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Identification of PCB's in the Presence of DDT-Type Compounds Using Low Temperature Luminescence

J. T. Brownrigg, J. Guilfoyle and A. W. Hornig

Baird-Atomic, Inc.
125 Middlesex Turnpike
Bedford, Mass. 01730

INTRODUCTION

Polychlorinated biphenyls (PCB's) have emerged as ubiquitous environmental pollutants having been widely used as plasticizers, lubricants, flame retardants, and as heat transfer media (1, 2). These compounds are insoluble in water, but are soluble in lipids. PCB levels found in fish typically range from 0.01 to 10 ppm and from 1 to 100 ppm in fish-eating birds and are comparable to DDE levels found in the same species (3, 5). The presence of PCB's in the environment is a matter of concern for two reasons. First, they have been found to be highly toxic to certain marine animals. For example, exposure for 48 hours to 0.1 ppm Aroclor® 1254 (a commercial PCB mixture) in sea water produces 100% mortality in juvenile pink shrimp, and strongly depresses the rate of shell growth in oysters (6). Second, PCB's have been found to interfere with gas chromatographic determination of DDT and related compounds, requiring a pre-separation step which usually involves thin-layer or column chromatography (3).

The objective of the present investigation was to assess the applicability of low temperature (77° K) luminescence spectroscopy to the problem of identifying the PCB's in the presence of DDT-type compounds. Basic studies completed to date have focused upon the documentation of important pesticide and PCB spectra, including various mixtures of these. The results obtained are very encouraging and suggest that a rapid and sensitive method for PCB determination can be developed using this approach.

EXPERIMENTAL

The p, p'- and o, p'-derivatives of DDD, DDE, and DDT were obtained from the EPA Primate Research Branch, Perrine, Florida.

PCB isomers studied have included biphenyl; 2- and 4-chlorobiphenyl; 4, 4'-dichlorobiphenyl; 2, 5, 2', 5'-tetrachlorobiphenyl; 2, 4, 5, 2', 5'-pentachlorobiphenyl; and 2, 4, 5, 2', 4', 5'-hexachlorobiphenyl. With the exception of biphenyl (Aldrich Chemical Co.) samples were obtained from Drs. R. G. Webb and O. Hutzinger. All of these compounds have been identified in commercial PCB mixtures (7-9).

Samples of Aroclor 1221, 1242, 1248, 1254, and 1260 were provided by Drs. R. G. Webb and E. S. Tucker.

Methylcyclohexane, hexane, and heptane were Matheson, Coleman, and Bell Spectroquality grade solvents. Methylcyclohexane (MCH) forms a clear, rigid glass upon cooling slowly (about two minutes) to 77° K. Under similar conditions, the n-alkane matrices produce highly scattering "snows" and are therefore less suitable for quantitative studies.

Luminescence measurements were performed using a Baird-Atomic SF-100 (or SF-1) Fluorispec fluorescence spectrophotometer.

RESULTS

In general, halogenation results in diminished fluorescence yields and enhanced phosphorescence yields, probably a result of enhanced intersystem-crossing rates (10, 11). Room temperature luminescence measurement is less useful for these compounds since phosphorescence emission is quenched. At low temperature, phosphorescence appears, and spectra are often more highly structured. All spectra appearing in this paper were obtained at 77° K, and have not been corrected for instrumental response.

PCB Isomers

Emission spectra of biphenyl, 4-chlorobiphenyl, and 4,4'-dichlorobiphenyl were found to be considerably sharper in heptane than in methylcyclohexane(MCH). Spectra of the 4,4' isomer in these two solvents appear in Figures 1 and 2. (Spectra obtained using hexane were very slightly broader than in heptane.) The sharper vibronic structure revealed in the n-alkane matrices is an example of quasilinear spectra, often called the "Shpolskii" effect (12). Usually, quasilinear spectra are obtained in n-alkane matrices whose molecules have dimensions similar to that of the guest (solute) molecule, and spectral bandwidths become increasingly narrow as the temperature is reduced. This phenomenon is extremely useful for identification purposes, since narrowing results in enhanced specificity and sensitivity.

In contrast, spectra of 2-chlorobiphenyl and the more highly chlorinated isomers display rather diffuse emission both in MCH and in heptane. Spectra of 2, 5, 2', 5'-tetrachlorobiphenyl in these solvents appear in Figures 3 and 4. Since the same isomer was found to exhibit similar diffuse emission in octane and nonane matrices as well, the emission of this isomer may be intrinsically diffuse.

PCB Mixtures (Aroclors)

Absorption commences in the 290-300 nm region for the Aroclors studied, with phosphorescence maxima in the region 440-480 nm. The spectrum of Aroclor 1254 in MCH at 77° is fairly typical, and is shown in Figure 5.

Solvent effects noted above for PCB isomers are reflected in the spectra of Aroclors. For example, the emission spectrum of Aroclor 1221 in heptane at 77° K revealed considerable fine structure which did not appear in MCH. Comparison with isomer spectra (in heptane) identified biphenyl and 4-chlorobiphenyl as principal constituents of this Aroclor (1221). In contrast, the emission spectra obtained for Aroclor 1248 were diffuse both in MCH and in heptane, paralleling the result obtained for 2, 5, 2', 5'-tetrachlorobiphenyl (Figures 3 and 4). It seems likely that spectra of Aroclors having even greater chlorine content will also remain diffuse in heptane so that for these compounds MCH would be an equally suitable matrix. Heptane, however, should prove useful in helping to identify Aroclors having relatively low chlorine content (e.g., 1221 and 1232).

Although emission spectra of the more highly chlorinated PCB isomers are diffuse, the excitation spectra are usually more highly structured as compared with compounds of low chlorine content. Spectral characteristics of emission and excitation thus enable those Aroclors studied to be distinguished.

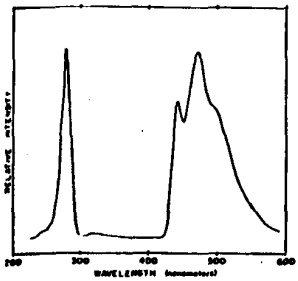

Figure 1. Excitation/emission of 4, 4'-dichlorobiphenyl in MCH glass (100 ppm) at 77° K

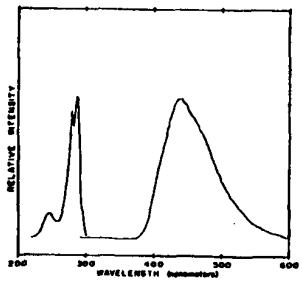

Figure 3. Excitation/emission of 2, 5, 2', 5'-tetrachlorobiphenyl in MCH glass (100 ppm) at 77° K

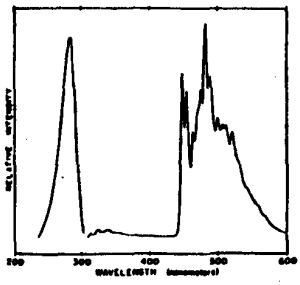

Figure 2. Excitation/emission of 4, 4'-dichlorobiphenyl in heptane (100 ppm) at 77° K

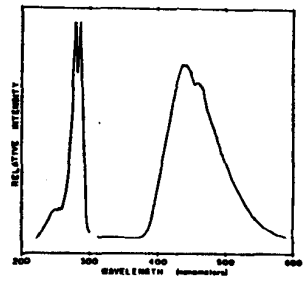

Figure 4. Excitation/emission of 2, 5, 2', 5'-tetrachlorobiphenyl in heptane (100 ppm) at 77° K

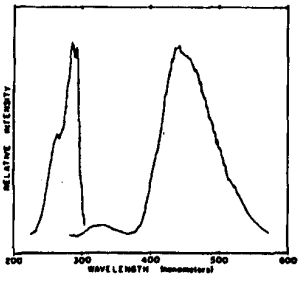

Figure 5. Excitation/emission of Aroclor 1254 in MCH glass (approx. 5 ppm) at 77° K

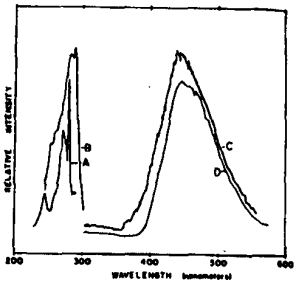

Figure 7. Mixture of 50 ppm p, p'-DDT and 50 ppm Aroclor 1254 in MCH at 77° K. Curves A and B: Excitation spectra monitored at 380 and 445 nm. Curves C and D: Emission spectra excited at 240 and 290 nm

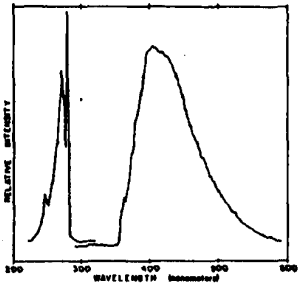

Figure 6. Excitation/emission of p, p'-DDT in MCH glass (100 ppm) at 77° K

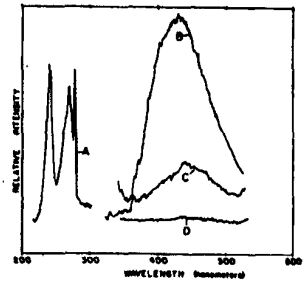

Figure 8. Mixture of 5 ppm p, p'-DDT and .05 ppm Aroclor 1254 in MCH at 77° K. Curve A: Excitation spectrum monitored at 380 nm. Curves B and C: Emission spectra excited at 275 and 295 nm. Curve D: Emission of solvent excited at 295 nm

Pesticides

Emission observed from DDE was found to be at least 100 times weaker than the phosphorescence of comparable concentrations of DDD or DDT, suggesting that the weak emission which we observe may in fact be due to an impurity. Our results are not in agreement with those reported by Moye and Winefordner (13).

Spectra of the four DDD and DDT compounds are very similar. As an example, the spectrum of p, p'-DDT in MCH is shown in Figure 6. Phosphorescence origins are in the region 355-365 nm. The band systems are slightly structured to the short wavelength side of the maximum but become stronger and more diffuse at longer wavelengths. Phosphorescence intensities are about ten times weaker than for Aroclors.

The excitation spectra characteristically show prominent narrow (3-4 nm half-widths) in MCH at 275-278 nm. Our results are in reasonable agreement with those of Moye and Winefordner (13), and the excitation spectra resemble the absorption spectrum of the parent hydrocarbon, diphenyl methane, as given by Berlman (14). Spectra of p, p'-DDT in heptane revealed no additional sharpening, in contrast to some of the PCB isomers discussed previously.

Analysis of Mixtures: Aroclor 1254 and p, p'-DDT

Several mixtures of the above materials were studied at various relative concentrations of the components in order to assess the potential of the low temperature method. Excitation/emission spectra of a mixture consisting of 50 ppm p, p'-DDT and 50 ppm Aroclor 1254 appear in Figure 7. Since DDT has relatively little absorption at wavelengths longer than 280 nm, excitation of the mixture at 290 nm excites the Aroclor phosphorescence with virtually no interference from DDT. In addition, by monitoring the 380 nm emission, where the Aroclor has practically no emission intensity, the excitation spectrum of DDT is obtained with little interference from Aroclor. Figure 8 shows spectra obtained for a mixture consisting of 5 ppm p, p'-DDT and 0.05 ppm Aroclor 1254. Selective excitation of the Aroclor phosphorescence permits the Aroclor to be identified in the presence of 100 X greater concentrations of DDT.

Continued studies are in progress to establish analytical curves and detection limits for the components, requiring a better understanding of possible energy-transfer processes. (In those mixtures studied, no evidence of significant energy transfer was observed.)

Detection Sensitivities

In our work, interference from emitting solvent (MCH) impurities limited detection sensitivities to approximately 1 ppm for DDT and DDD and approximately 0.01 ppm for Aroclors. With suitable solvent purification, these sensitivities should be improved by two orders of magnitude and work in this direction is in progress.

The very low emission yield of the DDE compounds makes these difficult to determine with sensitivity; however, DDE should produce little interference with PCB determination.

SUMMARY

Low temperature luminescence offers a simple, sensitive method for determination of DDT-type compounds, PCB's and for DDT/PCB mixtures. As such, it should constitute a useful independent analytical approach, and might also be employed as an adjunct to other methods such as gas chromatography. For example, this technique should in principle be applicable

to the analysis of polychlorinated terphenyls (PCT's) present in certain PCB preparations. At column temperatures convenient for gas chromatographic analysis of PCB's, the PCT's have much longer retention times, resulting in either very broad peaks or secondary interference (3). Chlorinated terphenyls are expected to luminesce at low temperature, and have emission displaced to longer wavelengths from that of the biphenyls. Low temperature luminescence involving the selective excitation of PCT's in the presence of PCB's might thus avoid complications which arise in gas chromatography.

ACKNOWLEDGEMENTS

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