, 1993). In methanol solution and in the presence of Methylene Blue as a sensitizer, the irradiation gave rise to the appearance of dimethyl oxalate, ABZ, BZ, *N*,*N*′-dimetoxycarbonylguanidine, *N*-methoxycarbonylguanidine, *N*-methoxycarbonylurea and 2-guanidinobenzimidazole. In parallel, the importance of the nature of the substituent at position 2 in the BZ ring was unambiguously demonstrated (Abdou et al., 1985). Nevertheless, no systematic kinetic or mechanistic studies have been carried out on the sensitized photooxidation process applied to CBZ, although these studies could help to foresee the decay of this fungicide and, combined with the study of other SBZ's, could contribute to the design of CBZ analogs with variable resistance towards visible-light-induced photodegradation.

The main aim of the present work was to examine the experimental conditions that maximize the photodegradation efficiencies of CBZ and several related benzimidazoles (Fig. 1), with special emphasis on the CBZ photodegradation products ABZ and 2-hydroxybenzimidazole (HBZ). The study was carried out under dye-sensitized photooxidation conditions similar to those frequently found in nature, i.e. in the presence of the natural dye sensitizer riboflavin (Rf, vitamin B_2), a pigment usually present in natural waters (Benassi et al., 1967; Chacón et al., 1988) or of the synthetic sensitizer Rose Bengal (RB), employed for auxiliary determinations.



	R
CBZ	$NHCO_2Me$
BZ	H
HBZ	OH
MBZ	Me
ABZ	NH_2
PBZ	$(CH_2)_2CO_2H$

Fig. 1. Structure of the studied benzimidazoles.

2. Materials and methods

2.1. Materials

Riboflavin (Rf), deuterium oxide 99.9% (D_2O), superoxide dismutase (SOD) from boverythrocytes, carbendazim (CBZ), benzimidazole (BZ), 2-aminobenzimidazole (ABZ), 2-methylbenzimidazole (MBZ), 2-hydroxybenzimidazole (HBZ) and 2-benzimidazolepropionic acid (PBZ) were purchased from Sigma Chem. Co. (St. Louis, MO, USA). Rose Bengal (RB) and furfuryl alcohol (FFA) were from Aldrich (Milwaukee, WI, USA). Water was triply distilled. All the measurements were carried out with freshly prepared solutions at room temperature. Buffered aqueous solutions with pH/pD 6, 10 or 12 were prepared as described (Weast and Astle, 1981).

2.2. Absorption and fluorescence measurements

Ground state absorption spectra were registered employing a Hewlett Packard 8452A diode array spectrophotometer. Stationary fluorescence was measured with a Spex Fluoromax spectrofluorometer at 25 ± 1 °C in air-equilibrated solutions. Fluorescence lifetimes were determined with a time-correlated single photon counting technique (SPC) on an Edinburgh FL-9000CD instrument. Excitation and emission wavelengths for Rf were 445 and 515 nm, respectively. A classical Stern–Volmer treatment of the data was applied through Eq. (1), where ${}^1\tau$ and ${}^1\tau_0$ are the respective fluorescence lifetimes of Rf in the presence and in the absence of a SBZ, and ${}^1k_{\mathrm{qSBZ}}$ is the rate constant of the quenching of excited singlet Rf (${}^1\mathrm{Rf}^*$) by SBZ.

$$ {}^1\tau_0/{}^1\tau = 1 + {}^1k_{\mathrm{qSBZ}}\ {}^1\tau_0[\mathrm{SBZ}] \quad (1) $$

2.3. Stationary photolysis

Stationary aerobic photolysis of aqueous solutions containing a SBZ and Rf were carried out in a Photon Technology International (PTI) unit provided with a high pass monochromator and 150 W Xe lamp, irradiating at 440 ± 10 nm, or in a home made photolyser for non-monochromatic irradiation of a 150 W quartz-halogen lamp, cut off >400 nm. The reactive rate constant k_r for the reaction of each SBZ with $O_2({}^1\Delta_g)$ (Scheme 1), generated by RB-sensitization, was determined using the method described by Tratniek and Hoingé (1991) Eq. (2), for which the knowledge of the reactive rate constant for the photooxidation of a reference compound R, studied at the same concentration, is required:

$$ \mathrm{slope}/\mathrm{slope}_{\mathrm{R}} = k_{\mathrm{r}}/k_{\mathrm{rR}} \quad (2) $$

where slope and $\mathrm{slope}_{\mathrm{R}}$ are the respective slopes of their first-order plots of SBZ and R consumption, or oxygen consumption, respectively, under sensitized irradiation. Oxygen uptake in water was monitored with a 97-08 Orion