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Photodecomposition of 4-amino-1,2,4-triazin-3,5-diones and -thiones in oxygenated aqueous solutions

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Abstract

The photodecomposition of newly synthesized 4-amino-1,2,4-triazinthione **1** and -dione **2** was examined in oxygenated aqueous solutions at various pH values. The degradation pathway of these compounds was compared with the photochemical decomposition of the herbicide metribuzin. Side-chain degradation by deamination, decarboxylation, sulfoxidation and dealkylation is typical for photolysis. Structurally similar compounds display substantial differences with respect to degradation. The pH value has an accelerating or inhibiting effect on the degradation rate. After the rapid formation of basic metabolites by the deamination of **1** and the decarboxylation of **2**, selective decomposition takes place in alkaline and acidic solutions, whereas a non-selective course was detected under neutral conditions. The radicalic mechanisms of important reaction steps are discussed. Several metabolites with intact heterocyclic ring systems were identified as photochemically stable final products by the addition of a standard compound, such as 6-azauracile or 6-azathymine. In contrast to side-chain degradation, ring cleavage was only observed after long irradiation times. Carboxylic and ketocarboxylic acids as well as some inorganic ions were identified in the irradiated solution as the degradation products of side-chain degradation and ring cleavage.   © 1998 Elsevier Science S.A. All rights reserved.

1. Introduction

Much information is available concerning the photodecomposition of environmental compounds [1–6]. Structures often contain heterocyclic ring systems which are considered to be extraordinarily stable against photolytic cleavage. Symmetric triazines have in particular been thoroughly investigated as photochemically very stable compounds. Side-chain degradation by deamination, dehalogenation, decarboxylation, desulfuration and dealkylation is characteristic for photolytic degradation.

In contrast to s-triazines, little is known about the photolysis of 1,2,4-triazines. 1,2,4-Triazines are a class of compounds with a number of different physiological properties [7–17]. Great importance is especially attached worldwide to the herbicidal activity of 1,2,4-triazin-5-ones. The photochemical side-chain degradation of the herbicide metribuzin [4-amino-6-(1.1-dimethylethyl)-3-methylthio-1,2,4-triazin-5(4H)-one] by deamination and desulfuration has been described and leads to the loss of herbicidal activity [18–

22]. Derivatives of 6-azauracile [1,2,4-triazin-3,5-diones] result from this degradation. The photohydration of 1,2,4-triazin-3,5-diones was detected at elevated temperatures followed by the hydrolytic ring cleavage of the hydrated compounds in alkaline solution [23,24]. In the case of metamitron [4-amino-3-methyl-6-phenyl-1,2,4-triazin-5(4H)-one], a tetrazine is formed by ring transformation in conjunction with photochemical decarboxylation [25]. Scheme 1 summarizes known photochemical reactions.

In order to obtain herbicidally active structures, we synthesized the compounds **1** and **2**. Both compounds contain the structure $CO-N-NH_2$ as a herbicidally active element of 1,2,4-triazinone herbicides. As is well-known, this structural element of metribuzin is rapidly degraded by photochemical deamination. We compared the degradation pathway of our new compounds with the degradation of metribuzin.

2. Experimental details

The compounds **1–3** were synthesized by the reaction of 2-oxoglutaric acid [26] with semicarbacide or thiosemicar-
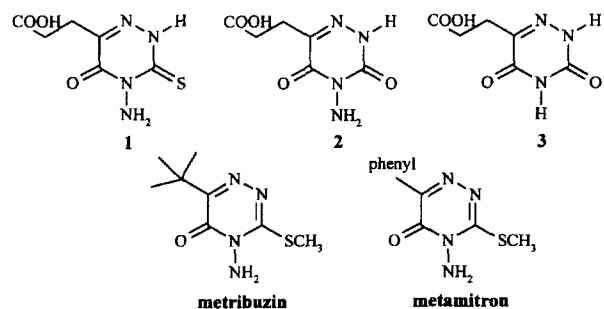
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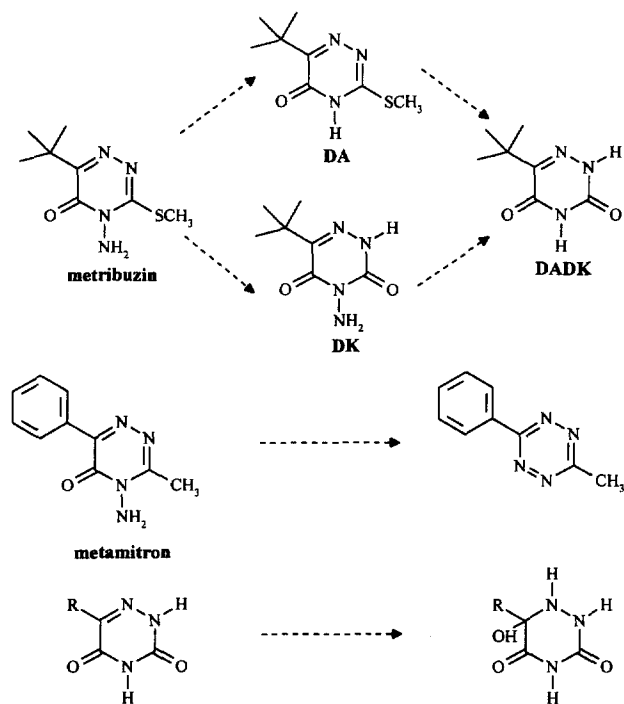
Scheme 1. Photochemical degradation pathways of 1,2,4-triazinones.

Scheme 2. Structures of metribuzin, metamitron and compounds 1–3.

bacide [27]. The structures were checked by MS, IR and NMR. The purity of these compounds was higher than 99.9% as confirmed by HPLC. Methanol, water (both HPLC-grade), NaOH and HCl were obtained from Merck (Darmstadt, Germany). The photolytic degradation experiments were carried out in quartz glass apparatus. The photon flux I of the low-pressure mercury lamp was 1.15×10^{-6} Einstein/s (0.53 W) at a wavelength of 254 nm. To estimate the photon flux of the mercury lamp, we applied the 1,3-dimethyluracile actinometer using the following procedure: 166 ml of a 5.5×10^{-4} M 1,3-dimethyluracile solution ($\varphi = 0.0125$ at 254 nm) was irradiated at 20°C for 1 h. 3.13×10^{-4} M 1,3-Dimethyluracile was degradated during this time (mean of seven measurements) [28]. On basis of these values we calculated the photon flux I by the equation: $I = (dcV)/(t\varphi)$.

The degradation of a standard was checked every 20–25 working hours to monitor burner stability. Compounds were dissolved in distilled water (10^{-4}–10^{-3} M) and irradiated for up to 10 h at various pH values. Alkaline (pH 11.0) and acidic (pH 2.0) pH values were adjusted by adding 1 M NaOH and HCl, respectively.

The photoproducts of irradiated solutions were separated with a Beckman HPLC (Gold system) using reversed phase conditions with water/methanol-gradient. Structures of all photoproducts detected were identified by standard addition. Syntheses of the standard compounds are described in Refs. [29–33]. In dependence of their concentration, the indisputable detection of photoproducts shown in Schemes 3 and 4 was done by adding 20–50 µl of a 100-ppm standard solution to 1 ml sample solution. Ionic organic and inorganic compounds were determined on a Dionex 4000i with suppressed

conductivity. The identification of ionic compounds was carried out in the same way. Calibration curves for each compound were recorded between 10^{-3} M and 10^{-5} M.

To compare the velocity of degradation under identical experimental conditions we have used an iteration method in accordance with Eq. (1).

$$[A] = \left[[A]_0^{1-n} - (1-n)kt \right]^{\frac{1}{1-n}} \tag{1}$$

The calculation is based on the initial concentration $[A]_0$ and the measured concentrations $[A]$ during photolysis. Eq. (1) is derived from a rate law of nth order. The half-lives $t_{1/2}$ were estimated on the basis of the calculated function [1] by Eq. (2).

$$t_{1/2} = \frac{(2^{n-1}) - 1}{(n-1)k[A]_0^{n-1}} \tag{2}$$

Theoretical calculations of the molecular structures and energy parameters were performed with the program HyperChem using the PM 3 method [34].

3. Results and discussion

3.1. Photolysis of metribuzin

In our earlier metribuzin photolysis experiments, we identified amongst the known metabolites deaminometribuzin (DA), diketometribuzin (DK) and deaminodiketometribuzin (DADK) in acidic and neutral aqueous solutions another six degradation products which have not been previously described in literature (Scheme 4, compounds A–F). Summarizing it may be said that the photolysis of metribuzin leads to a change of substituents by side-chain degradation, forming new compounds while maintaining the heterocyclic ring system. Ring degradation plays a growing role as photolysis increases. Ring transformation as described for metamitron or diazines was not found [35–37].

3.2. Photolysis of compounds 1 and 2

Compounds **1** and **2** (Scheme 2) were irradiated in aqueous oxygenated solutions at pH 2.0, pH 5.9 and pH 11.0. The

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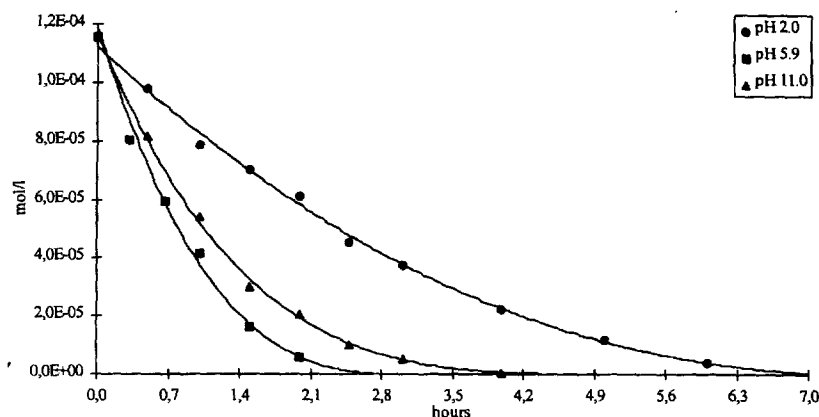[1] T. Berndt, private communication, 1994.

Fig. 1. Measured (points) and calculated (lines) degradation function of compound 1.
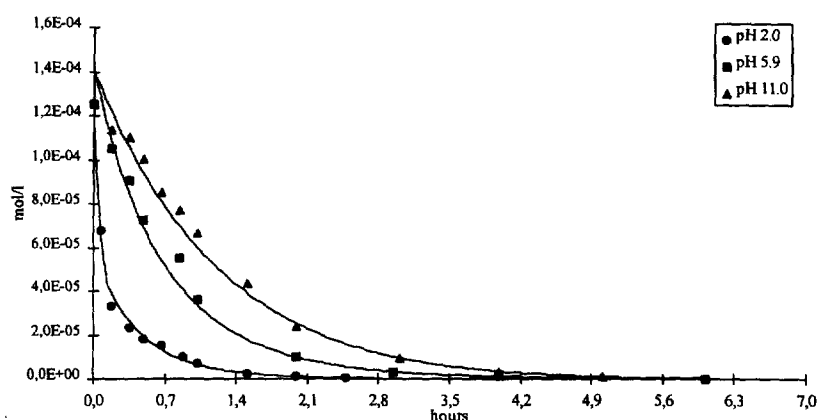

Fig. 2. Measured (points) and calculated (lines) degradation function of compound 2.

measured points and calculated curves of photolytic degradation are shown in Figs. 1 and 2. Table 1 contains a summary of the calculated parameters n and k. Both values describe only the process of degradation for each compound as the sum of all current processes under identical experimental conditions. Therefore, n and k are only values with mathematical character. Predictions of reaction kinetics and photochemical reaction mechanisms as well as the characterizations of single processes are not possible. From Figs. 1 and 2, it is recognizable that slight structural modifications lead to substantial differences of the degradation rate as well as the pH influence. As with metribuzin, fast deamination producing metabolite G (Scheme 3) is characteristic. The reaction rate of deamination is higher in neutral and alkaline than in acidic solutions. By contrast, the photolysis of compound 2 (Fig. 2) is characterized by fast decarboxylation with the formation of metabolite H (Scheme 4), which was identified by standard addition. In this case, the reaction rate was higher in acidic and neutral than in alkaline solutions.

Owing to the very fast deamination of metribuzin with the loss of biological activity in the environment, it is important to know the chemical structures for which this reaction pathway is preferred. In our experiments, we observed that the deamination by photolysis of 4-amino-substituted 1,2,4-triazinones and -thiones with different substituents in position 6

Table 1
Parameters for calculation of degradation curves and half-lives of compounds 1–3 and metabolite G

	n	k $[(h(mol/l)^{n-1})^{-1}]$	Half-life [h]
Compound 1			
pH 2.0	0.53	0.0039	2.01
pH 5.9	0.66	0.0414	0.68
pH 11.0	0.74	0.0739	0.82
Compound 2			
pH 2.0	1.13	11.44	0.20
pH 5.9	1.07	2.89	0.46
pH 11.0	0.95	0.54	0.81
Compound 3			
pH 2.0	0.96	0.1050	4.73
pH 5.9	0.33	0.0001	9.71
pH 11.0	0.33	2.38	6.21
Metabolite G			
pH 2.0	0.74	0.0036	17.01
pH 5.9	0.95	0.0726	5.96
pH 11.0	0.47	0.0039	1.26

only takes place in compounds with single or double bonded sulfur in position 3. The rate of deamination is very slow if sulfur is replaced by another substituent, for example methyl
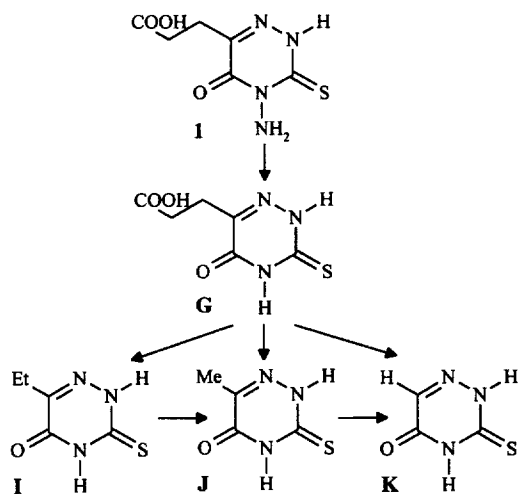
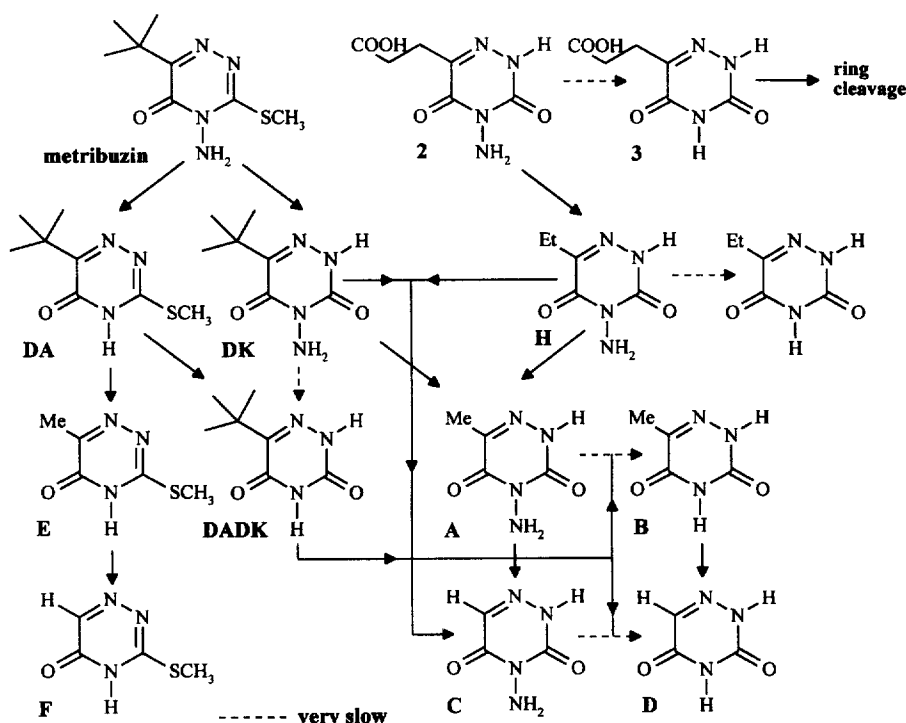Scheme 3. Degradation pathway of compound 1.

(metamitron) or oxygen (compound 2). The actual type of substituent at position 6 has no impact on the deamination rate. We performed calculations of energy parameters and molecule geometry using HyperChem® to establish a theoretical explanation for this different behavior. Similar bonding energies were calculated for all N_4–NH_2-bonds. Thus energetic parameters can not have an important influence on deamination rate. With exclusion of 4-amino-1,2,4-triazin-3,5-diones we found a planar or weak angled ring system. Our experiments showed a slow deamination for 4-amino-1,2,4-triazin-3,5-diones. The slow deamination was also detected for planar compounds without single or double bounded sulfur in position 3, for example metamitron. Our

calculations and experiments led us to the conclusion that the presence of single or double bonded sulfur combined with an almost planar ring system is essential for fast deamination.

Although deamination has been described for many compounds, there is a lack of detailed information about potential reaction mechanisms. Only peptides have been extensively investigated in view of their cancerogenic action as a result of degradation by UV-irradiation. Photoinduced hydrolytic deamination has been detected to be one such important reaction [38–42]. The amino group is reduced to ammonia during this process. In the case of 4-amino-1,2,4-triazinones we found that the amino group is oxidized to nitrate with nitrite as an intermediate product. The measurement of nitrite and nitrate by ion chromatography detected those unique. First the rising of the nitrite concentration was observed. The concentration of nitrite decreases during increasing photolysis time, while the nitrate concentration rises. We therefore assume that different mechanisms exist in both cases.

According to literature, the sulfoxidation of compound 1 should be expected, forming 1,2,4-triazin-3,5-diones [43,44]. However, the oxidation of sulfur was not observed. It was found that sulfoxidation only takes place if sulfur is single bonded.

In contrast to deamination, the mechanism of photochemical decarboxylation (generally known as the 'photo-Kolbe reaction') has been studied intensively [45–48]. Carboxylic acids were decomposed to an alkane and carbon dioxide in the presence of a photocatalyst. Although no photocatalyst was applied in our experiments, we assume that identical processes take place in the case of compound 2.

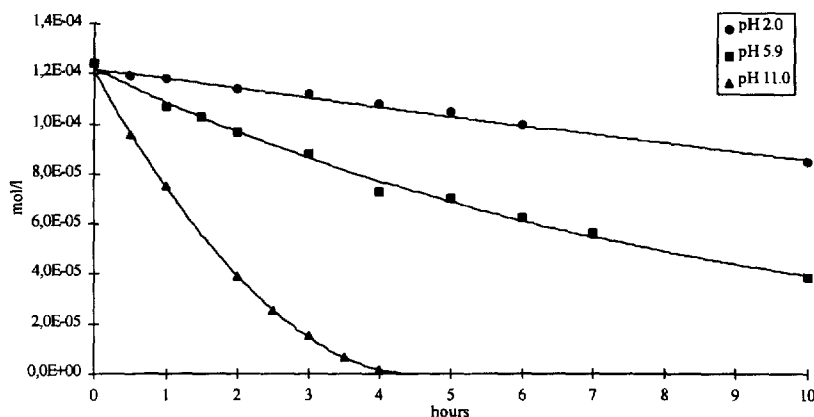Scheme 4. Degradation pathway of compound 2 and metribuzin.

Fig. 3. Measured (points) and calculated (lines) degradation function of metabolite G.

3.3. Photolysis of metabolites G and H

The compounds G and H were further decomposed by side-chain degradation with increasing irradiation time. Compared with compounds 1 and 2, the rate of degradation was noticeably slower.

An example of the course of degradation is given for metabolite G in Fig. 3 (parameters in Table 1). The number of formed photoproducts depends on the pH value. Decomposition proceeds non-selectively in neutral solutions and becomes increasingly selective as the concentrations of oxonium or hydroxyl ions rise.

We also studied other aspects of photolysis in neutral solutions. The photolysis of compound G results in the simultaneous formation of seven degradation products. The structure of three of them was established by adding standard compound (Scheme 3). Metabolite I is a result of decarboxylation by the photo-Kolbe reaction. The rise of metabolites I–K is caused by concurrent reactions, because their simultaneous formation is detectable. By the investigation of the individual reactions was proven that dealkylation also takes place at the metabolites I and J. In line with literature [49–52], we suggest that the mechanism for this photoprocess is an oxidative dealkylation pathway as shown in Scheme 5. As has been previously described for metabolite G, no sulfoxidation was detected for photoproducts I–K.

Metabolite H is decomposed by deamination and dealkylation (Scheme 4), but both processes proceed very slowly. We found the photoproducts 6-azauracile, 6-azathymine and their 4-aminosubstituted derivates (compounds A–D),

which were also formed by the photolysis of metribuzin. These compounds are known as genotoxic. We detected a simultaneous formation of A–D, but concentrations of A and C are essential higher than concentrations of B and D. As described for metabolite G before, further single experiments with metabolites A–C were necessary to clear up their photochemical behaviour. Deamination and dealkylation was detected. Scheme 4 shows the known reactions, but we cannot rule out that further reactions take place.

3.4. Ring cleavage

We could observe the degradation by ring cleavage only indirectly as removal of the concentrations of all UV-active compounds because the degradation of ring system leads to the destruction of chromophoric system. The analytical detection and structural elucidation of short-chain and UV-inactive metabolites is very problematic. Ring decomposition by α-cleavage of the keto groups positions 3 and 5 is not very significant for degradation. Investigation of photolysis of metabolite D has shown these clearly. Long irradiation times are necessary to detect measurable cleavage. We only detected ring cleavage as a characteristic degradation process for compound 3 (Scheme 2). UV-active metabolites caused by side-chain degradation were only formed in very small traces. The degradation function is given in Fig. 4 (for parameters, see Table 1). The rate of ring decomposition is comparable with the rate of the dealkylation of photoproduct G.
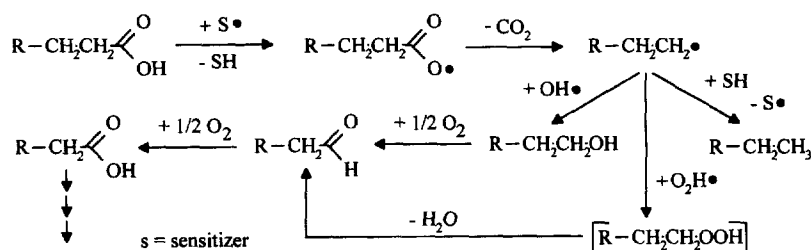
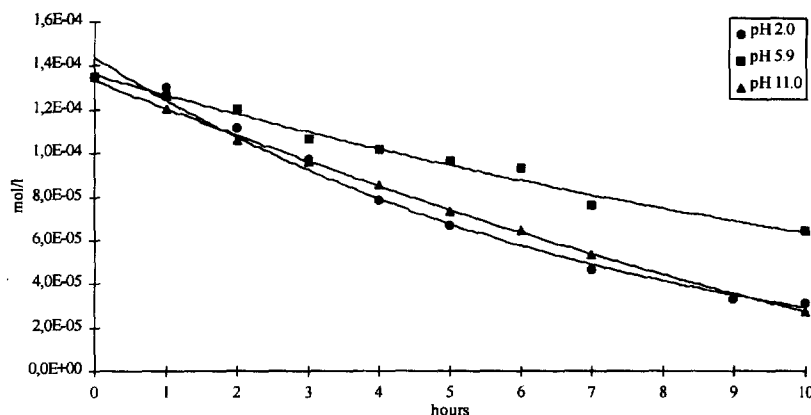Scheme 5. Supposed pathway of oxidative side-chain degradation.

Fig. 4. Measured (points) and calculated (lines) degradation function of compound 3.
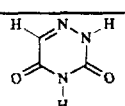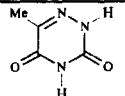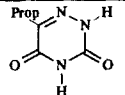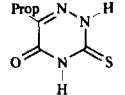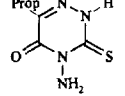
3.5. Short-chain degradation products

The neutral solution of compound 2 after 4 h of irradiation was analyzed by ion chromatography. It is known from humic substances to form several carboxylic and ketocarboxylic acids by photolysis [53]. We also found several carboxylic acids and inorganic ions in the solution of compound 2. We assume that both ring cleavage and side-chain degradation are responsible. Although formic acid is the main product, acetic, oxalic, lactic, pyruvic, succinic and glutaric acids were also found. Further we detected formaldehyde and acetaldehyde in the solution after derivatization with 2,4-diphenylhydrazine. Besides nitrite and nitrate we are sure that other nitrogen-containing compounds must be formed, for example urea or formamide. At present we work at the development of methods to determine these compounds. Investigations by several authors have revealed also the possibility that aldehydes and ketones are changed under conditions of photolysis [54–62]. Our investigations with selected carboxylic acids are in accordance with these results. Further experiments must be carried out to identify carboxylic acids, aldehydes and ketones which are not actually formed as the result of triazine degradation.

3.6. Quantum yield

Because it was not possible to identify all photoproducts by standard addition, the mathematical correction of quantum yield could not be carried out. Therefore, we had extrapolated the quantum yield of the time $t = 0$. The small turnover by use of differential small reaction times in our calculations ensure, that the formed concentrations of metabolites and thus their individual adsorption are insignificant during this time. Calculations of quantum yields show that compounds with selectively proceeding degradation reactions such as deamination or decarboxylation have approximately 10-fold higher quantum yields compared with compounds degraded by non-selective processes (Table 2). The same phenomenon has been found for the selective dehalogenation of 5-iodouridine, which has an 8-fold larger quantum yield than uridine [63].

Table 2
Quantum yields of selected 1,2,4-triazinones and -thiones

	pH	quantum yield
	2.0	$2,150*10^{-4}$
	5.9	$6,449*10^{-4}$
	11.0	$2,436*10^{-3}$
	2.0	$1,275*10^{-4}$
	5.9	$5,738*10^{-4}$
	11.0	$9,564*10^{-4}$
	2.0	$8,316*10^{-4}$
	5.9	$3,939*10^{-4}$
	11.0	$5,252*10^{-4}$
	2.0	$5,379*10^{-3}$
	5.9	$8,271*10^{-3}$
	11.0	$1,620*10^{-3}$
	2.0	$1,209*10^{-4}$
	5.9	$6,043*10^{-4}$
	11.0	$2,055*10^{-3}$
	2.0	$1,285*10^{-3}$
	5.9	$4,445*10^{-3}$
	11.0	$3,374*10^{-3}$
metribuzin	2.0	$6,838*10^{-3}$
	5.9	$6,962*10^{-3}$
	11.0	$3,330*10^{-3}$

4. Conclusions

Our investigations show that side-chain degradation is not only characteristic of the photolysis of metribuzin. Generally speaking, deamination, decarboxylation and dealkylation are important photochemical reactions of triazinones and -thiones. Small differences in the substituents at the heterocyclic ring lead to considerable differences in photolytic degradation; whether deamination or decarboxylation proceeds very fast and selectively or very slowly and non-selectively depends on the structure. The dealkylation of all investigated compounds is a slow, non-selective process. The formation

of compounds with new physiological action is possible as the detection of 6-azauracile and 6-azathymine shows.

Acknowledgements

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