Phosphorimetry of Chloro- and Nitro-Aromatic Fungicides[1]

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Summary

Low temperature fluorescence and phosphorescence properties of 19 chloro- and nitro-aromatic fungicides have been investigated. Five compounds (chloroneb, 1-chloro-2,4-dinitronaphthalene, daconil 2787, DCNA and dyrene) show luminescence, strong enough to be used for sensitive analytical procedures. The lowest detection limit (5×10^{-9} g/ml) is shown by DCNA. In all cases phosphorescence was more intense than fluorescence suggesting the former as the preferred method.

Introduction

Phosphorimetry, one of the most sensitive analytical methods (for general references see 1-4, biological applications are discussed in 5) has been suggested and used for the analysis of pesticides. Phosphorescence excitation and emission wavelengths for a number of pesticides has been measured (6-9) and analytical procedures involving phosphorescence measurements developed for biphenyl (10), the parathion metabolite p-nitrophenol (11), insecticide synergists (7) and carbamates (8). The application of phosphorimetry to pesticides has been briefly reviewed (12).

Phosphorescence characteristics for the major chloro- or nitro-aromatic fungicides are not known. Since analytical methods for these compounds are generally scarce (cf. 13) we have measured the luminescence properties of 19 important compounds of this type.

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Materials and Methods

Fungicides

The following compounds[1] were investigated: binapacryl, blastin, chloranil, chloroacetaldehyde-2,4-dinitrophenylhydrazon, 1-chloro-2,4-dinitronaphthalene, chloroneb, daconil 2787, DCNA, dichlone, 2,4-dinitrophenyl thiocyanate, dinobuton, DNOC, dyrene, HCB, oryzon, PCNB, PCP, 2,3,5,6-tetrachloronitrobenzene and tricamba. Oryzon (hexane-acetone, 4:1, R_f 0.41) and pentachloronitrobenzene (hexane, R_f 0.42) were purified on silica thin layer plates. All other compounds were repeatedly recrystallized.

Fluorescence and Phosphorescence Measurements

Fluorescence emission spectra were obtained with an Aminco-Bowman spectrophotofluorimeter[2] and the phosphorescence spectra with an Aminco-Keirs phosphoroscope. A Hanovia mercury xenon arc lamp (901 B-1) was used as an excitation source and a photomultiplier tube (RCA 1P 28) as a detector.

The spectra were measured with the following slit widths (in the order from excitation monochromator to emission monochromator): 3,2,1,3,0.5 mm. For measurements of the limits of detection slit widths of 3,3,1,3,0.5 mm were used.

The instrument was calibrated with a mercury arc lamp. Wavelengths recorded are accurate to ±2 nm. Ethanol/isopentane/ether 2/5/5 (vol) (EPA) was used as a solvent for all measurements. Liquid nitrogen (77°K) was the coolant.

Results and Discussion

Five of the fungicides investigated show significant luminescence properties (see Table 1). Phosphorescence in all of these cases was of considerably higher intensity than fluorescence making it the analytically more useful property. The low detection limit of DCNA being particularly noteworthy.

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[1] Whenever possible compounds are listed by their established common names and abbreviations [cf. J. Neumeyer, D. Gibbons, and H. Task, Chemical Week, April 12 (1969) p. 28 and April 26 (1969) p. 38].

[2] American Instrumental Company Inc., 8030 Georgia Avenue, Silver Spring, Md. 20910.

TABLE 1

Fungicide	Luminescence characteristics of five fungicides λ max at 77°K in mμ		Phosphorescence Detection limit g/ml[b]
	Fluorescence	Phosphorescence[a]	
DCNA (2,6-Dichloro-4-nitroaniline)		508, 526	5×10^{-9} (365)
Dyrene	325	410	5×10^{-8} (295)
Daconil 2787 (Tetrachloroisophthalonitril)	330, 344	423, 448, 474	5×10^{-8} (313)
Chloroneb (1,4-Dichloro-2,5-dimethoxybenzene)	330	482	5×10^{-7} (300)
1-Chloro-2,4-dinitronaphthalene		538, 575	5×10^{-7} (365)

a) The bands useful for analytical purposes have been underlined.

b) Excitation wavelength used is given in parentheses (nm).

For these compounds phosphorescence seems a useful property for detection and quantitative determination in natural samples considering the well known advantages of phosphorimetry i.e. (i) the method is sensitive, (ii) interferences can be avoided by the selective excitation (iii) the procedure is fast (ca. 15 minutes when standard curve is known).

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