[Chem. Pharm. Bull. 21(12)2613—2616(1973)]

UDC 546.221.04.08 : 547.286' 546.98.04

Studies on the Sulfur-containing Chelating Agents. XXXVI.[1] Reaction of Palladium Monothioacetylacetonate with Sulfide Ion and Its Application for Determination of Sulfide Ion

SHOSUKE KAWANISHI, NAOKO HONGO, AKIRA YOKOYAMA and HISASHI TANAKA

Faculty of Pharmaceutical Sciences, Kyoto University[2]

(Received December 22, 1972)

Palladium monothioacetylacetonate ($Pd(SAA)_2$) was found to be converted into palladium dithioacetylacetonate ($Pd(SSAA)_2$) in the presence of sodium sulfide. It was indicated that this reaction follows first order kinetics with respect to the concentrations of $Pd(SAA)_2$ and sodium sulfide, respectively and on the whole, second order kinetics. A new spectrophotometric method of determination of sulfide ion, which is applicable in the range from 8 μg to 240 μg of sulfide ion, was devised by the measurement of the absorbance of $Pd(SSAA)_2$ formed (510 mμ).

In the previous paper,[3] we reported that palladium dithioacetylacetonate (abbreviated as $Pd(SSAA)_2$ hereafter) is obtained together with palladium monothioacetylacetonate (abbreviated as $Pd(SAA)_2$ hereafter) in the reaction of palladium ion with excess of monothioacetylacetone (abbreviated as SAA hereafter) in acidic solution. In the course of the investigations on the mechanism of this reaction, it was found that $Pd(SAA)_2$ is also converted into $Pd(SSAA)_2$ in the presence of sodium sulfide instead of SAA in acidic solution, whereas $Pd(SAA)_2$ is stable in-acidic solution in the absence of sodium sulfide. We prompted to study this reaction in detail by the novelty of this reaction which may be called as "ligand atom replacement reaction". We investigated, in the first place, the effect of pH to the formation of $Pd(SSAA)_2$ and the kinetics of this reaction through the spectral change, and in the second place, the possibility of the application of this reaction for the determination of sulfide ion.

The formation of $Pd(SSAA)_2$ occurred most readily in the pH range from 5 to 6. The formation of $Pd(SSAA)_2$ was detected by the increase of the absorbance at 510 mμ (λ_{max} for $Pd(SSAA)_2$) and the decrease of that at 400 mμ (λ_{max} for $Pd(SAA)_2$).[3] As shown in Fig. 1, in the pH range from 2 to 5, the increase of the absorbance at 400 mμ and the decrease of that at 510 mμ was observed in accord with the increase of pH with isosbestic points at 292, 362, and 450 mμ, and the color change from yellow to red was clearly observed. In the region higher than pH 5, the absorption spectra did not show the isosbestic point at 292 mμ and at pH 9 an absorption maximum was observed at 350 mμ. The spectral change is probably due to the formation of water soluble thio-complex of palladium.

On the basis of the results mentioned above, kinetic study was carried out with the solution containing $Pd(SAA)_2$ and sodium sulfide with various ratios in the region of pH 4—5 at various temperatures, by the measurement of the absorbance at 510 mμ at regular time intervals. The spectral change with the formation of Pd(SAA)(SSAA) which is presumed to be an intermediate was not recognized in the reaction of $Pd(SAA)_2$ with sulfide ion. Pd(SAA) (SSAA) is considered to be converted into $Pd(SSAA)_2$ immediately, and the easiness of this conversion is reasonably explained by *trans* effect. Accordingly, it may be reasonable to presume the steady state with respect to Pd(SAA)(SSAA) and hence equation 1 is obtained.

$$\frac{1}{b-2a}\ln\frac{a(b-2x)}{b(a-x)}=kt \qquad (1)$$

---

[1] Part XXXV: A. Yokoyama, M. Chikuma and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), 20, 2000 (1972).

[2] Location: *Yoshida, Shimoadachi-cho, Sakyo-ku, Kyoto.*

[3] S. Kawanishi, A. Yokoyama and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), 20, 262 (1972).

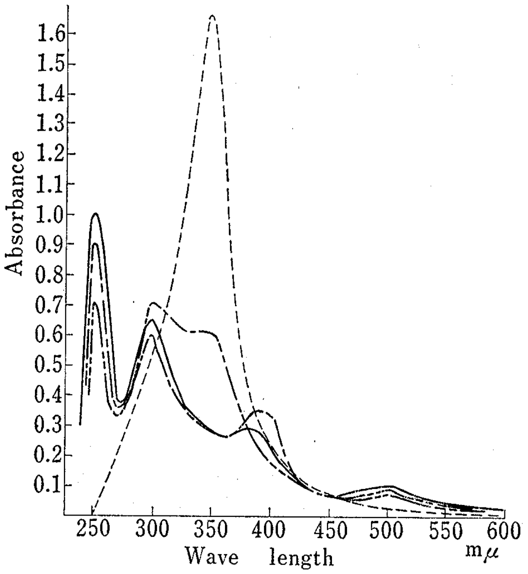

Fig. 1. Change in Electronic Spectra with pH in the Reaction of $Pd(SAA)_2$ with Sulfide Ion

buffer		4 ml
dioxane		4 ml
$Pd(SAA)_2$	5×10^{-4}M	1 ml
Na_2S	5×10^{-3}M	1 ml

pH

———: 2.17 —·—·—: 4.96

—··—··: 6.18 ———: 8.72

1 hour after reaction at room temperature

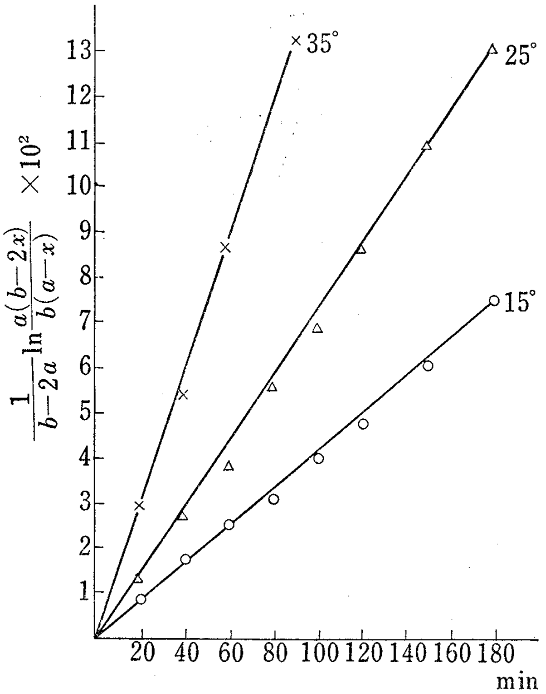

Fig. 2. Rates of Reaction of $Pd(SAA)_2$ with Sulfide Ion

a : the initial concentration of $Pd(SAA)_2$

b : the initial concentration of sodium sulfide

X: the concentration of $Pd(SSAA)_2$

$Pd(SAA)_2$	2×10^{-3}M	1 ml
buffer	pH 4.09	3 ml
dioxane		5 ml
Na_2S	10^{-3}M	1 ml

where a and b represent the initial concentration of $Pd(SAA)_2$ and sodium sulfide respectively and x represents the concentration of $Pd(SSAA)_2$ at certain time t. The results are shown in Fig. 2. The second order rate constants (k) were calculated to be 6.5×10^{-2} l. mole^{-1} sec^{-1} at 15°, 1.2×10^{-1} l. mole^{-1} sec^{-1} at 25° and 2.4×10^{-1} l. mole^{-1} sec^{-1} at 35° respectively, from the slopes of the straight lines in Fig. 2. This result indicates that this reaction is first order with respect to the concentrations of $Pd(SAA)_2$ and sodium sulfide respectively and on the whole, second order. As the mechanism of this reaction, a bimolecular mechanism is reasonable for the progress of this square planar replacement. The occurrence of this replacement is made possible by an expansion of the coordination number for an entering ligand, namely sulfide ion. Thus, it may be reasonable to presume a five-coordinated complex as a transitional state. This presumption may be reasonable, being referred the fact that strong π-bonding ligands are generally found in five-coordinated low-spin d^8 complex.[4] The reaction mechanism is shown in Chart 1.

Oxidation of sulfide ion to sulfur is greatly influenced by the reaction medium. When the concentration of sulfide ion is 5×10^{-3}M, about 13% of sulfide ion was oxidized in 1 hr in distilled water, whereas in the solution containing dioxane and buffer solution of pH 4.07 in the ratio of 1 to 1, the oxidation ratio of sulfide ion was about 83% and almost quantitative in 90 min and in 2 hr respectively. Being considered these facts, as the reactant other than sulfide ion in the formation of $Pd(SSAA)_2$, some species which is formed by the oxidation of sulfide ion may be taken into account. Further, an equilibrium between sulfide ion and some oxidation product of sulfide ion may also be considered. However, polysulfide ion which is

---

4) F. Basolo and R.G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sonc, Inc. New York, 1967, p. 375.

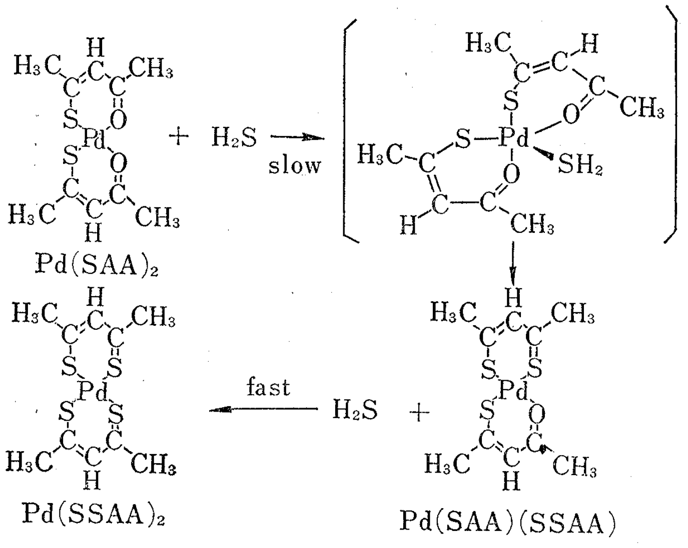

Chart 1

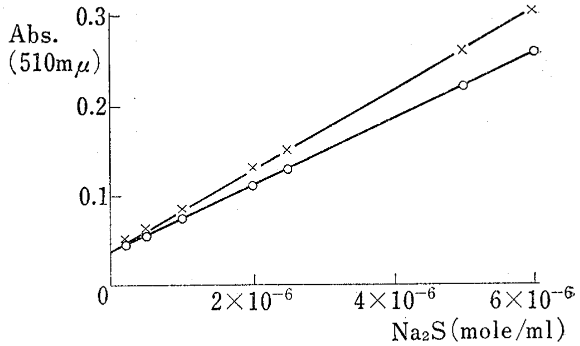

Fig. 3. Calibration Curves for the Determination of Sulfide Ion

×: 120 min after reaction
○: 90 min after reaction

readily produced with the oxidation of sulfide ion is unstable in acidic medium to form very stable elemental sulfur. On the other hand, it has been reported[5] that the oxidation ratio of 0.0001 M sulfide ion in EDTA solution is about 5% in 4 hr and 15% in 24 hr, respectively and after that time during 10 days, no appreciable loss of sulfide ion is observed. In this connection, an equilibrium may be considered between sulfide ion and polysulfide ion which is formed by the reaction of sulfide ion with elemental sulfur. The determination of sulfide ion by the use of the reaction with Pd(SAA)$_2$ is expected to be possible, provided that the proportion of sulfide ion which participates in the reaction in total sulfide ion present is constant, regardless of the concentration of total sulfide ion, notwithstanding the complexity of the behavior of sulfide ion in solution as mentioned above.

From the above-mentioned investigations, a possibility of the application of this reaction for the spectrophotometric determination of small amount of sulfide ion can be considered. On the basis of the results, calibration curves for the determination of sulfide ion were obtained as shown in Fig. 3, in the range from 8 μg to 240 μg of sulfide ion, by the measurement of the absorbance at 510 mμ. When the concentration of sulfide ion is more than 6×10^{-3} M, Pd(SSAA)$_2$ formed decomposes slowly and when that is less than 2×10^{-4} M, the absorbance of Pd(SSAA)$_2$ is influenced appreciably by that of Pd(SAA)$_2$ which remains unchanged. Accordingly, this method of determination is available, when the molar ratio of sulfide to Pd(SAA)$_2$ is in the range from 0.1 to 3.0, and about 10% of sulfide in total sulfide present participates in the reaction.

Various methods of the determination of sulfide ion have been known, and recently several improved spectrophotometric[6] and fluorometric[7] methods were reported. However, these methods are not satisfactorily simple in their procedures. A merit of the method presented here may be the simplicity in the procedure.

Experimental

Materials——Pd(SAA)$_2$ was prepared by the procedure described previously.[3] Standard sulfide solution was prepared by dissolving 2402 mg of reagent grade $Na_2S\cdot9H_2O$ in H_2O and the solution was diluted to 1000 ml. Concentration of sulfide was checked by the titration with 0.001 N iodine solution.

---

[5] R.E. Humphrey, W. Hinze and W.M. Jenkines IV, *Anal. Chem.*, 43, 140 (1971).
[6] S.A. Rahim and T.S. West, *Talanta*, 17, 851 (1970).
[7] *a*) J.S. Hanker, A. Gelberg and B. Witten, *Anal. Chem.*, 30, 93 (1958); *b*) H.D. Axelrod, J.H. Cory, J.E. Bonelli and J.P. Lodge, Jr., *Anal. Chem.*, 41, 1856 (1969).

Apparatus——Absorption spectra were measured on a Hitachi recording spectrophotometer model EPS-2 at room temperature. Absorbance was measured by Shimadzu spectrophotometer model QV-50. A Hitachi-Horiba pH meter model F-5 was used for the pH measurement.

Synthesis of Pd(SSAA)$_2$ from Pd(SAA)$_2$ and Na$_2$S——To a solution of Pd(SAA)$_2$[3] (20 mg in 200 ml acetone), 150 ml of acetate buffer solution of pH 4.57 and a solution of Na_2S (120 mg in 50 ml H_2O) were added. The reaction mixture was allowed to stand for 2 hr, and acetone was removed from the resulted red solution. Pd(SSAA)$_2$ (10 mg) was obtained by the extraction with CH_2Cl_2 and the evaporation and purified with dry column chromatography by the use of benzene as the solvent and recrystallized from acetone. mp 240°.

Effect of pH on the Reaction——Pd(SAA)$_2$ (5×10^{-4}M, 1 ml), dioxane (4 ml), buffer solution of various pH (4 ml) and Na_2S (5×10^{-3}M, 1 ml) were mixed, and the absorbance at 510 mμ was measured after 1 hr.

Determination of Rate Constant——To 1 ml of dioxane solution of 2×10^{-3}M Pd(SAA)$_2$ in a test tube with stopper were added 5 ml of dioxane and 3 ml of acetate buffer solution of pH 4.09. To this solution, 1 ml of solution of Na_2S (2×10^{-3}M, 1×10^{-3}M, 2×10^{-4}M) was added and the reaction mixture was kept at 15°, 25° or 35° in a thermostat. The absorbance at 510 mμ was measured at 20 min intervals.

Calibration Curve——To 1 ml of dioxane solution of 2×10^{-3}M Pd(SAA)$_2$ in a test tube with stopper, 5 ml of dioxane, 3 ml of buffer solution of pH 4.55 and 1 ml of standard sulfide solution (2×10^{-4}M, 5×10^{-4}M, 1×10^{-3}M, 2×10^{-3}M, 2.5×10^{-4}M, 5×10^{-3}M and 6×10^{-3}M) were added. The absorbance at 510 mμ was measured after 1.5 hr or 2 hr.