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Determination of Palladium(II) with Coproporphyrin III by Using Zephiramine-Perchlorate Ion-Pair Scum as a New Medium for Room Temperature Phosphorescence

Kazutoshi ENDO, Shukuro IGARASHI, and Takao YOTSUYANAGI*
Department of Applied Chemistry, Faculty of Engineering,
Tohoku University, Aoba, Aramaki, Sendai 980

Palladium(II) complex of coproporphyrin III was adsorbed on zephiramine-perchlorate ion-pair scum, on which the complex emitted room temperature phosphorescence (RTP). The peak to peak height calibration curve of the first-derivative of the RTP spectra was linear over the concentration range of 10^{-7} mol dm^{-3} to 10^{-8} mol dm^{-3} of Pd(II).

Several methods have been used to "immobilize" triplet molecules in a rigid medium in order to reduce radiationless deactivation and to measure the phosphorescence. Low temperature rigid matrices have been most popular, however, need of refrigerant such as liquid nitrogen makes them inconvenient. If this inconvenience could be removed, phosphorimetry will become one of the most useful and versatile methods for trace analysis. Schulman and Walling observed RTP of some organic compounds spotted and fixed on filter paper, silica gel, and alumina.$^{1)}$ Other examples of media for RTP measurements were crystals of inorganic or organic salts, polymer-salt mixtures,$^{2)}$ lauryl sulfate micelles,$^{3)}$ sensitizer solutions,$^{4)}$ etc.$^{5,6)}$

Mechanism of immobilizing molecules on solid supports for RTP has scarcely been understood; a hydrogen bonding may stabilize a triplet molecule.$^{7)}$ Desirable properties for RTP media are empirically known as, 1) the inside hydrophobic field for liquid RTP media and 2) surface functional groups such as hydroxyl groups and carboxyl groups for the solid supports.$^{8)}$ Heavy atoms are important for RTP media suitable for nonpolar aromatic compounds.

On the course of systematic survay of RTP media, we found a new RTP medium of zephiramine-perchlorate ion-pair scum. When large hydrophobic counter anions, such as iodide and perchlorate ions, were added to quarternary ammonium salt solutions, the solutions became turbid. Then, the scum was formed and was adsorbed at the air-liquid interface by shaking it. Palladium(II) coproporphyrin III (Copro III) complex, which had the strongest phosphorescence intensity among the metal-Copro III complexs, was quantitatively concentrated on the scum, when carbon numbers of the n-alkyl chain of quarternary ammonium ion were more than 14 for benzyldimethyl-n-alkyl type quarternary ammonium salt, 12 for trimethyl-n-alkyl type, and 5 for tetra-n-alkyl type. When the carbon number of the n-alkyl chain was less than those described above, the scum did not formed because of their too large hydrophilicity. The scums as RTP media have the advantages as follows: 1) concentration of phosphors by adsorption on the course of formation, 2) moisture insensitive compared with the other conventional solid supports. Zephiramine was chosen as a quarternary ammonium salt from the view point of the favorable balance of hydrophobicity and hydrophilicity. Based on these findings, RTP determination of 10^{-8} mol dm^{-3} level of Pd(II) with Copro III was developed.

Luminescence measurements were made with a Hitachi 850 fluorescence spectrophotometer equipped with a phosphoroscope attachment and powder sample holder, with an excitation light source of a 150 W xenon arc lamp, and an R-928F photomultiplier detector tube. The reagent, Copro III, was obtained as sodium salt by hydrolysis of coproporphyrin III tetramethylester (Nihon Sekiyu Co. Ltd.) in 1 mol dm^{-3} NaOH solution. The standard Pd(II) solution (1.0×10^{-2} mol dm^{-3}) was prepared by dissolving $PdCl_2$ (Wako Pure Chemical Co. Ltd.) in hydrochloric acid. Zephiramine (Dojindo Laboratory Co. Ltd.) was used as obtained. All of other reagents used were of guranteed reagent grade.

Recommended Procedure: A 20 cm^3 of sample solution containing not more than 3.2 µg of Pd(II) is taken into 50 cm^3 Erlenmeyer flask. One cm^3 of 1 mol dm^{-3} acetate buffer solution (pH = 5.0), 0.5 cm^3 of 10^{-4} mol dm^{-3} Copro III solution and 0.5 cm^3 of 10^{-2} mol dm^{-3} L-ascorbic acid solution are added. The solution is boiled for 2 min and allowed to cool to room temperature. After the solution is transferred to a 25 cm^3 volumetric flask, 2.5 cm^3 of 0.1 mol dm^{-3} zephiramine solution (pH = 5.0) is added and diluted to the mark with water. The solution is transferred to 30 cm^3 cylindrical glass vial fitted with plastic cap. One cm^3 of 5 mol dm^{-3} $NaClO_4$ solution is added and the mixture is shaken for 1 min. The scum is filtrated and dried for 60 min at 60 °C. After cooling to room temperature in a silica gel desiccator, the scum is packed in a powder sample holder and the first-derivative curve of RTP spectrum is measured at 20°C (excitation wavelength is 395 nm).

Fluorescence spectrum of Copro III and RTP spectrum of Pd(II)-Copro III complex on the scum are shown in Fig.1. And the first-derivative spectra are shown in Fig.2. The peak to peak height difference between the signal intensity of the first-derivative spectra for Pd(II)-Copro III complex at 660 nm and 674 nm, was used for the determination. The signal intensity of the complex were corrected for reagent blank(Copro III), so as to eliminate the effect of reagent fluorescence.[9] Because the measurements with a chopper could not be applied to the solid supports system due to the mechanical restriction of the apparatus.

According to the recommended procedure, Pd(II)-Copro III complex was quantitatively formed within 1 min. L-ascorbic acid was essential for rapid complexation. When the perchlorate ion more than equivalent amounts to zephiramine was added, the scum was formed and the complex was quantitatively adsorbed on it at pH = 5.0. The yield of the adsorption was confirmed from the absorbance of the filtrate. The RTP intensity increased with increase in the concentration of perchlorate ion. And the appearance of the scum changed from

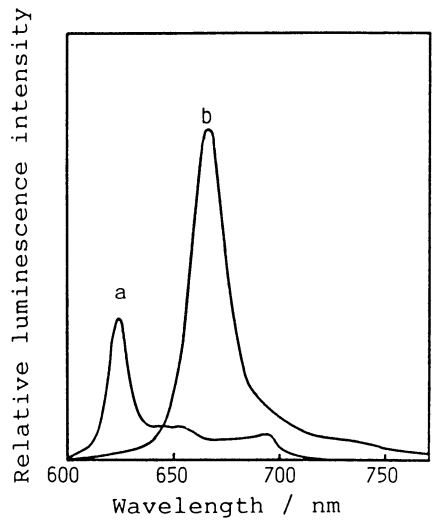

Fig. 1. Emission spectra of Pd-Copro III and Copro III.
a : Fluorescence of Copro III, λex = 402 nm
b : RTP of Pd-Copro III, λex = 395 nm
[Pd-Copro III] = 2×10^{-6} mol dm^{-3}
[Copro III] = 2×10^{-6} mol dm^{-3}

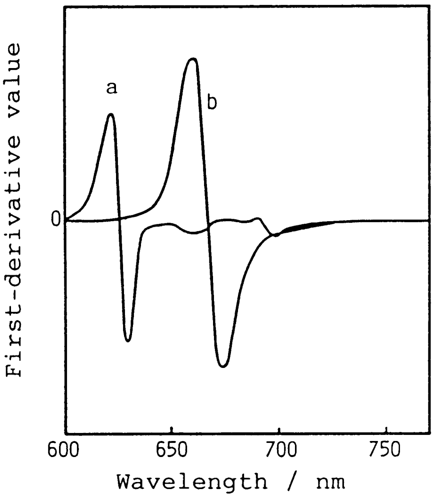

Fig. 2. The first-derivative spectra of Pd-Copro III and Copro III.
a : Fluorescence of Copro III, λex = 402 nm
b : RTP of Pd-Copro III, λex = 395 nm
[Pd-Copro III] = 2×10^{-6} mol dm^{-3}
[Copro III] = 2×10^{-6} mol dm^{-3}

foam like structure to cotton wool like one. Thus, the increase in RTP intensity should be attributable to the change in the form of the scum. The intensity was also affected by pH condition of the solution, as shown in Fig.4. At pH region of 4.0 to 5.5, RTP intensity was constant. Above pH 6.5, Pd(II)-Copro III complex was not adsorbed and remained in the solution. Such pH dependence can be ascribed to the acid dissociation of peripheral propionic acid groups of Copro III.

The constant RTP intensity was obtained by drying it at 60°C for 30 min or more. The scum was a moisture insensitive RTP support compared with the conventional solid ones. For example, even just after the filtration, Pd(II)-Copro III complex on the moisted scum exhibited RTP, its intensity being 85 % of that on the dried one.

A linear calibration curve was obtained between the concentration range of 10^{-7} mol dm^{-3} to 10^{-8} mol dm^{-3} of Pd(II) for a peak to peak height of the first-derivative curve of the RTP spectra. The relative standard deviations were 5.5% for 1×10^{-6} mol dm^{-3} Pd(II) (8 determinations) in the 20 cm^3 sample solution.

A new RTP medium such as an ion-pair scum of the quarternary ammonium salt may be applied to various kinds of materials. This finding will be expected to contribute to the extension of the phosphorimetry.

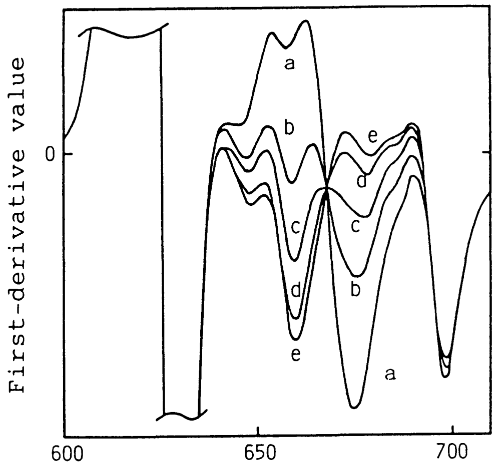

Fig. 3. The first-derivative spectra of Pd-Copro III system.
[Pd(II)] in the 20 cm^3 of sample solution:
a = 2.5 x 10^{-7} mol dm^{-3}
b = 1.25 x 10^{-7} mol dm^{-3}
c = 7.5 x 10^{-8} mol dm^{-3}
d = 2.5 x 10^{-8} mol dm^{-3}
e = 0 mol dm^{-3}

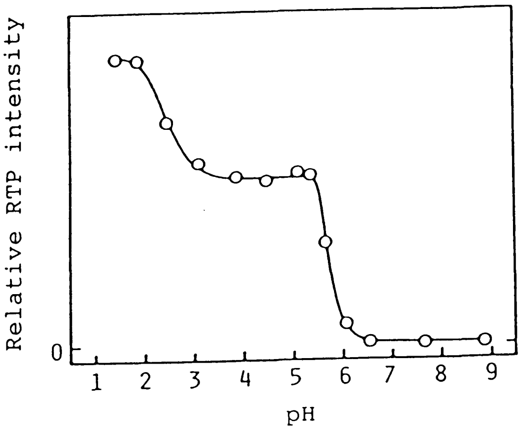

Fig. 4. Effect of pH on RTP intensity of Pd-Copro III system.
[Zephiramine] = 0.01 mol dm^{-3}
[$NaClO_4$] = 0.2 mol dm^{-3}
[Copro III]$_T$= 2 x 10^{-6} mol dm^{-3}
[Pd(II)] = 8 x 10^{-7} mol dm^{-3}

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