An innovative way of obtaining room-temperature phosphorescence signals in solution

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Abstract

This manuscript presents an innovative way of obtaining room temperature phosphorescence (RTP) in solution. For the first time, the RTP of naphthalene derivatives have been observed in solution without using any kind of organized media. The RTP signals are a consequence of intermolecular protection when analytes are exclusively in the presence of a heavy atom salt and sodium sulfite is employed as an oxygen scavenger to minimize RTP quenching. A rigorous study of numerous experimental and instrumental variables has been carried out. © 1998 Elsevier Science B.V.

1. Introduction

Until recently, all the methodologies proposed to obtain room temperature phosphorescence (RTP) signals in fluid solution have involved the use of some kind of organized medium. Apart from sensitized RTP [1], RTP in fluid solution has been observed only under special conditions, such as in highly pure solutions [2], or for a very small number of compounds such as biacetyl, which is a well-known example [3]. The rest of the proposed methodologies involve the use of some kind of organized medium such as micelles [4–10], microemulsions [11–13] or cyclodextrins [14–22], combined with thallium, silver or bromoalcohols as external ‘heavy atoms’, and N₂ or sulfite as oxygen scavenger. The use of sodium sulfite for deoxygenation instead of passing nitrogen through the solution as before, was introduced by Sanz-Medel research group [7] and has permitted the determination of different ions such as niobium [8] and aluminium [9], also giving satisfactory results when implemented in flow injection analysis (FIA) systems [10].

We have recently observed, for some kinds of compounds that it is possible to obtain phosphorescence signals in solution by using exclusively aqueous solutions of the analytes in the presence of a heavy atom and sodium sulfite as oxygen scavenger. This has been named as heavy atom induced RTP (HAI-RTP). In the present work, this innovative way of obtaining RTP signals in solution has been demonstrated with three naphthalene derivatives, a pharmaceutical compound (naphazoline, NPZ), a plant growth regulator (naphthoxyacetic acid, NOA) and a polycyclic aromatic hydrocarbon (acenaphthene, Ace). Until now, no phosphorimetric method for naphazoline has been described in the literature, and there are only a few...
for naphthoxyacetic acid [21,23] and acenaphthene [11,20,22] in solution. All need a special kind of organized medium, which make them more complicated and expensive while the methods proposed in the present paper represent an interesting alternative because of their simplicity, low cost and speed.

2. Experimental

2.1. Instrumentation

All recordings of uncorrected luminescence spectra and measurements of HAI-RTP intensities were carried out with an Aminco Bowman series 2 luminescence spectrometer equipped with a 7 W pulsed xenon lamp, and a thermostated cell holder. The system was controlled with a personal computer with 40 MB hard disk, 4 MB RAM memory, 3.5-inch 1.44 MB floppy disk drive, VGA color monitor with VGA graphics adapter card, serial 2-button mouse, DOS 6.0, OS/2 version 2.0, and a GPIB (IEEE-488) interface card for computer instrument communication. An ultrasonic bath ULTRASONS (Selecta) was used for sample sonication.

2.2. Reagents

Reagent grade thallium(I) nitrate, potassium iodide, potassium bromide, potassium chloride, sodium iodide, sodium bromide, sodium chloride and anhydrous sodium sulfite (Sigma) were used as received. Aqueous solutions were made with doubly distilled water. The sodium sulfite solutions were prepared daily and kept in tightly stoppered containers.

NPZ, NOA and Ace (Sigma) were used without further purification; $3.66 \times 10^{-4} \text{ M}$ and $4.95 \times 10^{-4} \text{ M}$ stock solutions of naphazoline and NOA, respectively, were prepared in water. A $6.48 \times 10^{-5} \text{ M}$ stock solution of Ace was prepared in cyclohexane.

2.3. Method

A 100 \( \mu \text{l} \) aliquot of NPZ stock solution with 5 ml of 2 M potassium iodide and 1 ml of 0.1 M sodium sulfite or a 100 \( \mu \text{l} \) aliquot of NOA stock solution with 5.00 ml of 0.5 M thallium nitrate and 1 ml of sodium sulfite or a 1 ml aliquot of Ace stock solution with 1 ml of 0.5 M thallium nitrate and 1 ml of sodium sulfite, was introduced into a 10 ml calibrated flask and made up to

Fig. 1. Excitation and emission spectra of NPZ (-----), NOA (---) and Ace (- - -). (-----) [NPZ]=4.95 \times 10^{-6} \text{ M}, [KI]=1 \text{ M} and [Na$_2$SO$_3$]=1 \times 10^{-2} \text{ M}. (---) [NOA]=7.32 \times 10^{-6} \text{ M}, [TlNO$_3$]=0.25 \text{ M} and [Na$_2$SO$_3$]=1 \times 10^{-2} \text{ M}. (- - -) [Ace]=1.30 \times 10^{-5} \text{ M}, [TlNO$_3$]=0.05 \text{ M} and [Na$_2$SO$_3$]=1 \times 10^{-2} \text{ M}. $t_{ex}$ 200/200 \( \mu \text{s} \), slits 16/16 nm, detector voltage=1100 V.
volume with water. Standard 10 mm fused silica cells were filled with these analyte solutions.

The intensities of the samples (see Fig. 1) and the corresponding blanks were measured at phosphorescence wavelength maxima $\lambda_{ex}/\lambda_{em}$ 288/488 nm for NPZ, 336/500 nm for NOA and 290/500 nm for Ace (fluorescence wavelength maxima of the three compounds are 294/323 nm for Ace, 290/350 nm for NPZ and 326/346 nm for NOA). The half life time of the phosphorescence emission in the experimental conditions were 417 ms for Ace, 632 ms for NPZ and 307 ms for NOA. The gate time ($t_g$) and delay time ($t_d$) were kept constant at 200 ms for the three compounds.

Excitation and emission slits of 16 nm were used throughout.

3. Results and discussion

3.1. Influence of heavy atom

The influence of heavy atom salts (KI, NaI, KBr, NaBr, KCl, TlNO$_3$, Pb(NO$_3$)$_2$ and AgNO$_3$) concentration on the HAI-RTP of NPZ, NOA and Ace were studied. Pb(NO$_3$)$_2$ and AgNO$_3$ precipitated in the presence of SO$_3$$^-$$^2$ so they cannot be used, while with KCl no phosphorescent signals were observed.

The study of the rest of the heavy atom salts is represented in Fig. 2. In all cases, it has been proved that non-phosphorescence responses of the analytes are obtained in the total absence of a heavy atom while, in general, the HAI-RTP intensity increased with increasing heavy atom concentration. Concentrations of 1 M for KI and 0.25 and 0.05 M for TlNO$_3$ were found as optima for the three compounds, NPZ, NOA and Ace, respectively, because maximum intensities are obtained, and were selected for the rest of the experimental work.

3.2. Influence of sodium sulfite concentration

The influence of sodium sulfite concentration has been performed by monitoring the RTP signal as a function of time until the HAI-RTP signal was stable for at least 5 min. Various amounts of sodium sulfite were added to a solution with a fixed amount of NPZ, NOA or Ace and heavy atom salt while the concentration of sodium sulfite was varied from $1.0 \times 10^{-3}$ to $2.0 \times 10^{-2}$ M. The concentrations of NPZ, NOA and Ace were $4.95 \times 10^{-6}$ M, $7.32 \times 10^{-6}$ M and $1.30 \times 10^{-5}$ M, respectively, and the concentrations of KI, TlNO$_3$, and again TlNO$_3$ were 1, 0.25 and 0.05 M, respectively. They were transferred into a 10 ml flask, with the appropriate amounts of 0.1 M sodium sulfite stock solution to obtain the final desired concentration. The development of the HAI-RTP emission was followed kinetically by monitoring at 488, 500 and 490 nm for NPZ, NOA and Ace, respectively.

Fig. 3(a) shows the influence of sodium sulfite concentration on the RTP emission from naphazoline in the presence of KI and Fig. 3(b) for NOA with TlNO$_3$. It has been observed in both cases that the Na$_2$SO$_3$ concentration does not influence the intensity of phosphorescence. However, it influences the time of appearance of the emission in such a manner that by increasing sodium sulfite concentration, phosphorescence signals are more rapidly obtained due to more effective deoxygenation. A 0.01 M sodium sulfite concentration was selected as optimum. The behaviour of Ace–TlNO$_3$ is very similar to that obtained for NOA–TlNO$_3$, so its presentation has been omitted.

3.3. Effect of temperature on HAI-RTP intensities

For obtaining the HAI-RTP signals of the three phosphors, a detailed study of temperature was carried out. The HAI-RTP intensities decrease almost linearly with an increase in temperature. This effect is more marked for the NPZ–KI system than the NOA–TlNO$_3$ or Ace–TlNO$_3$ systems and is mainly due to molecular motion and intermolecular energy conversion because of the collisional deactivation of the phosphors. A temperature of 25°C was selected for the rest of the experimental work.

3.4. Analytical figures of merit

Calibration graphs were constructed for standards of the three compounds containing 0–1.00 $\mu$g ml$^{-1}$ of NPZ, 0–2.00 $\mu$g ml$^{-1}$ for NOA and 0–2.00 $\mu$g ml$^{-1}$ for Ace, with the regression equations of $\log P=0.100+1.64 \log C$, $\log P=0.074+0.49 \log C$ and $\log P=0.059+0.52 \log C$, respectively, where $P$ is the relative phosphorescence intensity and $C$ is the concentration in $\mu$g ml$^{-1}$. The more important analy-
Fig. 2. Influence of different heavy atoms on the HAI-RTP of NPZ (a), NOA (b) and Ace (c). (a) [NPZ] = 4.95 \times 10^{-6} \text{ M} and [Na}_2\text{SO}_3 = 1 \times 10^{-2} \text{ M}. (b) [NOA] = 7.32 \times 10^{-6} \text{ M} and [Na}_2\text{SO}_3 = 1 \times 10^{-2} \text{ M}. (c) [Ace] = 1.30 \times 10^{-5} \text{ M} and [Na}_2\text{SO}_3 = 1 \times 10^{-2} \text{ M}. \lambda_{ex}/\lambda_{em} 288/488 \text{ nm for NPZ, 336/500 nm for NOA and 290/500 nm for Ace, } t_{ag} 200/200 \mu \text{s, slits 16/16 nm, detector voltage } = 1100 \text{ V.}
Fig. 3. Influence of Na$_2$SO$_3$ concentration on the HAI-RTP of NPZ (a) and NOA (b). (a) [NPZ] = 4.95 x 10$^{-6}$ M and [KI] = 1 M. (b) [NOA] = 7.32 x 10$^{-6}$ M and [TINO$_3$] = 0.25 M. $\lambda_{ex}/\lambda_{em}$ 288/488 nm for NPZ and 336/500 nm for NOA, $t_{delay}$ 200/200 $\mu$s, slits 16/16 nm, detector voltage = 1100 V.
tical parameters [24] for the different compounds are summarized in Table 1.

The repeatability of the proposed method was determined. The precision was assessed for 0.50 µg ml⁻¹ NPZ, 1.00 µg ml⁻¹ NOA and 1 µg ml⁻¹ Ace from seven independent determinations. The relative standard deviations were 2.41, 3.78 and 1.83% respectively.

4. Conclusions

This paper present an innovative way of obtaining RTP from various phosphors in solution, without using any kind of organized media. This important finding opens possibilities of RTP measurements in solution in the future and provides simple and useful conditions for obtaining some very attractive analytical characteristics.

References