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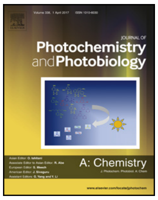

Oxygen dependence in the photoreaction of the pesticide metamitron

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The dependence of the quantum yield of metamitron on oxygen concentration in the range $c_{O_2} = (0.005–12.6)\cdot 10^{-4}$ M in aqueous solution was investigated with a polychromatic Xe-light source in the wavelength region 270–376 nm. The quantum yield of $\Phi = 0.022 \pm 0.002$ mol mol^{-1} at $T = (293 \pm 3)$ K and $c_{O_2} = 2.8\cdot 10^{-4}$ M is independent from metamitron concentration in the range of $c_M = 8\cdot 10^{-8} - 1.8\cdot 10^{-4}$ M. A weak temperature dependence of the photolysis of metamitron at constant oxygen concentration was found with an activation energy of $E_A = (3 \pm 1)$ kJ mol^{-1}. The yield ($\nu = 0.91$) of the main product desamino-metamitron does not depend on start concentration of metamitron, oxygen concentration or temperature (in the range of $T = 281.5–327$ K). Oxygen is necessary in the photolysis of metamitron. Quantum yields for the photoreaction of metamitron increase from practically zero at low oxygen concentrations ($\Phi = 0.002$ mol mol^{-1} at $c_{O_2} < 3\cdot 10^{-6}$ M) to a maximum of $\Phi_{max} = 0.042$ mol mol^{-1} at $c_{O_2} = 5.1\cdot 10^{-5}$ M and declines with increasing oxygen concentration to a value of $\Phi = 0.006$ mol mol^{-1} in oxygen saturated solutions. Two reaction sequences with a reaction from the triplet state T_1 and from a recently proposed transient triplet state T_1' were used to explain the oxygen-dependent rate constants of metamitron. Both sequences explain the oxygen dependence equally well and it was not possible to distinguish between both mechanisms. Aqueous solutions of metamitron are recommended as a promising actinometric system, especially suitable for measurements in sunlight.

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1. Introduction

Triazinone derivatives are known to be important structures with herbicidal activity. As for other triazinones [1], photolysis of metamitron (see Fig. 1) is a main degradation pathway and has been extensively investigated in the past [2–8].

The main photolysis product of metamitron is desamino-metamitron [3–6,9], also found besides metamitron itself [10–12] in environmental samples [12,13]. Metamitron is one of the few examples of a pesticide with available information not only with respect to the photolysis leading to e.g. defined products but also for photophysical details to explain the photochemical reaction. A recent study [8] explained the necessity of water [5] and the dependence on oxygen by an unusual reaction of the enol of metamitron from a transient triplet state T_1'.

Experiments presented here were motivated by the use of metamitron as a promising actinometer in our laboratory. For corresponding measurements, metamitron was chosen as a reference pesticide employed as an actinometric system. Metamitron is easy to analyze with high sensitivity, the photolysis lifetime is short leading to desamino-metamitron as the main product and the UV-spectrum of metamitron covers the important wavelength range for sun-light irradiation below 370 nm.

Besides metamitron [5,8] the influence of oxygen on quantum yields of related thiomethyl-substituted triazinones [14] were reported. However, detailed conditions in photolysis experiments of metamitron in the presence of TiO_2 [6], in photocatalytic degradation reactions in ZnO water suspensions [7], in the presence of soils and soil components [4] and in pure aqueous solutions [3,6], including our own measurements [5], were not well defined or insufficiently reported with respect to concentration and influence of oxygen. On the other hand, even transformation rates and metamitron sorption in soil were found to be oxygen dependent [15].

It soon became apparent from preliminary experiments that the influence of oxygen on the photolysis of metamitron, hitherto reported for a few in particular oxygen-saturated concentrations at a given temperature, is essential for the application of metamitron as a short-lived actinometer in aqueous solutions. Hence, detailed investigations were performed and a reaction scheme is presented and discussed to explain the oxygen dependence.

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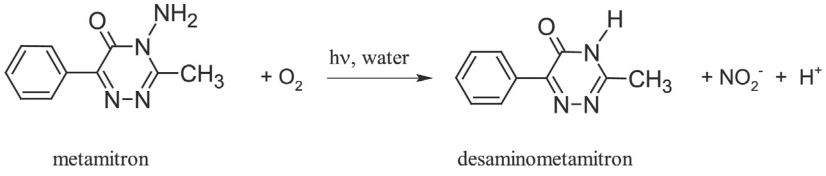

Fig. 1. Photolysis of metamitron leading to the main products desamino-metamitron and nitrite.

Oxygen concentrations in aqueous solutions are dependent on temperature. To distinguish between the potential influence of decreasing oxygen concentration with increasing temperature in natural samples irradiated by sunlight and the intrinsic influence of temperature on the photoreaction of metamitron in aqueous solution, the temperature dependence was investigated. In addition, experiments to investigate the concentration dependence on photolysis-quantum yields and influences on the yield of the main product desamino-metamitron were performed. The comparison with sunlight was a further boundary condition and a polychromatic Xe-light source was used throughout the study.

2. Experimental

2.1. Analytical setup

Metamitron and the main product desamino-metamitron were analyzed by HPLC with a DAD-detector. Analysis was performed with an Agilent HPLC 1100, column Eclipse XDB8, 150 × 4.6 mm, 5 μm-particles, flow 1 mL min^{-1}, 50 μL injection volume, isocratic eluent 20% acetonitrile/80% water, detection wavelength $\lambda = 300$ nm. Typical retention times for metamitron were $RT_M =$ 5.74 min and for desamino-metamitron $RT_D = 4.51$ min. External calibrations were used, with a response factor for metamitron of $R_M = (2.96 \pm 0.01) \cdot 10^7$ areas M^{-1} (from linear calibration between $(9.8–490) \cdot 10^{-8}$ M, $N = 9$, $r^2 > 0.9999$) and a response factor for desamino-metamitron of $R_D = (2.09 \pm 0.01) \cdot 10^7$ areas M^{-1} (from linear calibration between $(3–160) \cdot 10^{-7}$ M, $N = 8$, $r^2 > 0.9999$).

Nitrite and nitrate were analyzed by ion chromatography (Dionex DX120 with AS14 column and guard column AG14) with detection limits of 60 μg L^{-1}. In addition, samples were analyzed for nitrite in parallel by a classical wet chemical analysis using sulfanilic acid and naphthylethylene diamine dihydrochloride (detection limit 20 μ g L^{-1}).

Oxygen in solution was detected by an oxygen electrode (Cellox 325, WTW, Weinheim, Germany). Absolute oxygen concentrations obtained by the oxygen electrode were checked by the classical Winkler procedure. From measurements between $c_{O_2} = 3–10$ mg L^{-1} oxygen concentrations from the electrode were found to be 98 ± 2 % of the Winkler procedure.

pH-values were obtained with a common pH-electrode (SenTix81, WTW, Weinheim, Germany) after calibration with standard buffer solutions at pH = 4, 7, and 9.

UV-spectra (double-beam spectrometer Lambda 45 with pre monochromator, Perkin Elmer) were measured with a resolution of 2 nm in 1 nm steps at $d = 1$ cm in quartz cuvettes at ambient temperature with water as reference. The wavelength accuracy has been checked by a holmium filter to be better than $\Delta\lambda = \pm 1$ nm.

Metamitron will be abbreviated as M and desamino-metamitron as D. Errors are always given as one standard deviation σ.

2.2. Photolysis experiments

For photolysis experiments, a photolysis apparatus on an optical bench (Amko, Tornesch, Germany) with a Xe-lamp XBO 1000 (1000 W, Osram, Germany) was used. Although 1000 W were available, the electrical power of the light source was always set to 500 W (±2%). Light was focused by mirrors through a water filter (equipped with quartz windows) and an optical glass-filter with known absorbance (A_{filt}) into a 500 mL round-bottomed flask made of quartz glass, positioned 6.5 cm behind the optical filter. The quartz flask was found to be transparent in the wavelength region 220–700 nm. The optical path-length of the quartz-flask was determined to be $d = 9.9$ cm using a method proposed by Zepp [16], details of the measurement are given on page S5 in the supplementary information.

The Xe-lamp, mirrors and the water filter were cooled by tap water. The light beam (height 3 cm, width 6 cm) was adjusted above the middle of the flask. Throughout the study 500 mL of an aqueous solution was used and the beam was always below the surface of the solution. The flask was thermostated by an open water bath, placed on a magnetic stirrer. The water bath was connected to a thermostat, maintaining a constant temperature (usually $T = 293 \pm 3$ K). Stirring of the solution provided homogeneous concentrations and constant temperatures between $T = 281.5–327$ K (for temperature dependent measurements).

The quartz flask was stoppered with a quick-fit stopper and equipped with the oxygen electrode, a needle (15 cm, luer-lock adapter) for a syringe (1 mL gas-tight Hamilton-syringe) to take samples and a Pasteur pipette made of glass to provide the necessary gas mixture. Temperatures of the solution were measured by the temperature sensor inside the oxygen electrode, occasionally checked by a calibrated thermometer.

Oxygen-mixing ratios of 0–100% were provided by a mass-flow controller (Tylan FC-260, 100 SCCM) for oxygen and a second mass-flow controller for nitrogen (Tylan FC-260 1 SLM). After mixing both flows in a mixing flask (500 mL) the gas mixture was transferred to the solution of the 500 mL quartz flask. The total flow was kept within the range of 100–300 mL min^{-1}.

Experiments always started with an equilibrium period to stabilize the light source and temperature and oxygen concentration in solution. Within the equilibrium period, the light beam was shut off with a shutter behind the optical filter. With solubility data of oxygen in aqueous solution [17] and the desired oxygen concentration in solution, a theoretical oxygen concentration in the gas phase was provided by suitable adjustment of both flow controllers. The stirred solutions usually only needed small readjustments within an equilibrium period of about 30 min. The end of the equilibration period was defined by constant (±2%) oxygen concentrations for about 5 min. Then oxygen electrode and Pasteur pipette were pulled out from the solution into the gas phase, thereby maintaining the necessary oxygen concentration in the gas phase. After taking a sample (1 mL) for irradiation time $t = 0$, the shutter was opened and the solution was irradiated. Irradiation times with an accuracy of about one second were applied. After a given irradiation time, 1 mL of the solution was removed and analyzed directly by HPLC. A maximum of 10 samples were taken after a maximum irradiation time of 60 min. At the end of an experiment, oxygen concentration and temperature were measured again. Errors in oxygen concentrations were defined as

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