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Photochemical Degradation of Imazamox in Aqueous Solution: Influence of Metal Ions and Anionic Species on the Ultraviolet Photolysis

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Imazamox [5-methoxymethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl) nicotinic acid] is one of the later pesticides of the imidazolinone family. The fate of imazamox has been studied upon UV irradiation. The degradation of a 10 mg L^{-1} imazamox solution leads to pyridine derivatives, which remain in solution for 50−100 h. Most of the photoproducts occurring during the photodegradation have been characterized by means of liquid chromatography coupled with mass spectrometry. The degradation scheme is very similar to that observed for the analogous imazapyr pesticide [2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl) nicotinic acid]. Nevertheless, imazamox shows a greater stability than imazapyr. More, complexation interactions between imazamox and metal ions such as Cu^{2+} or Ca^{2+} increase the persistence of the pesticide.

KEYWORDS: Imazamox; imidazolinone; photodegradation; complex

INTRODUCTION

Under typical field application conditions, a portion of the applied pesticide reaches its final target, but the majority is released in the environment. Pesticides are then subjected to biotic and abiotic degradation processes, in particular in water, including photolysis.

Imazamox [5-methoxymethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl) nicotinic acid] is a broad-spectrum herbicide in the imidazolinone family, which was developed by the American Cyanamid Co. (Princeton, NJ) (*1*). It is formulated as the isopropylamine salt or as the free acid and is the active ingredient in commercial formulations of Raptor, Sweeper, Odyssey, and Bolero (*1*−*3*). Imazamox is selective for many leguminous crops such soybeans, field peas, alfalfa, dry beans, and peanuts (*4*). The activity of imidazolinone herbicide family is associated with inhibition of acetohydroxyacid synthase, an enzyme essential for the production of branched chain amino acids (valine, leucine, and isoleucine) (*2*). Imazamox has no aquatic uses; however, it could potentially enter surface water by spray drift during application or by runoff after application (*3*). Therefore, determination of kinetics and route of photodegradation in water is important in defining its environmental impact.

This study completes our previous work (*5*) on the photostability in water of imazapyr [2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl) nicotinic acid], another pesticide of the imidazolinone family. The photolytic degradation of imazapyr has been previously studied under different conditions (*5*−*8*), including the role of ionic species such as metal ions (*9*) leading to complexation interactions (*10*−*13*).

The aim of this work was to investigate the photodegradation of imazamox in aqueous media, with or without metal salts. The influence of metal ions (Cu^{2+} and Ca^{2+}) and of their concomitant anionic species (NO$_3^-$ and Cl$^-$) as well as that of the pesticide to metal ion molar ratio was studied using a chemometric approach. A factorial design considers the main effects as well as interactions of the influential parameters, thus conducting a more thorough investigation of the method than the common step-by-step approach. More, liquid chromatography−mass spectrometry (LC-MS) coupling was used to identify photoproducts and this determination permitted the identification of possible photolytic pathways of imazamox. In addition, these results are compared to those obtained for the imazapyr parent pesticide. Although this study does not exactly predict the behavior of pesticides under environmental conditions, the aim of this work is to consider the importance of the metal salts on the pesticide persistence.

MATERIALS AND METHODS

Reagents and Solutions. Imazamox (purity 99%) was purchased from Chemservice, Inc. (West Chester, PA) and was used as received. Copper(II) nitrate, copper(II) chloride, calcium(II) nitrate, calcium(II) chloride, sodium nitrate, and sodium chloride were supplied by Prolabo and have analytical quality. Ultrapure water (18.2 MΩ cm) was used

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Table 1. Factors and Levels Considered for the Chemometric Study

	levels	
factors	(−1)	(+1)
molar ratio pesticide/metal ion	2	1
concomitant anion	Cl^-	NO_3^-
metal ion	Cu^{2+}	Ca^{2+}

for the preparation of all aqueous solutions. The mobile phase used for chromatographic experiments was a mixture of acetonitrile (high-performance liquid chromatography grade, SDS Carlo Erba) and water adjusted to pH 2.6 with formic acid (98%, Fisher Scientific).

Photodegradation under Artificial Light. Irradiations were carried out in a 3 L Pyrex glass immersion photochemical reactor, cutting the radiation shorter than 290 nm. The molar absorption coefficient ϵ_{290} was 3400 L mol^{-1} cm^{-1} for the wavelength of 290 nm. The photoreactor was charged with 2 L of a 10 mg L^{-1} (3.3×10^{-5} mol L^{-1}) aqueous solution of imazamox, with or without metal salts. The pesticide/metal ion molar ratio was varied from 1 to 2. A high-pressure mercury lamp (HPK 125 W Philips), which emitted in the range of 250−600 nm with maximum emission at 365.5 nm, was placed in a water-jacketed Pyrex tube (diameter 3 cm) centered in the reactor. The reaction medium was continuously stirred and remained in contact with air. Several runs of experiments were necessary to observe the 100 h of degradation. The advance of reaction was followed by successive samplings (1 mL). A dark control was performed by covering flasks with aluminum foil to ensure that imazamox did not degrade by hydrolysis. Before the experiments, the light emission effectiveness of the irradiation system was tested by using the uranyl oxalate actinometry method (*14*, *15*).

Analysis. The degradation of imazamox was followed using a HP1100 chromatograph equipped with a photodiode array detector (LC-DAD). The flow rate was 0.4 mL min^{-1}, and the injection volume was 20 μL. The eluent was a water, pH 2.6 (formic acid), and acetonitrile (ACN) mixture using the following gradient profile: 0−5 min, 0% ACN; 5−15 min, 0−5% ACN; 15−20 min, 5% ACN; and 20−30 min, 5−100% ACN. The column was an Aquasil C18 (100 mm × 2.1 mm i.d., 5 μm) preceded by a precolumn Uptisphere HDO C18 (10 mm × 2.0 mm i.d., 5 μm). The UV detection was centered at 266 nm. Samples from reaction solutions were injected into the chromatograph without any further preparation.

Extraction Procedure and Characterization of Photoproducts. Some samples were preconcentrated by solid phase extraction in order to improve the detection of the products in low concentration. A strong anion exchange SAX cartridge (3 mL, 200 mg) from STRATA Phenomenex was first conditioned by 5 mL of ACN, followed by 5 mL of pure water. A sample of 50 mL of irradiated solution was adjusted to pH 10.2 (NaOH) and was then passed through the cartridge. Elution was achieved by 5 mL of acid solution (pH 1.4 HCl).

The characterization of intermediate products was carried out on a HP 1100 series LC-MSD under the same chromatographic conditions. A postcolumn addition, with an external pump, of a mixture of 2-propanol and ammonium formate (10^{-2} mol L^{-1}, pH adjusted to 7.8 with diluted ammonia) was used in order to improve chemical ionization. Mass spectrometry detection was carried out in positive and negative electrospray modes.

Chemometric Study. When metal salts were added into the solution, the study of imazamox photodegradation involved new parameters, which could not be considered separately. Thus, a chemometric strategy using factorial design was very useful, allowing us to increase the information with a limited number of experiments.

Factors Considered for the Study and Experimental Domain. With a classical two levels full factorial design of eight experiments (2^3), it was possible to study three experimental factors: the metal ion [copper-(II) or calcium(II)], the associated anion (chloride or nitrate), and the pesticide to metal ion molar ratio R (2 or 1) and their interaction. The different levels (X_i) of the three factors are presented in **Table 1**. The observed response (Y) is the degradation half-life ($t_{1/2}$) of imazamox (A), this time being the main characteristic of the degradation curve.

Model and Strategy Used. The synergic model used was as follows: $Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3$
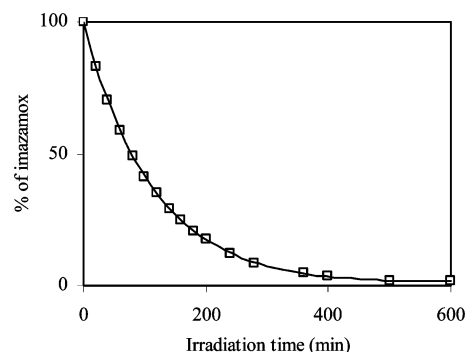
Figure 1. Photodegradation of imazamox (O, 10 mg L^{-1}) in deionized water followed by LC-DAD.
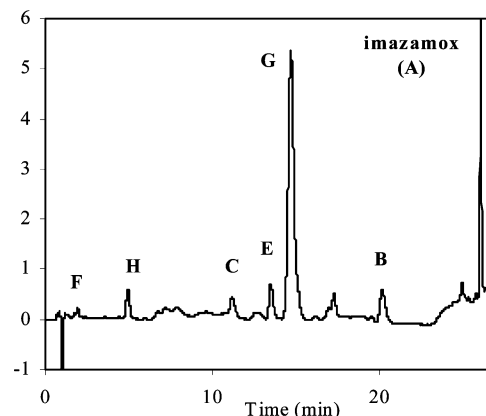
Figure 2. LC-DAD chromatogram of an irradiated aqueous solution of imazamox (10 mg L^{-1}; irradiation time = 480 min; λ = 266 nm).

$+ b_{123}X_1X_2X_3$. The coefficients b_i represent the effects of factor X_i on the observed answer Y, and the coefficients b_{ij} and b_{ijk} are the interactions between these factors. The statistical results were analyzed with NemrodW software (*16*). To observe reproducibility, the design was replicated, and each irradiation was carried out twice.

RESULTS AND DISCUSSION

Photolytic Degradation by UV Radiation. Dark controls were stable over the kinetic period indicating that hydrolysis is not a factor in the imazamox degradation in agreement with the literature about imidazolinone hydrolysis (*5*, *6*, *17*). The photolysis shows a complete disappearance of imazamox after 10 h for an initial concentration of 10 mg L^{-1} (**Figure 1**). Degradation data are well-fitted by an exponential curve suggesting a first-order model. The linear plot of $\ln[(\% C_{imazamox})_t]$ vs irradiation time ($r^2 = 0.996$) allows us to determine the first-order rate constant, $k = 0.0089 \pm 0.0005$ min^{-1}, and the half-life $t_{1/2} = 78 \pm 4$ min for imazamox photolysis.

Under the same degradation conditions, imazamox is more stable than imazapyr (*5*), which degrades completely within 6 h ($t_{1/2} = 40 \pm 2$ min). This relative stability of imazamox may be correlated to the single structural difference between both pesticides with substitution of the pyridinic ring by a methoxymethyl group for imazamox. Nevertheless, it can be noted that imazethapyr, where the substitutent is an ethyl group, degrades faster than imazapyr (*7*).

Characterization and Evolution of Imazamox Intermediates. During the irradiation of imazamox, different photoproducts were detected by LC-DAD. **Figure 2** shows a characteristic chromatogram of an irradiated imazamox solution. On the basis of the LC-MS analyses carried out at different degradation times

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Table 2. Retention Times and Masses of Photoproducts of Imazamox[a]

			LC-MS			
			mass (*m/z*)			
			positive mode		negative mode	
product no.	formula	t_R (min)	$(M + H)^+$	fragments or adduct	$(M - H)^-$	fragments
A	$C_{15}H_{19}N_3O_4$	26.0	306	328 $(M + Na)^+$	304	260 $(M - H - CO_2)^-$
B	$C_{14}H_{19}N_3O_3$	20.2	278	300 $(M + Na)^+$	276	232 $(M - H - CO_2)^-$
C	$C_{14}H_{18}N_2O_3$	11.3	263	285 $(M + Na)^+$	261	NF
				221 $(M + H - C_3H_6)^+$		
E	$C_1H_{21}N_3O_2$	13.6	252	274 $(M + Na)^+$	250	232 $(M - H - H_2O)^-$
				234 $(M + H - H_2O)^+$		
F	$C_9H_{11}N_3O_3$	2.0	210	232 $(M + Na)^+$	NF	NF
				193 $(M + H - NH_3)^+$		
G	$C_9H_9NO_4$	14.7	196	178 $(M + H - H_2O)^+$	194	176 $(M - H - H_2O)^-$
						150 $(M - H - CO_2)^-$
H	$C_9H_9NO_5$	5.0	212	234 $(M + Na)^+$	210	166 $(M - H - CO_2)^-$
				194 $(M + H - H_2O)^+$		122 $(M - H - 2CO_2)^-$
				168 $(M + H - CO_2)^+$		

[a] NF, not found.

and by comparison with the previous identification work for imazapyr photoproducts (*5*), the structures of six detected products are suggested. All of the results are summarized in **Table 2** where each compound is referenced by its code letter (**Scheme 1**), its formula, and its retention time.

The characterization of photoproducts suggests that the degradation schemes for imazamox and imazapyr are similar. The methoxymethyl group substituting the pyridinic ring is not involved in the photochemical degradation. This phenomenon was already observed for other compounds of the imidazolinone family (*6, 17*). Indeed, the group substituting the pyridinic ring, which differentiates the imidazolinone pesticides, remains grafted on the pyridinic ring throughout the first steps of the degradation process.

The main six compounds (B, C, and E−H; **Figure 2**) have been followed during the photodegradation and measured as their peak areas by LC-DAD. A few hundred minutes are necessary to reach the maximum concentration of the majority of degradation compounds. These products are very stable because, even though imazamox is completely degraded in 10 h; after 100 h, only the compound E disappeared. Although their concentrations are decreasing, compounds B, C, F, and G remain in solution after 100 h. Only the concentration of H continues to increase. Under these photochemical conditions, H (5-methoxymethyl-2,3-pyridinedicarboxylic acid) is the last product of the imazamox photodegradation. Indeed, the compound does not absorb above 290 nm.

Degradation Pathway. Following the identification of the different photoproducts by LC-MS, a general scheme including several competitive pathways is proposed for the photolytic degradation of imazamox in water (**Scheme 1**). Imazamox is noted A. The first step corresponds to the opening of the imidazolinone ring and the loss of the lactam C=O (decarbonylation process) to give photoproduct B. Then, two ways labeled 1 and 2 are possible. First, the photoproduct B loses its amino group to form compound C (route 1). This compound leads probably to G by successive oxidations.

Route 2 probably involves the hydration of the alkene group of B leading to D (not detected). The next step is either a decarboxylation, which gives the compound E, or an α-cleavage of the N−C bond to give compound F. The competitive oxidation of the amidino group in F forms 5-methoxymethyl-2-formyl-nicotinic acid (**G**) whose facile oxidation gives the 5-methoxymethyl-2,3-pyridinedicarboxylic acid (H). This com-

Table 3. Imazamox Half-Lives for Chemometric Study

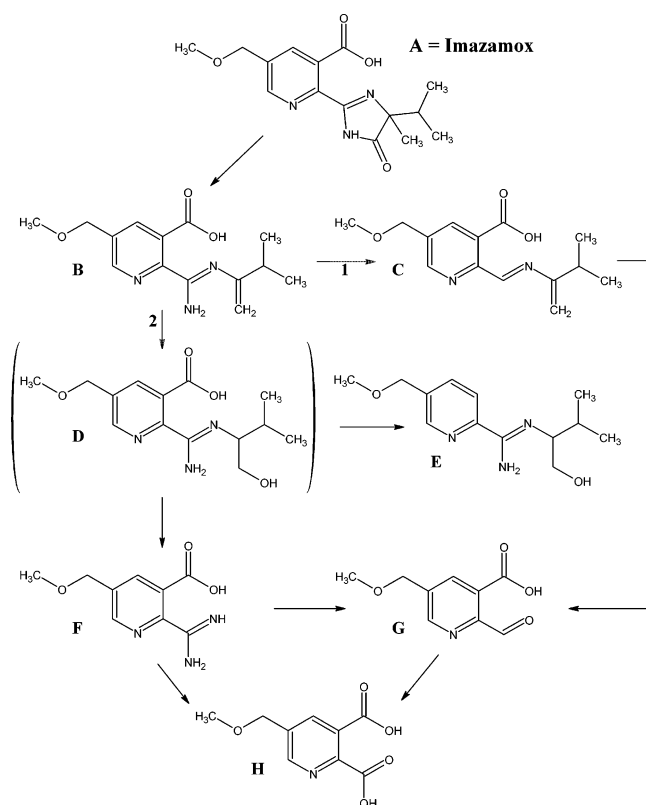| experiment	$R = [A]/[M^{2+}]$	X_1	anion	X_2	M^{2+}	X_3	$Y = t_{1/2}$ of imazamox (min)[a] Try 1	Try 2
1	2	−1	Cl^-	−1	Cu^{2+}	−1	265	278
2	1	1	Cl^-	−1	Cu^{2+}	−1	390	423
3	2	−1	NO_3^-	1	Cu^{2+}	−1	223	239
4	1	1	NO_3^-	1	Cu^{2+}	−1	572	542
5	2	−1	Cl^-	−1	Ca^{2+}	1	91	96
6	1	1	Cl^-	−1	Ca^{2+}	1	148	155
7	2	−1	NO_3^-	1	Ca^{2+}	1	110	115
8	1	1	NO_3^-	1	Ca^{2+}	1	110	105

[a] Standard deviation = 13.

pound **H** may also be obtained by direct hydrolysis of compound F. A similar degradation scheme has been already proposed for the imazapyr photolysis (*5*) and showed that the analogue of H, the 2,3-pyridinedicarboxylic acid, was not degraded.

Influence of Complexation on Imazamox Photodegradation. As it is not possible to observe the influence of metal ions independently of their associated anion, it is necessary to study at the same time the influence of the metal ions, the associated anions, and also their interactions. Therefore, a chemometric study including these two parameters (metal ion and associated anion) and the pesticide to metal ion molar ratio has been carried out.

Chemometric Study. The experiments were carried out with copper(II) and calcium(II) associated to chloride and nitrate. On one hand, copper(II) is known for its strong interaction with ligands such as imidazolinone (*10−13*). On the other hand, calcium(II) is generally in relatively high concentrations in environmental media. Nitrate ions lead to reactive hydroxyl radicals under UV irradiation while chloride ions are supposed to be inert species.

The imazamox half-lives obtained for each experiment are reported in **Table 3**, and calculated coefficients for the model are summarized in **Table 4**. These coefficients evaluate the weight of the main factors (X_1, X_2, and X_3) and of their interactions (X_1X_2, X_1X_3, X_2X_3, and $X_1X_2X_3$). From the eight experiments, twice repeated, the Student's values ($t_{Student}$) show that all of the X_i main factors and X_iX_j interaction factors have a high significance level (significance ≤ 0.96).

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Scheme 1. Proposition of Imazamox Photodegradation Pathway in Aqueous Medium

Table 4. Coefficient Values of Model

coefficient	values[a]	$t_{Student}$	significance (%)
b_0	241.4	76.7	<0.01
b_1	64.3	20.4	<0.01
b_2	10.6	3.4	0.96
b_3	−125.1	−39.7	<0.01
b_{12}	16.0	5.1	0.11
b_{13}	−51.0	−16.2	<0.01
b_{23}	−16.9	−5.4	0.08
b_{123}	−31.8	−10.1	<0.01

[a] Standard deviation = 3.1.

Figure 3. Degradation kinetics for 10 mg L^{-1} imazamox without metal salts (□) and in the presence of CaCl$_2$ (◇) or CuCl$_2$ (◆); pesticide to metal salt molar ratio $R = 1$.

Figure 4. Representation of the one-order interaction effect pesticide to metal ion molar ratio (R).

In all cases (**Table 3**), the presence of metal salts decreases the imazamox degradation rate ($t_{1/2}$ = 78 min for imazamox alone). As shown in **Figure 3**, the most important effect is obtained with copper(II) ions. The presence of metal ions such as Cu^{2+} stabilizes imazamox probably by means of a chelating effect. Indeed, it is expected that as well as for imazapyr (*13*) the coordination mode between imazamox and copper(II) involves a five-membered chelate ring by means of N pyridine and N lactam atoms. Other studies have shown the influence of metal ions such as copper(II) but also lead(II), cobalt(II), or manganese(II) (*18−21*) on stabilization of organic compounds by complexation. Nevertheless, these works have not considered the influence of the associated anions and have sometimes been carried out in the presence of photosensitized substances such as humic acids or iron oxides inducing difficult interpretations.
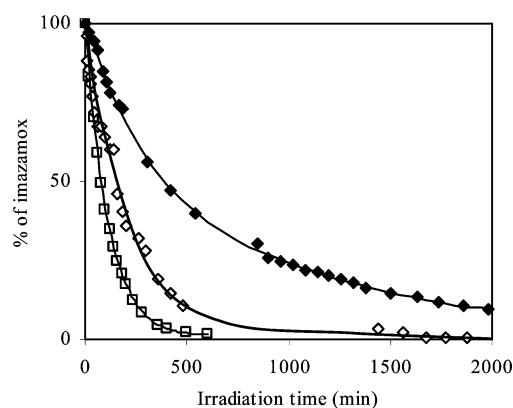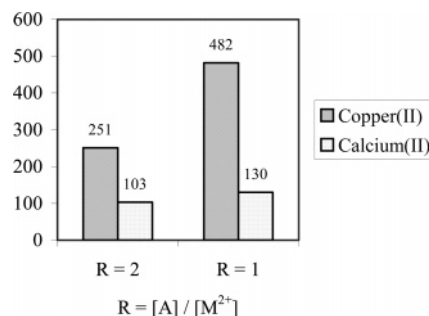
Interpretation of the Main Effects. The calculated coefficients show that the metal ion is the most important parameter in the degradation of imazamox ($|b_3| > |b_1| > |b_2|$). The degradation rate is slower in the presence of copper(II) whatever the anion or the molar ratio. This correlates with the high complexation constants generally observed between such ligands and copper-(II). The calcium(II) effect is weaker because the copper(II) complexes are generally more stable than those with calcium (*22*). The stronger the stability constant of the complex is, the more the molecule is stable for the degradation. The same difference has been observed between copper(II) and iron(II) for organic drinking water contaminants (*23*) and between copper(II) and manganese(II) or cobalt(II) for organophosphorus pesticides (*20*).

The coefficient value b_1 indicates that the degradation rate decreases when the amount of metal ions increases, i.e., $R = 2$ to $R = 1$. Indeed, an increase in metal ion concentration favors the imazamox complexation. The next coefficient b_2 indicates that the degradation rate is slower with chloride than with nitrate.

Indeed, chloride ions are not known to have any effect on degradation whereas nitrate ions lead to photooxidations accelerating the degradation mechanisms of organic compounds (*24*).

Interpretation of the Interaction Effects. The b_{13} coefficient (**Figure 4**), which represents the one-order interaction effect ratio/metal (X_1X_3), shows clearly a stabilizing combination ($t_{1/2}$ = 482 min) when the solution contains copper(II) ions and the molar ratio R is equal to 1.

Influence of Metal Salts on Photodegradation Products. The six photoproducts previously detected (B, C, and E−H) when imazamox is only in solution have also been analyzed in the presence of metal salts. These six compounds may be classified in two groups according to their behavior with metal salts. The first group, including the compounds B, C, and E, is always detected when copper(II) or calcium(II) salts are involved. The second group, including the compounds F−H, disappeared when copper(II) was present.

The kinetic formation of the three compounds of the first group is slowed by copper(II) and calcium(II). For example, **Figure 5** shows the concentration of compound E vs time. This
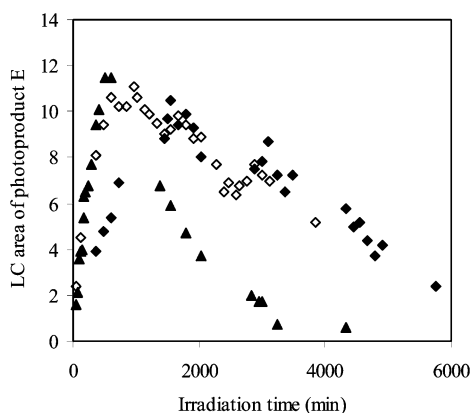
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Figure 5. Degradation kinetics of photoproduct E for 10 mg L^{-1} imazamox without metal salts (▲) and in the presence of Ca(NO$_3$)$_2$ (◇) or Cu-(NO$_3$)$_2$ (◆) with $R = 2$.

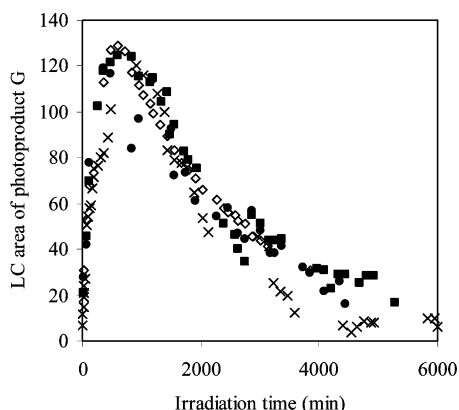**Figure 6.** Degradation kinetics of photoproduct G in the presence of calcium salts: CaCl$_2$ (×) or Ca(NO$_3$)$_2$ (●) with $R = 1$ and CaCl$_2$ (■) or Ca(NO$_3$)$_2$ (◇) with $R = 2$.

phenomenon is evidently correlated to the influence of the metal salts on the degradation of the initial imazamox molecule. It can be noticed that the photoproducts are themselves stabilized by the metal salts showing that they are also involved in metal ligand interactions.

The three compounds (F−H) of the second group are not detected when copper(II) is involved. It may be suspected that their mother molecules are blocked by copper(II). **Figure 6** shows the concentration for compound G. Calcium(II) salt does not show clearly any influence on the photodegradation of this compound.

ACKNOWLEDGMENT

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