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### PHOTOCHEMICAL REACTIONS OF METAMITRON

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### Summary

Photochemical reactions of metamitron (a 4-amino substituted as-triazin-5(4H)-one) were investigated including UV- and phosphorescence spectroscopy, determination of quantum yields, comparison with measurements in sunlight and products found. The photolysis of metamitron is found to be strongly dependent on solvent and oxygen, as known for other 4-amino-triazin-5(4H)-ones. No photoreaction was found in methanol, acetonitrile and hexane. Photolysis rate constants were obtained using a xenon light source by analysis of the UV-spectra and HPLC. Quantum yields found in water and at pH=4 and 9 are comparable ( $\Phi = 0.014 - 0.018$ ) and at pH=7 about a factor of 2 higher, probably influenced by the phosphate buffer used. Photochemical mechanisms are discussed. With the strong indication of a highly probable pH-independent quantum yield found, the involvement of hydroperoxyl radicals in the first step of the photoreaction, discussed before, is assumed to be unlikely. Besides desamino metamitron a second, minor (and by GC/MS and UV-spectra tentatively assigned) ring cleavage product was found. © 1997 Elsevier Science Ltd

# Introduction

Derivatives of 4-amino substituted asymmetric triazin-5(4H)-ones are known for their herbicidal activity. Especially two pesticides of this class are still used worldwide, metribuzin (4-amino-6-tert-butyl-1,2,4-triazin-5-one), and metamitron (4-amino-6-phenyl-3-methyl-1,2,4-triazin-5-one).



Metribuzin: R=C(CH<sub>3</sub>)<sub>3</sub>, R'=SCH<sub>3</sub> Metamitron: R=C<sub>6</sub>H<sub>5</sub>, R'=CH<sub>3</sub>

As for all pesticides, a potential degradation reaction in the environment is the photolysis by sunlight, and a main research field is the investigation of the corresponding products. In general, the photolysis of 4-amino substituted asymmetric triazin-5-ones with wavelengths  $\lambda > 290$  nm is a relatively fast process (half-lives of a few hours to days [1, 2]), and the main products are the corresponding desamino derivatives [3, 4, 5, 6, 7].

On the other hand, the photochemical reaction mechanism is less well understood and a couple of investigations were performed for 4-amino-3-thiomethyl substituted asymmetric triazin-5(4H)-ones only (i. e. for metribuzin and related compounds). The first assumption to explain the desamination reaction was a Norrish-Type-II reaction [4], i. e. a pure intramolecular mechanism. However, it soon became apparent, that an intramolecular mechanism alone was not able to explain the photochemical reaction and an intermolecular mechanism should hold. In principle two experimental facts were responsible for this mechanism [2, 8, 9]:

- 4-NR<sub>2</sub> substituents, independent on the nature of R are necessary for the formation of desaminotriazin-5(2H)-ones which excludes a Norrish-Type-II reaction
- both water and oxygen are necessary for the photoreaction; the quantum yield in other solvents or in oxygen-free water decreases by more than a factor of 10

As oxygen and water are involved in the photoreaction, hydroperoxyl radicals were postulated to take part in the first step of the photoreaction [2, 8, 9], although a detailed mechanism could not be given. For metamitron corresponding investigations of the photoreaction (with the exception of the early work on formation of the corresponding desamino derivative [6]) are not available, a very recent publication investigated the influence of soil components on the photolysis [7]. In this paper we present first results of the investigation of the photoreaction of metamitron, which include UV-spectra, phosphorescence spectra, quantum-yields in different solvents, products formed, comparison of the laboratory experiments with irradiations by direct sunlight and the discussion of the photochemical mechanism.

# Experimental

UV-spectra (double beam spectrometer Uvikon 860, Kontron Instruments) were measured at l=1 cm in quartz cuvettes with the corresponding solvent as reference at ambient temperature (T  $\approx$  298 K).

Phosphorescence spectra were taken with a a Perkin Elmer MPF-44 fluorimeter at T=77 K in nmrtubes in an ethanol:methanol=4:1 glass. The absorbance at the excitation wavelengths was always below 0.2. To remove any short-lived emission (fluorescence), the chopper-method was used. However, without chopper no fluorescence was detected at room temperature in the same solvent.

HPLC-analysis was performed for comparison with UV-spectroscopy to follow the conversion by the photoreaction with a Waters QA-1 autosampler system (UV-detection at 254 nm, column: C18-4 $\mu$ m, injection volume: 50 $\mu$ l, flow: 1.5 ml/min, solvent: 50/50 acetonitrile/water).

Wavelength resolved HPLC was performed with a micro-HPLC (Brown Lee Micro Pump Model G, column: RP 18 Chrompac-column, UV-detector Uvikon 810, injection volume:  $2 \mu l$ , flow:  $100\mu l/min.$ , gradient using A=30/70 CH<sub>3</sub>CN/buffer pH=3 and B=70/30 CH<sub>3</sub>CN/buffer pH=3 with: 1 min 30% B - in 7 min to 80% B - hold 2 min - in 1 min to 50% B) using the stopped-flow technique at the corresponding retention times.

Mass spectra were obtained with a NERMAG R10-10C GC/MS-system consisting of a Delsi DI700 gas-chromatograph with cryo-preconcentration, the corresponding Nermag R10-10C mass spectrometer (pos. ion, 70 eV) and a PDP11 micro-computer.

A modified merry-go-round apparatus (DEMA, Bornheim; Germany) with simultaneous irradiation of 10 cuvettes (optical pathlength 1cm) has been used for all irradiation experiments with a xenon lamp XOP7 (500W, Philips, Germany) as the light source. The distance of the light source from the cuvettes is about 5 cm, the irradiated volume was always 3.5 ml. Cooling is accomplished by three cooling circuits: the xenon lamp by pressurized air and tap water, the temperature bath with the cuvettes by a thermostat. With this setup the temperature in the cuvettes was maintained at T=295K. Different cut-off wavelengths were achieved using double walled cooling jackets for the xenon lamp made of Duran- or quartz-glass and additional optical filters with selected thickness made of Duranglass. The measurement of the relative light intensities and the corresponding absolute light intensities (using the ferrous oxalate actinometer), the method to obtain rate constants from the UV-spectra and the calculation of quantum yields was described in detail elsewhere [10].

Briefly, rate constants  $k_{\lambda}$  were obtained from a non-linear fit of the absorbances  $E_{\lambda,t}$  versus irradiation time t according equation 1.

$$\mathbf{E}_{\mathbf{t}} = (\mathbf{E}_{\mathbf{0}} - \mathbf{E}_{\infty}) \cdot \exp(-\mathbf{k}_{\lambda} \cdot \mathbf{t}) + \mathbf{E}_{\infty} \tag{1}$$

with  $E_0$  taken from the UV-spectrum at t=0 and  $E_{\infty}$  obtained as second fit parameter.

A mean rate constant k (with no weighting) was calculated from the rate constants  $k_{\lambda}$  obtained in the wavelength region  $\lambda = 302$  - 328 nm. The wavelength region was chosen due to the highest absorption change observed (see below).

Quantum yields  $(\Phi)$  were calculated from a plot of the left hand side of equation 2 versus irradiation time t (with c(0) and c(t) as the corresponding concentrations (in mole/l), N<sub>A</sub>/mole<sup>-1</sup> the Avogadro constant, and  $J'_{abs,\lambda}/photons s^{-1} nm^{-1} cm^{-3}$  as absolute, absorbed wavelength dependent light intensities).

$$\frac{[\mathbf{c}(0) - \mathbf{c}(\mathbf{t})] \cdot \mathbf{N}_{\mathbf{A}}}{1000 \cdot \sum_{\lambda_1}^{\lambda_2} \mathbf{J}'_{\mathbf{abs},\lambda}} = \overline{\Phi} \cdot \mathbf{t}$$
<sup>(2)</sup>

For comparison with the laboratory measurements, photolysis experiments by true daylight were performed outside on Sept. 1, 1995 (overcast, rain) and Sept. 12, 1995 (clear sky, bright and sunny the whole day). Quartz-cuvettes (l=1cm) were placed in a blackened cuvette holder on the roof at the institute in Hannover  $(9.8^{\circ}E/52.4^{\circ}N)$  always in direction to the sun.

Metamitron and desamino metamitron (99%, Ehrenstorfer, Germany), solvents (HPLC quality, Aldrich) and buffer solutions for pH=7 and pH=9 (Merck) were used as received. For pH=4 solution, sulfuric acid prepared from a Titrisol standard solution (Merck) was used.

Ammonium concentrations were determined using the Spectroquant kit (Merck, No. 14752, Germany). Solutions for the irradiation experiments were prepared from a stock solution of metamitron in acetonitrile (1g/l). The acetonitrile stock solutions were diluted with the corresponding solvent (water, buffer, acetonitrile, hexane) to concentrations of  $1.61 \cdot 10^{-5}$  mol/l of metamitron with an amount of the cosolvent always below 1%. No cosolvent was used for solutions in methanol and ethanol/methanol = 4/1. Various concentrations were used for UV-spectra to calculate the molar absorption coefficients.

### **Results and Discussion**

### UV, fluorescence, phosphorescence and quantum yields

The UV-spectra of metamitron (I) and desamino metamitron (II) in water are shown in Figure 1. A bathochromic shift of up to 7 nm for the UV-band around 310 nm was found with decreasing polarity of the solvent (water, methanol, acetonitrile and hexane, see Table 1).

Fluorescence and phosphorescence was not observed for both compounds at room temperature. However, at 77K in the glassy solvent methanol:ethanol = 1:4 a weak phosphorescence was observed, shown in Figure 1. The singlet energy and the triplet energy of metamitron was tentatively assigned to be  $E_S \approx 325 \text{ kJ/mol}$  and  $E_T \approx 245 \text{ kJ/mol}$  which leads to  $\Delta E_{ST} \approx 80 \text{ kJ/mol}$ . For desamino metamitron a hypsochromic shift of about 20 nm was found for the first UV-band as well as for the phosphorescence spectrum (see Figure 1).

Metamitron was stable in all solutions in the dark during the time of investigation. Furthermore, within an irradiation time of 4-5 hours no degradation of metamitron was found in acetonitrile, hexane or methanol and in oxygen free (by three freeze and thaw cycles) aqueous solutions.



Figure 1: UV- and phosphoresence-spectra of metamitron (-) and desamino metamitron (- - -)

 Table 1: UV-minima and maxima of metamitron in different solvents and corresponding molar absorption coefficients

solvent	$\lambda/\mathrm{nm}(\epsilon/\mathrm{M}^{-1}~\mathrm{cm}^{-1})$			
	min	max		
water	261 (3130)	306 (11290)		
methanol	264 (3040)	312 (11790)		
acetonitrile	265~(2901)	312 (11740)		
hexane	265 (2690)	313 (11880)		

This is in accordance with photolysis experiments for the corresponding 3-thiomethyl substituted compounds [8].

As a representative example, the UV-spectra of metamitron in water measured at different irradiation times and the absolute intensities of the xenon lightsource used are shown in Figure 2.

An isosbestic point was found in the UV-spectra at  $\lambda_{iso}(water) = 285.5 \text{ nm} (\lambda_{iso}(pH = 4) = 287 \text{ nm}, \lambda_{iso}(pH = 7) = 290 \text{ nm}, \lambda_{iso}(pH = 9) = 285 \text{ nm})$ . Straight lines were found for the differences of

absorbances in all aqueous solutions, indicating a uniform reaction, and a representative example for water with the data from Figure 2 is shown in Figure 3. The rate constants and the corresponding quantum yields are summarized in Table 2. The rate constants calculated from the UV-spectra and from HPLC are within an error of 10% comparable (see also Figure 5). In buffered solution at pH=7 a 2.5 fold higher quantum yield was found in comparison to all other aqueous solutions. As the quantum yield in water is within the error of the experiments comparable to the quantum yields at pH=4 and pH=9, we assume an influence of the phosphate buffer on the photoreaction. However, in contrast to the reported decreasing photoreactivity with increasing pH [6], rate constants and quantum yields found in this study at pH=4 and pH=9 are within the overall error of about 20% comparable.



Figure 2: UV-spectra of metamitron in water (T = 293 K,  $c_0$  = 1.61 · 10<sup>-5</sup> mol/l) at different irradiation times and the absolute light intensities of the Xe-light source used



Figure 3: Plot of the differences of absorbances of metamitron in water using the data from Figure 2. No change of absorption is indicated by the dotted line (isosbestic point at 285.5 nm). Straight lines indicate a uniform reaction.

Table 2: Photolysis rate constants k and quantum yields  $\Phi$  of metamitron at T = 293 K and  $c_0 = 1.61 \cdot 10^{-5}$  mol/l determined by UV-spectroscopy and HPLC

Solvent	$(k \pm \sigma)/min^{-1}$	Method	N <sup>a</sup>	$(\Phi \pm \sigma)$
pH=4	$(1.3 \pm 0.1) \cdot 10^{-2}$	HPLC	7	$(0.017 \pm 0.003)$
pH=4	$(1.5\pm0.1)\cdot10^{-2}$	$\mathrm{UV}^{b}$	7	$(0.020 \pm 0.003)$
pH=7	$(4.7\pm0.3)\cdot10^{-2}$	HPLC	10	$(0.036 \pm 0.005)$
pH=7	$(5.2 \pm 0.2) \cdot 10^{-2}$	$\mathrm{UV}^{b,c}$	6	$(0.039 \pm 0.003)$
pH=9	$(1.8 \pm 0.1) \cdot 10^{-2}$	HPLC	10	$(0.021 \pm 0.002)$
pH=9	$(1.7\pm0.1)\cdot10^{-2}$	$\mathrm{UV}^{b,c}$	7	$(0.018 \pm 0.002)$
water	$(1.7\pm0.1)\cdot10^{-2}$	HPLC	13	$(0.017 \pm 0.002)$
water	$(1.8\pm0.1)\cdot10^{-2}$	$\mathrm{UV}^{b,d}$	13	$(0.018 \pm 0.002)$

<sup>a</sup> number of irradiation time intervals; <sup>b</sup> 27 wavelengths used in the wavelength region  $302 \rightarrow 328$  nm; <sup>c</sup> two runs; <sup>d</sup> three runs

For the irradiation experiments in sunlight UV-spectra were measured before and after t = 15 min irradiation for different times of the day. The rate constants k were simply calculated from the UV-spectra at  $\lambda = 306$  nm using equation 3.

$$\mathbf{k} = -\frac{1}{t} \ln \left( \frac{\mathbf{E}_{t} - \mathbf{E}_{\infty}}{\mathbf{E}_{0} - \mathbf{E}_{\infty}} \right) \tag{3}$$

 $E_0$  is the absorbance before and  $E_t$  after t=15 min sunlight irradiation, whereas  $E_{\infty}$  is the absorbance at time infinity, determined in the laboratory as discussed before. The calculated rate constants versus time of the day for the 12th of September 1995 are shown in Figure 4.



Figure 4: Photolysis rate constants of metamitron for sunlight experiments performed at September 1, 1995 ( $\bullet$  clouds, overcast and rain) and at September 12, 1995 ( $\bullet$  clear sky and sunny). For comparison calculated rate constants using a mean quantum yield of  $\overline{\Phi} = 0.02$  and maximum (—) and mean (- - -) intensities were included (see text for further explanations).

We have also included the data of a day (1st of September 1995) with overcast sky (and finally in the afternoon with slight rainfall). The corresponding rate constants decrease drastically by more than a factor of 10. For comparison we calculated (at 52°N, 9°E for the 12th of September) the corresponding rate constants with a simple model described in [11]. Calculations were performed with  $\Delta\lambda = 2$  nm at the central wavelengths 280-348 nm and  $\Delta\lambda = 6$ -10 nm at 352-380 nm using the molar absorption coefficients of metamitron in water and a mean quantum yield of  $\overline{\Phi} = 0.02$ . Daily sunlight intensities  $J_{\lambda}/\text{photons s}^{-1}$  nm<sup>-1</sup> cm<sup>-2</sup> were calculated using 21 zenith angles between sunrise and sunset. Monthly mean values comparable to values published in [12] ("mean values" in Figure 4) were obtained using values of precipitable water w = 2.1 cm, dust particle factor d = 450, aerosol scatter  $\omega_0 = 0.5$  and an ozone column of 300 DU (see [11] for definition of variables, respectively). A global radiation for the 12th of September of G = 4400 Whm<sup>-2</sup> was calculated using this model. Maximum mean global radiations in September for German stations at latitude 52°N were reported to be G = 5000-5300 Whm<sup>-2</sup> [13]. These "maximum values" were reproduced (G = 5100 Whm<sup>-2</sup> at 12th of September) using w = 1.0 cm, d = 200,  $\omega_0 = 1.0$  and 300 DU. The corresponding calculated rate constants k (using equation 4) are included in Figure 4 also.

$$\mathbf{k} = 3.82 \cdot 10^{-21} \cdot \overline{\Phi} \sum_{\lambda} \mathbf{J}_{\lambda} \cdot \epsilon_{\lambda} \, \Delta\lambda \tag{4}$$

As quantum yields obtained with polychromatic irradiation are uncertain within an error of about 20%, the agreement of measured and calculated rate constants using general parameters is satisfactory. Besides the agreement of the rate constants determined in the laboratory and by sunlight, results should emphasize, that calculated rate constants for direct photolysis are only valid for clear sky scenarios, i. e. calculated rate constants are maximum values.

#### Products

Two products (II) and (III) were detected in the photolysis of metamitron (I) using GC/MS as well as HPLC. The mass spectrum of (I) was in accordance with a published mass spectrum [14], and the masses found for (I), (II) and (III) are summarized in Tab. 3.

Table 3: Mass spectra of metamitron (I), the main product desamino metamitron (II) and the second product (III).

	m/e (rel. intensity)
(I)	$42(58), 57(17), 63(22), 77(41), 89(17), 104(95), 174(35), 187(50), 202(100, M^+)$
(II)	$42(53), 56(12), 63(19), 69(10), 77(22), 89(19), 104(100), 119(11), 187 (99, M^+)$
(III)	43(18), 77(60), 105(100), 136(11), 178 (14, M <sup>+</sup> )

The main product is the desamino derivative (II), as described before in the literature [6, 7]. (II) was formed at all pH-values with a yield of  $80\pm5\%$ , confirmed by UV-spectroscopy and by HPLC. As we were not able to detect any other product, we assume a yield of (III) of about 15-25%. A measured concentration-time dependence in water of (I), (II) and (III) by HPLC is shown in Figure 5.



Figure 5: Concentrations found by HPLC for the photolysis of metamitron (I) and the corresponding products (II, III) in water. Yield of (II) is found to be 80% and for (III) a yield of 20% is assumed.

To demonstrate the good agreement of the kinetic analysis between UV-spectroscopy and HPLC the curves shown in Figure 5 are calculated with  $k = 0.018 \text{ min}^{-1}$  obtained by UV-spectroscopy. The triazinone chromophore is lost in (III), as obtained by wavelength resolved HPLC of (III), and a UV-spectrum typical of benzene-derivatives is observed. Hence, we assume (III) is a ring cleavage product of (I). A second, more polar product than (I) and (II) was also observed in [6] by TLC. From the mass spectrum we assigned a tentative structure of (III) as shown in Scheme 1.



Scheme 1: Structures of desamino metamitron (II) and the tentatively assigned product (III) from the photolysis of metamitron (I)

# Mechanistic considerations

As for other triazinones [8] water and oxygen are necessary in the photoreaction of metamitron. In one experiment performed the removal of oxygen by freeze and thaw cycles was apparently not sufficient. Interestingly we observed in this experiment by UV-spectroscopy a photoreaction which stops after a conversion of about 10 %. Hence, oxygen acts not as an catalyst but is consumed. The saturation concentration of oxygen in water ( $c = 2.7 \cdot 10^{-4} \text{ mol/l}$  at T = 298 K [15]) is by more than a factor of 10 higher compared to the concentration of metamitron in this study and the effect of oxygen on the reaction is not be observed in these experiments. As oxygen is not incorporated in desamino metamitron as the main product of the photolysis, up to now unknown products should be formed. However, we were not able to detect ammonium in irradiated aqueous solutions. High concentrations of metamitron should lead to a decrease of the photoreactivity, which in part can explain the inhibition of the photoreaction for high concentrated solutions (0.1%, at pH > 7) [6].

The dissociation energy of the N-NH<sub>2</sub> bond is known to be relatively low [16]. For metamitron we calculated a dissociation energy of about 200 kJ/mol using the AM1-method from the MOPAC package [17]. Hence, with the triplet energy obtained by phosphorescence spectroscopy we can not exclude a reaction from the triplet state. The hydroperoxyl radical was assumed to be involved in the primary step of the photoreaction of the related 3-methylthio triazinones, (e. g. metribuzin) [2, 8, 9]. The mechanism is in general described as the formation of singlet oxygen by a sensitized reaction of the excited organic molecule with a consecutive reaction to the hydroperoxyl radical. Main arguments for the mechanism in the case of triazinones are the involvement of water and oxygen and the formation of phenol from cumene [9] added to the solutions of a couple of 3-thiomethyl triazinones. On the other

hand, a Norrish Type-II reaction could be excluded. Metamitron reacts in a similar way as found for other triazinones and a comparable photoreaction should hold. However, the hydroperoxyl radical as a weak acid ( $pK_A = 4.7[18]$ ) is in equilibrium with the superoxide anion:

$$HO_2 \rightleftharpoons H^+ + O_2^-$$

and one would assume a strong effect of pH on the photoreaction, if only hydroperoxyl radicals are involved in the first step of the photodegradation. Unfortunately, quantum yields of 3-thiomethyl triazinones are only known in water. As shown in this study the quantum yield of metamitron is within the error of the experiment independent of pH (for  $4 \le pH \le 9$ ). Hence, the reaction of hydroperoxyl radicals alone can not explain the photodegradation of metamitron, which should also hold for other triazinones investigated so far. The dependence of the photoreaction of triazinones from oxygen and water are arguments against an intramolecular mechanism. On the other hand, the desamination of triazinones is in a formal view a  $\beta$ -cleavage reaction of a ketone with NH<sub>2</sub> as leaving group.

Up to now, the mechanism of the formation of (III) as well as the formation of (II) and the initial step in the photoreaction of metamitron and corresponding triazinones is still an open question.

## Conclusions

Comparable quantum yields of metamitron ( $\overline{\Phi} = 0.02$ ) in aqueous solutions were found at low and high pH (water and pH 4 and 9). A realistic overall error for the quantum yields of  $\pm$  20% takes into account the uncertainty of the absolute light intensities of the polychromatic light source. The two times higher quantum yield obtained at pH=7 is probably an effect of the phosphate buffer used. As for other 4-amino substituted asymmetric triazin-5(4H)-ones a strong solvent and oxygen dependence of the photoreaction was found. For photolysis times of 2-3 hours no reaction was found in methanol, acetonitrile or hexane as well as in oxygen free water. Evidence is presented from the pH-independent quantum yields, that the first step in the photolysis of metamitron can not be initiated by hydroperoxyl radicals alone, as assumed before in the literature. From the phosphorescence spectra a reaction from the triplet state can not be excluded. Quantum yields at different partial pressures of oxygen or for different concentrations of metamitron should be determined to investigate the quenching and influence of oxygen on the photolysis in water. UV-spectroscopy is a simple and fast tool to observe the photochemical reaction. With deeper and more information about the temperature-, wavelengthand oxygen dependence of the photoreaction, metamitron is in principle an attractive candidate for an actinometric system covering the important region from 290 - 380 nm.

Using clear sky sunlight intensities as described above, calculated mean half-lifes of metamitron are very low between 0.4 h (June,  $k = 5 \cdot 10^{-4} \text{ s}^{-1}$ ) and 3.4 h (December,  $k = 5.5 \cdot 10^{-5} \text{ s}^{-1}$ ). The measured half-life in sunlight at 12th of September 1995 range between 1 h in the morning and evening and 0.25 h

at noon.

Metamitron is a good example, that the variation of half-lives calculated for different seasons of the year could be lower than the variation of half-lives for cloudy with respect to sunny days as shown by measurements at two days in the month September 1995 (see Figure 4). Hence, it should be emphasized, that calculations of half-lives often performed for pesticides are maximum values and at least mean annual half-lives should be taken as more realistic values.

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