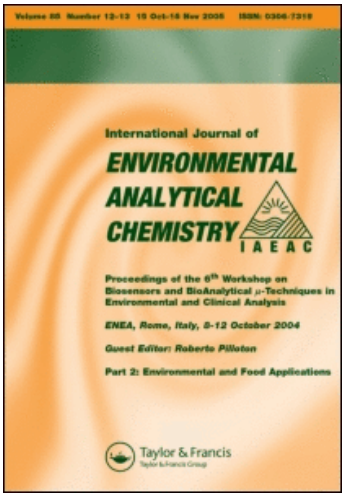

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Studies on the Photolytical Behaviour of Bromofenoxim in the Atmosphere

M. T. Oms-molla[ab]; M. Schilling[a]; J. Nolte[a]; D. Klockow[a]
[a] Institut für Spektrochemie und Angewandte Spektroskopie, Dortmund, Germany [b] Department of Analytical Chemistry, Universitat de les flies Balears, Palma de Mallorca, Spain

To cite this Article Oms-molla, M. T. , Schilling, M. , Nolte, J. and Klockow, D.(1995) 'Studies on the Photolytical Behaviour of Bromofenoxim in the Atmosphere', International Journal of Environmental Analytical Chemistry, 58: 1, 359 — 370
To link to this Article: DOI: 10.1080/03067319508033137
URL: http://dx.doi.org/10.1080/03067319508033137

Intern. J. Environ. Anal. Chem., Vol. 58, pp. 359-370
Reprints available directly from the publisher
Photocopying permitted by license only

STUDIES ON THE PHOTOLYTICAL BEHAVIOUR OF BROMOFENOXIM IN THE ATMOSPHERE

M. T. OMS-MOLLA*, M. SCHILLING, J. NOLTE and D. KLOCKOW

Institut für Spektrochemie und Angewandte Spektroskopie, P.O. Box 101352, 44013 Dortmund, Germany

(Received, 10 October 1993, in final form, 23 December 1993)

Photodecomposition of the herbicide bromofenoxim was studied in aqueous solution, solid state and in aerosol form. In all cases, bromoxynil and 2,4-dinitrophenol are the degradation products. Photodecomposition rate in solution is strongly dependent on the pH with a minimum at pH 8–10 and increasing at lower and higher pH values. Hydrolysis at pH 12 in darkness also yields 2,4-dinitrophenol and bromoxynil as products, while hydrolysis in acidic medium has not been observed to occur in absence of light. Photodecomposition of solid bromofenoxim deposited on an inert surface is also studied and linked to the irradiation time. A system for generation of test aerosols is described. Dry and droplet aerosols are collected, extracted and analyzed after different times of irradiation in order to study the possible photolytical behaviour of bromofenoxim in the atmosphere.

KEY WORDS: Bromofenoxim, photochemical decomposition, aerosols.

INTRODUCTION

Due to extensive use and physical properties of herbicides, these compounds can be nowadays found in all compartments of the natural environment. Investigations of environmental fate and behaviour of herbicides have been done mainly in water and soil samples, while information regarding their fate in the atmosphere is limited[1]. Their input into the atmosphere is caused due to agricultural practices and depends mainly on the application mode and the properties of the herbicide. Once in the atmosphere, it may suffer chemical transformations due to other pollutants and sunlight[2], and together with its metabolites, it may be removed by wet and dry deposition[3]. Another potentially important source of airborne pesticides can be the volatilization from formerly treated surfaces[4].

Bromofenoxim (FEM) [3,5-dibromo-4-hydroxybenzaldehyde-O-(2′,4′-dinitrophenyl)oxime] is an often used post-emergence herbicide[5,6]. Its photodecomposition in aqueous samples yields 2,4-dinitrophenol (DNP) and bromoxynil (BOX) (3,5-dibromo-

*To whom correspondence should be addressed. Present address: Department of Analytical Chemistry, Universitat de les Illes Balears, 07071-Palma de Mallorca, Spain.

4-hydroxybenzonitrile) as products[5,7]. Bromofenoxim is brought out to plants predominantly by spraying it as suspension or in dry form and therefore may remain in the atmosphere for a certain time. According to its physicochemical properties and application mode, bromofenoxim is expected to be found in the environment mainly in form of dry and droplet aerosol, in aqueous systems and also in solid form on soil and plant surfaces.

In this paper, results on photolytical degradation of bromofenoxim in aqueous solution, as a solid and in form of dry and droplet aerosol are presented.

EXPERIMENTAL

GC-MS analysis

A Varian gas chromatograph equipped with a programmable temperature vaporizer (PTV) injector and coupled to a Finnigan MAT MAGNUM^T Ion Trap Detector was used for GC-MS analysis. Separation was carried out on a 30 m capillary PTE-5 column from Supelco. GC-MS analytical conditions were as follows: PTV injection starting at 60°C and programmed after 0.1 min at 300°/min to 250°C; splitless; initial temperature 70°C maintained for 0.1 min, then programmed at 6°/min to 250°C and held there until the end of chromatogram (20 minutes).

HPLC analytical procedures

Analysis of bromofenoxim and its decomposition products was carried out on a SYCAM HPLC system equipped with a Reodyne injector (20 µL sample loop volume) and coupled to a PYE UNICAM UV-detector set at 250 nm.

The compounds were separated using a Nucleosil 300-5 C18 analytical column, 250 mm × 4.6 mm i.d., 5 µm particle size. A 2 cm long precolumn with the same characteristics was placed before the analytical column.

The mobile phase was acetonitrile/water (52:48, v/v) at pH 3.55, adjusted by adding acetic acid to the eluent containing 5×10^{-3} mol L^{-1} sodium acetate. The flow rate was 0.9 mL min^{-1} and the temperature 25°C. All solvents were previously distilled and degassed with helium.

Production of test aerosols

The experimental set-up for the production of test aerosols is shown in Figure 1.

A nebulizer operating with nitrogen at a flow rate of 240 L h^{-1} was used to nebulize a suspension of bromofenoxim in water (0.1587 g L^{-1}) thus producing a droplet aerosol with droplet diameters between 0.3 and 5 µm. Larger droplets were removed by impact within the device and drained back to the liquid reservoir. The water used as a solvent was removed by passing the wet aerosol through a diffusion dryer consisting of a screen tube surrounded by silica gel granules[8,9].

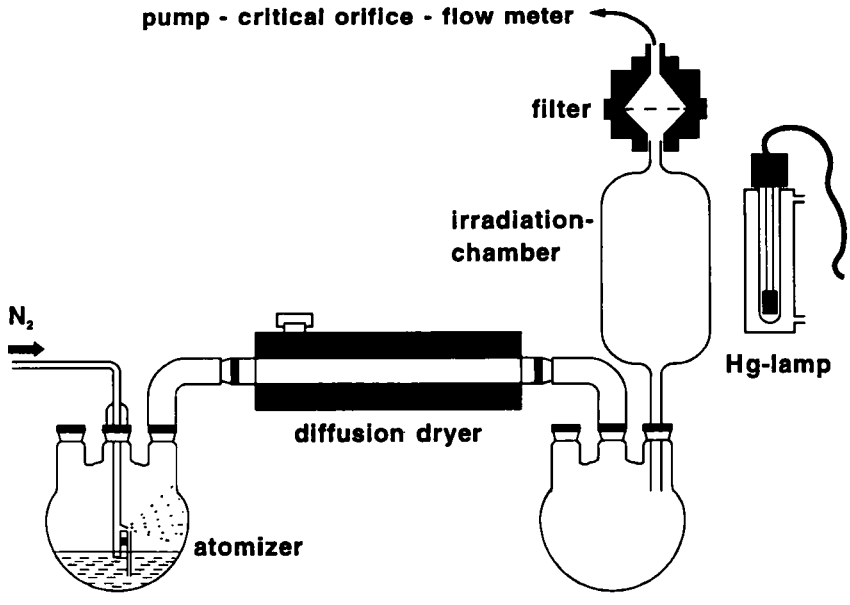

Figure 1 Experimental set-up for the production and irradiation of test FEM aerosols. For studies on droplet aerosol the diffusion dryer was replaced by a glass tube of similar dimensions.

Size characterization of aerosols was carried out with a particle size analyzer POLYTEC PSE-1500, that operates by measuring the scattered light from the particles passing through a focused beam of light. The POLYTEC PSE-1500 was calibrated with a monodisperse aerosol of latex. The latter was produced by the nebulization of a suspension of latex in ethanol supplied by the manufacturer for calibration purposes.

The particle size distribution of the generated bromofenoxim aerosol was obtained after calibration and is plotted in Figure 2 as a cumulative distribution. It shows that 50 per cent of the particles have diameters lower than 0.57 μm.

Studies on droplet aerosols were carried out by replacing the diffusion dryer by a glass tube of similar dimensions.

Photochemical experiments

Irradiation of bromofenoxim samples was achieved using a Hg Hanau TQ Z2 lamp from HERAEUS. The distance between the lamp and the irradiation chamber was 10 cm.

Stock solutions of bromofenoxim, 2,4-dinitrophenol and bromoxynil in methanol were prepared and stored in brown glass bottles for further use. The use of methanol was necessary for the preparation of stock solutions because bromofenoxim has a extremely low solubility in water. Solutions of bromofenoxim (65.1×10^{-6} M) containing 15% of methanol, were prepared from stock solutions, irradiated using the lamp described above and analyzed by HPLC. Adequate amounts of buffer solution were added to the solutions to adjust the pH to

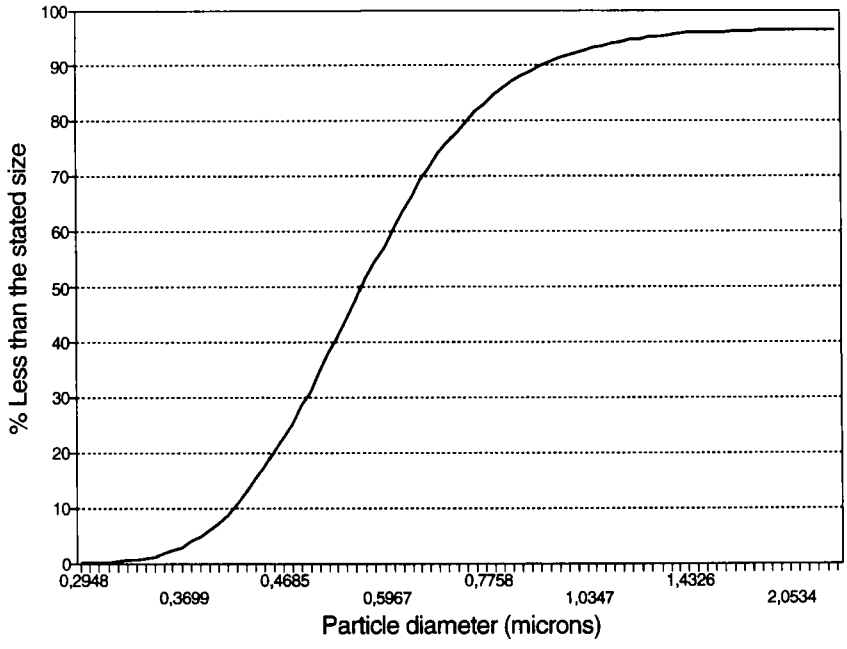

Figure 2 Cumulative distribution of the bromofenoxim aerosol generated by nebulization of a suspension containing 0.1587 g of bromofenoxim per liter of water. Spray flow = 240 L h^{-1}.

the desired values (HCl: pH 2, acetic acid/acetate buffer: pH 3.5, phosphate buffer pH: 6.2, borate buffer: pH 7.9, carbonate buffer: pH 10.2 and sodium hydroxide: pH 12). The buffered solutions were then irradiated for a period of time and analyzed by HPLC-UV.

Studies on photodecomposition of bromofenoxim deposited onto an inert surface, were achieved by placing 0.2 mL of a bromofenoxim solution in acetone (97×10^{-6} M) into a white glass vial and evaporating the solvent under a dry nitrogen flow. The vials were then closed and irradiated using the Hg-lamp. After different irradiation times the decomposition products together with undecomposed bromofenoxim were dissolved with 1 mL of methanol and analyzed by GC-MS and by HPLC-UV.

Irradiation of bromofenoxim aerosols was carried out using the set-up shown in Figure 1. The sample flow rate determined the residence time of the test aerosols inside the irradiation chamber (volume = 1138 mL). Decomposition products together with undecomposed bromofenoxim were collected on glass fiber filters (Schleicher and Schuell Inc, USA), extracted with 1 mL of methanol and analyzed by HPLC-UV.

RESULTS AND DISCUSSION

GC-MS investigation

Photodecomposition due to sunlight is an important conversion process for airborne pesti-

cides not only as a part of the removal process, but also because the products may be more toxic and persistent than the parent compounds. In this process, the incident light may be directly absorbed by the substrate itself, which undergoes then decomposition, or the reaction may take place via interaction with another photochemically generated intermediate that is in the system together with the herbicide.

With the aim to gain some knowledge about its photodecomposition in the atmosphere, solid bromofenoxim deposited on an inert surface, in solution and in dry and droplet aerosol form was irradiated and the resulting products were identified. GC-MS analysis of the irradiated samples showed that in all the cases bromofenoxim (FEM) undergoes molar decomposition to 2,4-dinitrophenol (DNP) and bromoxynil (BOX). Identification of the products was achieved by comparing their GC-MS data and HPLC retention times with those of standards. Figure 3 shows the GC-MS chromatogram obtained when a standard bromofenoxim solution was injected. The mass spectrum and the retention time of the peak eluting at 13.5 min corresponds to that of DNP. However, the mass spectra of the peaks eluting at 16.2 and 17.2 min were identical to that of BOX. The injection of a standard solution showed that BOX retention time under the described conditions was 17.2 min. The peak eluting at 16.2 min is thought to be due a product of thermal decomposition of FEM because, on one hand, its mass spectrum was the same as the one of BOX, but not its retention time and, on the other hand, it appears only when FEM is present in the sample. Small amounts of DNP and BOX were always found when standard solutions of FEM were analyzed by GC-MS, but not in the analysis by HPLC, and therefore they must to be due to thermal decomposition of FEM in the GC system. Figure 4 shows the GC-MS chromatogram

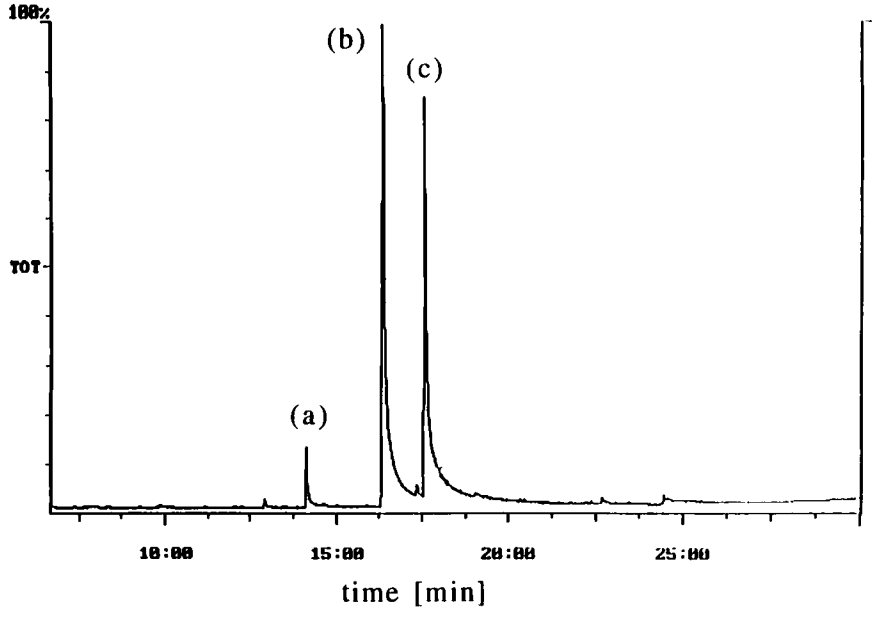

Figure 3 Total Ion Current (TIC) GC-MS chromatogram of a FEM standard injection; conditions: see text; detected compounds: (a) DNP; (b) thermal decomposition product of FEM (MS spectrum consistent with BOX); (c) BOX.

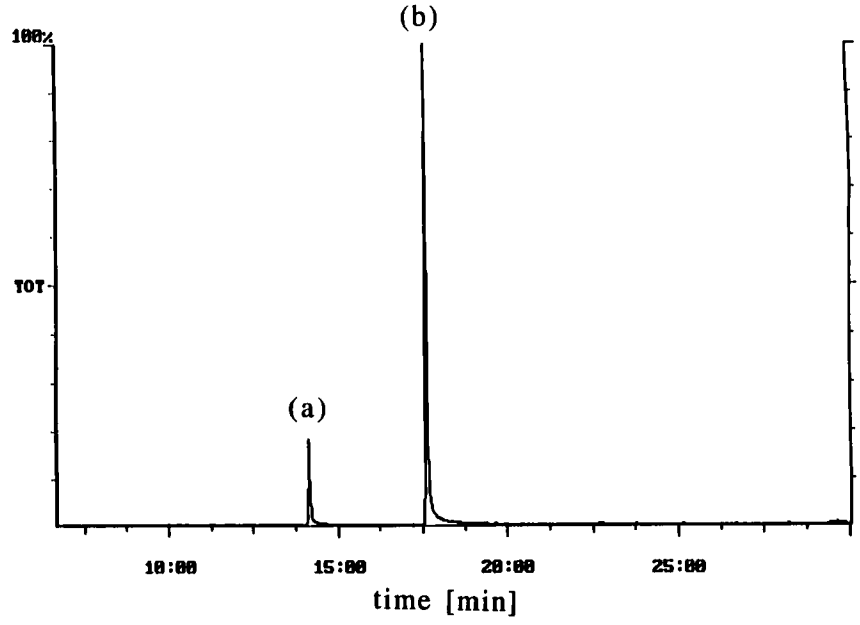

Figure 4 Total Ion Current (TIC) GC-MS chromatogram of FEM after irradiation in solid form for 12 hours. Identified photoproducts: (a) DNP, (b) BOX.

of a FEM solid sample after irradiation under the lamp for 12 hours to ensure total decomposition of the herbicide. It shows that only two decomposition products, DNP and BOX, were generated, while the peak at 16.2 min completely disappeared, thus helping to confirm that it is associated to the presence of FEM. The GC-MS analysis of irradiated samples of FEM in aqueous solution, methanol solution, and in dry and droplet aerosol form showed the same results with DNP and BOX as the only products found.

HPLC-UV investigation

An HPLC-UV method for studies on photodecomposition of FEM under different conditions was developed because of the difficulties described above for the GC-MS approach. Problems in the analysis of FEM have been recently pointed out by Benfenatti *et al.*[10] and up to now only one reference has been found which describes an HPLC method with amperometric detection of the eluting compounds[11]. Additional advantages of the HPLC-UV method described in this paper is that it provides a 10 fold higher sensitivity than GC-MS and avoids the problem of FEM thermal decomposition.

Calibration functions were obtained by injection of standard solutions of DNP, BOX and FEM in methanol. The wavelength at 250 nm was chosen as a compromise based on the corresponding UV spectra. The calibration was linear up to 80×10^{-6} M for the three compounds based on peak height measurements. The detection limits were 1.6×10^{-6} M for DNP (t_r 3.7 min), 1.1×10^{-6} M for BOX (t_r 4.5 min) and 1.1×10^{-6} M for FEM (t_r 18.5 min).

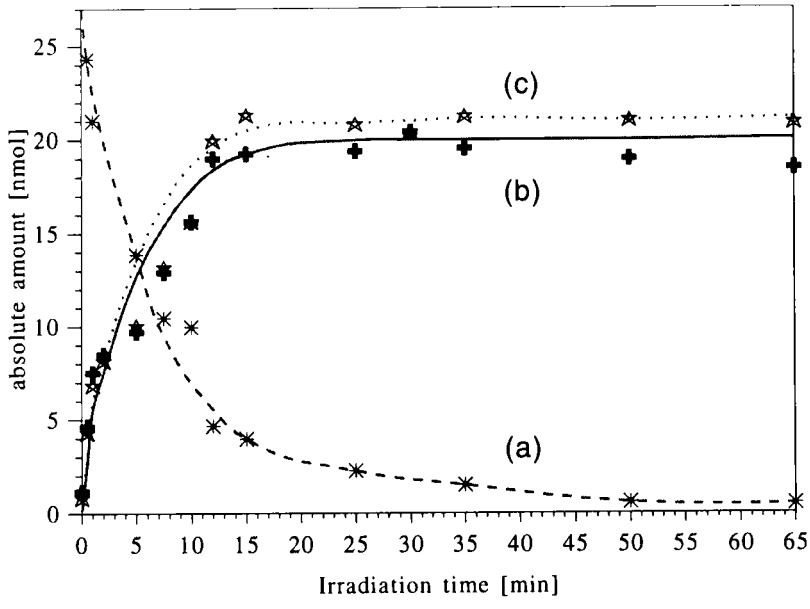

Figure 5 Decomposition of solid bromofenoxim when deposited on an inert surface as a function of the time of irradiation. (a) FEM, (b) DNP, (c) BOX.

Photodecomposition of FEM in aqueous solutions and solid form

The spectrum of the lamp used in these studies ranges from 220 to 600 nm. However, the lamp is cooled by water and the cool finger around it is made of glass. Thus, most of the radiation in the UV region is absorbed before reaching the test material. Under these conditions the most intense lines are in the visible range at 536 nm, 352 nm, 378 nm and 366 nm. The intensity at these wavelengths, according to the manufacturer report[12], are 12.6W, 5.6W, 3.8W and 3.2W.

Experimental results on decomposition of solid FEM when deposited on an inert surface showed that also in this case the only decomposition products were DNP and BOX. Figure 5 shows the decrease of FEM as a function of the irradiation time and the simultaneous appearance of the products (DNP and BOX) as a consequence of its photodecomposition.

The HPLC-UV analysis of the irradiated FEM solutions showed the rapid decrease of FEM concentration in water as well as in methanol and the simultaneous increase of DNP and BOX as a function of irradiation time (Figure 6). Figure 7 shows the photodecomposition of FEM after three different irradiation periods as a function of pH. It can be seen that the decomposition rate was minimal around pH 8–10 increasing towards higher and lower pH values. The experiments to determine the stability of bromofenoxim in absence of light showed that it is hydrolyzed at pH 12 according to a first-order reaction (Figures 8 and 9) which can be the reason for its greater decomposition observed at this pH also in light conditions. In contrast, hydrolysis at lower pH (2 to 10) was not observed in darkness within

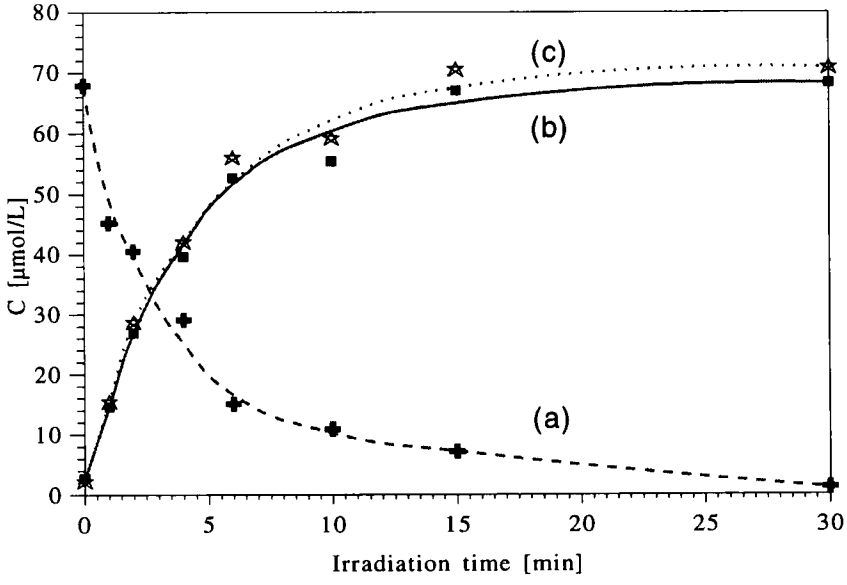

Figure 6 Changes in the concentration of FEM and its photoproducts in aqueous solution versus time of irradiation. Initial FEM concentration 65.1×10^{-6} M. (a) FEM, (b) DNP, (c) BOX.

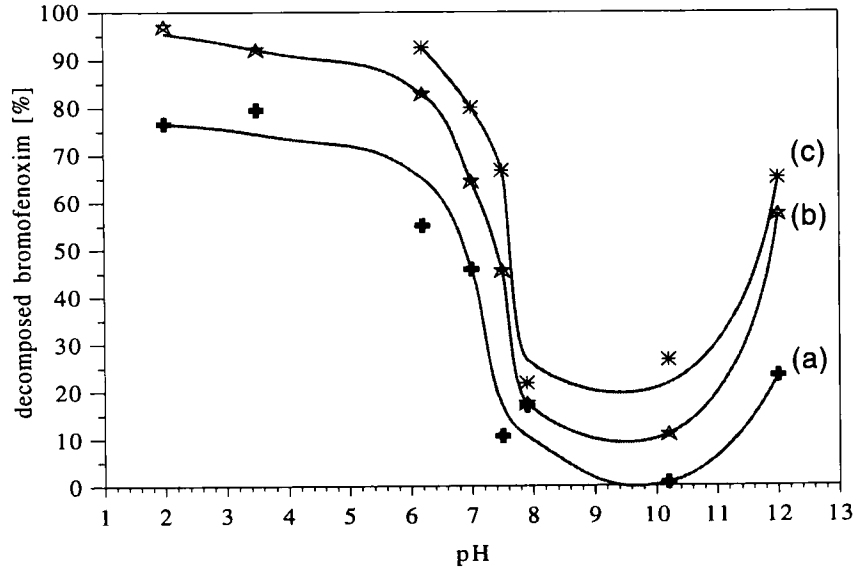

Figure 7 Influence of pH on the photodecomposition of FEM in aqueous solution after (a) 10 minutes, (b) 30 minutes and (c) 60 minutes exposures to radiation.

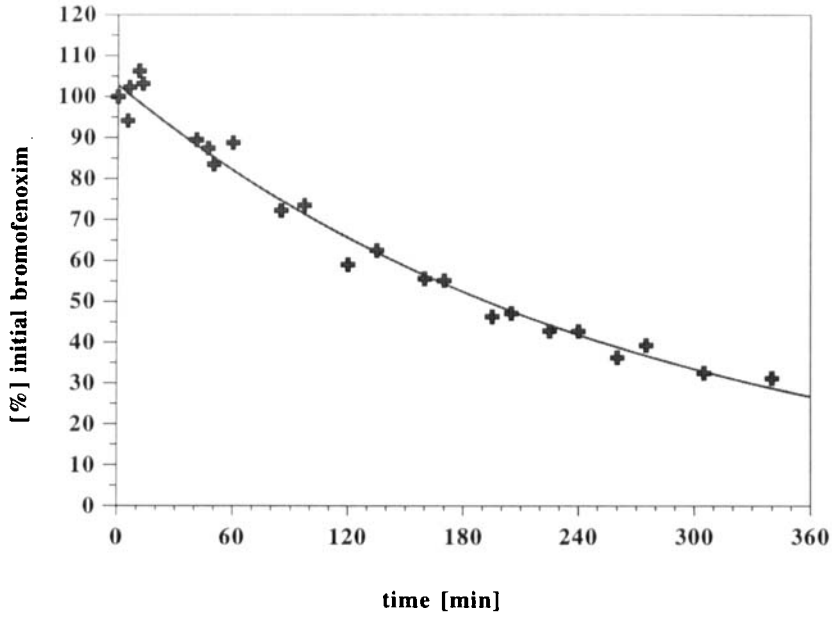

Figure 8 Hydrolysis of FEM in basic medium (pH = 12) in absence of light.

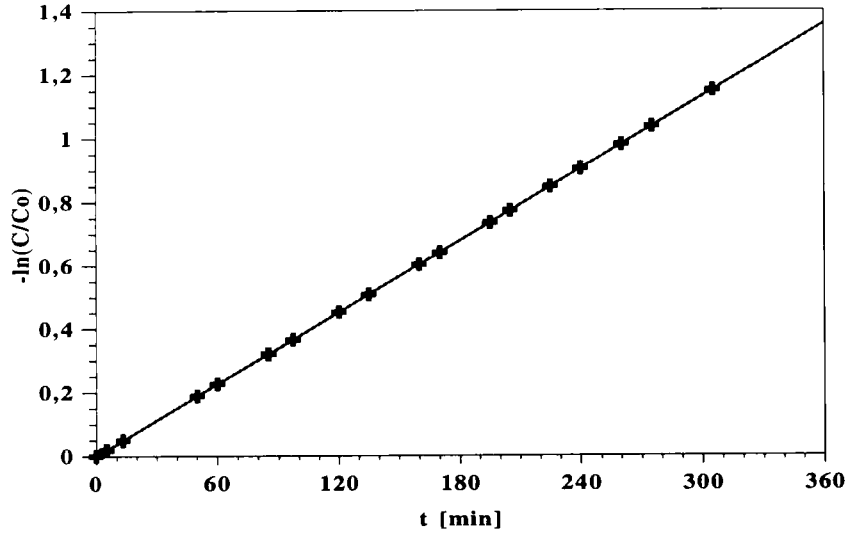

Figure 9 First-order plot of bromofenoxim hydrolysis in absence of light at pH 12.

the period tested (4 hours) and therefore it can not be the reason for the greater FEM photodecomposition rate at acidic pH. One possible explanation is that the reaction involves acid catalysis as it has been described for similar aromatic oximes[13]. However, the mechanism of the photodecomposition of bromofenoxim is not yet fully understood.

Regarding the products, the photodecomposition of bromoxynil by light at 313 nm has been reported[14] and it has been found to be affected by fulvic acids[15] and several ions such as Fe(III) and Mn(II)[16] while solar radiation >400 nm is not important in the presence or absence of soil fulvic acids. In the experimental conditions described in this paper, that is with light in the visible range, it was found that both DNP and BOX remained stable in aqueous samples after irradiation for a period time of 4 hours (maximum period tested).

Photodecomposition in aerosol form

Photodecomposition of airborne bromofenoxim can also occur when it is suspended as particulate matter and adsorbed or dissolved within atmospheric water droplets. It plays an important role in the atmospheric removal processes (together with dry and wet deposition) as FEM aerosols are totally exposed to sunlight.

Figure 10 plots the decomposition of FEM in dry particle and droplet aerosol form as a function of the irradiation time. Analysis of the collected samples after irradiation showed that the only decomposition products detected were again DNP and BOX. The influence of pH on the decomposition of FEM droplet aerosol was studied and it showed the same dependance as in solution (see above) with a minimal decomposition rate at pH 8–10.

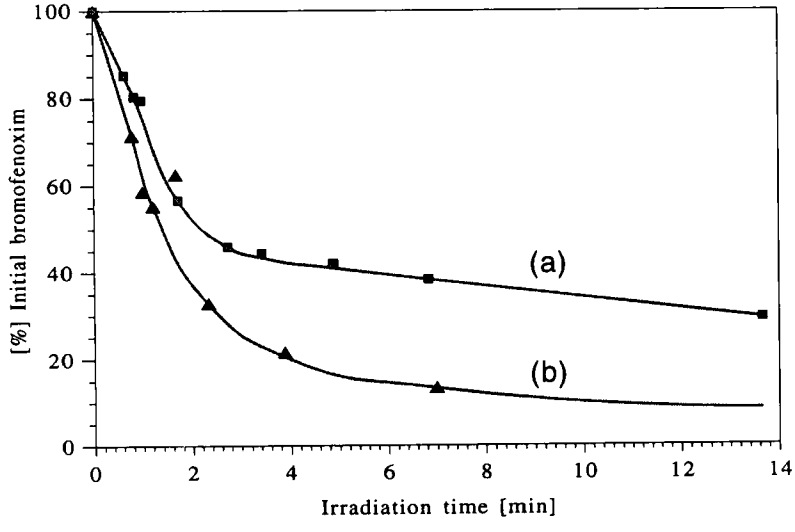

Figure 10 Photodecomposition of FEM in (a) droplet and (b) dry particle aerosols versus time of irradiation.

Influence of reactive trace gases

Further experiments were carried out in order to confirm that there is no artifact formation in the filters due to the presence of other atmospheric pollutants. With this purpose, air streams of controlled relative humidity (0 to 80% RH) and known concentrations of SO_2 (270 ppbv), NO_2 (350 to 490 ppbv) or O_3 (85 to 100 ppbv) were passed through a serial of filters spiked with bromofenoxim for a period of time (15 to 120 minutes) after which the filters were extracted and analyzed by HPLC and GC-MS. During all the procedure the filters and extracts were light-protected. Only FEM was found on the filters and at the same initial concentration showing that collected FEM aerosols are not decomposed by ozone, NO_2 or SO_2 present in the atmosphere.

CONCLUSIONS

Two analytical methods have been tested for the determination of bromofenoxim (FEM) and its metabolites bromoxynil (BOX) and 2,4-dinitrophenol (DNP). The first one, based on GC-MS, can be used for the determination of BOX and DNP. However, it is not adequate for the determination of FEM due to its thermal decomposition in the GC system that yields also DNP and BOX. The analysis by GC-MS provides information on the identity of the photoproducts after irradiation of FEM samples, but it is not suitable to quantify the three compounds present in a sample. For studies on the photolytical behaviour of FEM, the method based on the use of HPLC-UV has proved to be adequate for the determination of the three compounds in the same sample at concentrations in the micromolar range. Thus, this is the method recommended to be used in further studies on the fate and behaviour of bromofenoxim in the environment.

The results on photodecomposition studies do not allow to stablish photolytic rate constants, since the actinometryc fluxes under the experimental conditions have not been determined. However, the behaviour of bromofenoxim in solid, dissolved or aerosol form during irradiation and also the identity of the decomposition products could clearly be demonstrated. There is no doubt that these products will also be formed under real atmospheric conditions, and that correspondingly an analytical approach to bromofenoxim quantification in ambient air has to take into account the described observations.

Acknowledgment

The authors acknowledge the Ministry of Education and Science of Spain to support Dr. Oms Molla's stay at ISAS. The financial support of the Bundesministerium für Forschung und Technologie and of the Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen is also gratefully acknowledged.

References

1. M. S. Majewski in: *Pesticide Chemistry, Proceedings of the 7th International Congress of Pesticide Chemistry (IUPAC), Hamburg, 1990*; (H. Frehse ed., VCH, Weinheim, 1991) pp. 307–317.
2. J. E. Woodrow, D. G. Crosby and J. N. Seiber, *Res. Rev.*, **85,** 111–125 (1983).
3. J. Scharff, R. Wiesiollek and K. Bächmann, *Fres. J. Anal. Chem.*, **342,** 813–816 (1992).
4. J. H. Smith, D. Mackay and C. W. K. Ng, *Res. Rev.*, **85,** 73–88 (1983).
5. G. Jäger in: *"Pflanzenschutz und Schädlingsbekämpfung"*, (K. H. Büchel ed., Georg Thieme Verlag, Stuttgart, 1977) p. 165.
6. Ch. R. Worthing and S. B. Walker (eds.), *The Pesticide Manual*, (The British Crop Protection Council, Lavenham Press Ltd., Lavenham, UK, 1987), 8th ed.
7. B. A. Karlhuber, W. D. Hörman and K. A. Ramsteiner, *Anal. Chem.*, **47,** 2450–2452 (1975).
8. R. Niessner, PhD thesis, University of Dortmund, Germany, 1981.
9. R. D. Kaiser, PhD thesis, University of Dortmund, Germany, 1985.
10. E. Benfenati, V. Pistotti, M. Terreni and R. Fanelli, *"A Library Report on the Analysis of Pesticides Subject to Investigation for the European Communities Commission"*, presented at 4th Workshop on Chemistry and Fate of Modern Pesticides, Prague, 1993.
11. A. Meyer and G. Henze, *Fres. Z. Anal. Chem.*, **332,** 898–903 (1989).
12. *"Tauchlampen für photochemische Labor- und Herstellungsverfahren"*, (booklet) Heraeus, Hanau.
13. M. F. Haley and K. Yates, *J. Org. Chem.*, **52,** 1817–1824 (1987).
14. J. Kochany, G. G. Choudry and G. R. Webster, *Pest. Sci.*, **28,** 69–71 (1990).
15. J. Kochany, G. G. Choudry and G. R. Webster, *Intern. J. Environ. Anal. Chem.*, **39,** 59–74 (1990).
16. J. Kochany, *Chemosphere*, **25,** 261–270 (1992).