TRANS-EFFECT OF THIOCYANATE ION ON EXTRACTION KINETICS OF PALLADIUM WITH DIDODECYLMONOTHIO-PHOSPHORIC ACID

KAZUO KONDO, HIDEYUKI NISHIO AND FUMIYUKI NAKASHIO

Department of Organic Synthesis, Kyushu University, Fukuoka 812

Key Words: Extraction, Extraction Kinetics, Palladium Extraction, Platinum Group Metal, Interfacial Reaction Mechanism, Trans-Effect

Introduction

In a previous paper,³⁾ the extraction rate of palladium with didodecylmonothiophosphoric acid was measured. It was reported that the reaction rate constants of four chloro-palladium complexes with the extractant were obtained from analysis of experimental results by the interfacial reaction model in which the four chloro-palladium complexes take part in the extraction.

It is known that addition of soft ligand to aqueous solution enhances the extraction rate of palladium from chloride solution by the trans-effect.⁷⁾ Al-Bazi *et al.*¹⁾ studied the effect using the Kelex 100-palladium-thiocyanate system, but they only took one chemical species into consideration.

In this work, the trans-effect of thiocyanate ion on the extraction of palladium with didodecylmonothiophosphoric acid is studied, considering three kinds of chloro-thiocyno-palladium complexes which take part in the extraction reaction.

1. Experimental

The extractant, didodecylmonothiophosphoric acid (hereafter abbreviated as DDTPA or denoted by HR), was synthesized and its toluene solution was prepared according to the previous paper.³⁾ The aqueous solution was prepared by dissolving perchloric acid, lithium chloride, lithium thiocyanate and palladium chloride in deionized water. All organic and inorganic chemicals used were GR grade.

The same stirred transfer cell and the highly stirred tank as described in the previous paper³⁾ were used for measurement of the extraction rate of palladium. The experimental conditions are shown in Table 1. The interfacial area of the stirred transfer cell was 15.1 cm² and the specific interfacial area of the highly stirred tank was estimated as 2.73 × 10⁴ m⁻¹ in the same manner as in the previous paper.³⁾

2. Results and Discussion

Figure 1 shows the relation between the initial extraction rate of palladium, J_0 , and the thiocyanate-ion concentration, C_{SCNO} . J_0 increased with increase in C_{SCNO} in the low-concentration range and had a maximum value of about 2×10^{-6} mol/(m²s) at C_{SCNO} of about 2 mol/m³. After that, J_0 gradually decreased with increase in C_{SCNO} . The maximum value of J_0 was about six hundred times the extraction rate without thiocyanate ion. This result is very similar to that obtained by Al-Bazi *et al.*¹⁾

As mentioned previously,³⁾ palladium ion is known to form the complexes with chloride ion in aqueous solution. Under the experimental conditions shown in Table 1, PdCl₄²⁻ is mainly formed. When thiocyanate ion, which is a softer ligand than chloride ion, is added to PdCl₄²⁻ aqueous solution, the following ligand-exchange reaction occurs.²⁾

$$\beta_i = [\text{PdCl}_{4-i}(\text{SCN})_i^{2-i}] [\text{Cl}^-]^i / ([\text{PdCl}_4^{2-}] [\text{SCN}^-]^i) \quad (2)$$

where β_i is the stability constant of the complex ($\beta_1 = 10^{6.03}$, $\beta_2 = 10^{10.93}$, $\beta_3 = 10^{14.52}$ and $\beta_4 = 10^{17.55}$ at ionic strength of 1100 mol/m³).²⁾ Furthermore, thiocyanate ion is protonated in acidic aqueous solution, as follows.

Table 1. Experimental conditions

C_{Pd0}	=	0.5 mol/m ³
C_{HRO}	=	5 mol/m ³
C_{H0}	=	1000 mol/m ³
C_{Cl0}	=	1000 mol/m ³
C_{SCNO}	=	0.01–20 mol/m ³
Stirring speed in stirred transfer cell = 2.5 s ⁻¹ (150 r.p.m.)		
Stirring speed in highly stirred tank = 10 s ⁻¹ (600 r.p.m.)		
Temperature = 303 K		

* Received April 27, 1989. Correspondence concerning this article should be addressed to K. Kondo.

Fig. 1. Effect of thiocyanate ion concentration on initial extraction rate of palladium and distribution fraction of chloro-thiocyno-palladium complexes

$$K_{\text{SCN}} = [\text{HSCN}] / ([\text{H}^+][\text{SCN}^-]) \quad (4)$$

where K_{SCN} is the protonation constant of thiocyanate ion and has a value of $7.9 \times 10^{-3} \text{ m}^3/\text{mol}^6$ at ionic strength of zero. Using Eqs. (2) and (4), the distribution fractions of the complexes, f , were calculated as shown in Fig. 1, where f_0 to f_4 correspond respectively to the fractions of PdCl_4^{2-} , $\text{PdCl}_3(\text{SCN})^{2-}$, $\text{PdCl}_2(\text{SCN})_2^{2-}$, $\text{PdCl}(\text{SCN})_3^{2-}$ and $\text{Pd}(\text{SCN})_4^{2-}$.

It is anticipated from Fig. 1 that three species— $\text{PdCl}_3(\text{SCN})^{2-}$, $\text{PdCl}_2(\text{SCN})_2^{2-}$ and $\text{PdCl}(\text{SCN})_3^{2-}$ —enhance the extraction rate, while $\text{Pd}(\text{SCN})_4^{2-}$ decreases the rate. So the following interfacial reaction model for the extraction of palladium is proposed.

where subscripts *org* and *ad* denote organic phase and adsorption state, respectively. θ_v is the fraction of active vacant site at the interface. K_{HR} is the adsorption equilibrium constant of DDTA. k_1 to k_{s3} are the reaction rate constants corresponding to Eqs. (6) to (9), respectively. Assuming that Eqs. (6) to (9) are the rate-determining steps, according to the previous

Table 2. Values of constants for palladium extraction in the presence of thiocyanate ion

K_{HR}	$= 0.1 \text{ m}^3/\text{mol}^3$
S_{HR}	$= 4.0 \times 10^5 \text{ m}^2/\text{mol}^3$
k_1	$= 1.5 \times 10^{-3} \text{ m}^3/(\text{mol} \cdot \text{s})^3$
k_{s1}	$= 0.29 \text{ m}^3/(\text{mol} \cdot \text{s})$
k_{s2}	$= 14 \text{ m}^3/(\text{mol} \cdot \text{s})$
k_{s3}	$= 0.50 \text{ m}^3/(\text{mol} \cdot \text{s})$
k_{HR}	$= 8 \times 10^{-6} \text{ m/s}^4$
k_{Pd}	$= 7 \times 10^{-6} \text{ m/s}$

paper,³⁾ the following reaction rate equation is obtained.

$$r = (k_1 + k_{s1}\beta_1[\text{SCN}^-][\text{Cl}^-]^{-1} + k_{s2}\beta_2[\text{SCN}^-]^2[\text{Cl}^-]^{-2} + k_{s3}\beta_3[\text{SCN}^-]^3[\text{Cl}^-]^{-3}) / (1 + \sum_{i=1}^4 \beta_i[\text{SCN}^-]^i[\text{Cl}^-]^{-i}) \times \frac{K_{\text{HR}} C_{\text{HR}i} C_{\text{Pd}i}}{S_{\text{HR}} 1 + K_{\text{HR}} C_{\text{HR}i}} \quad (10)$$

where S_{HR} is the interfacial area occupied by unit mole of DDTA and subscript i denotes the chemical species close to the interface.

It is necessary to consider the effect of mass transfer on the extraction rate because the rate was enhanced by the addition of thiocyanate ion. At steady state, the initial extraction rate, J_0 , is correlated to the mass transfer rates as follows.

$$J_0 = r_0 = (k_{\text{HR}}/2)(C_{\text{HR}0} - C_{\text{HR}i}) = k_{\text{Pd}}(C_{\text{Pd}0} - C_{\text{Pd}i}) \quad (11)$$

where k_{HR} and k_{Pd} are the mass transfer coefficients of DDTA and palladium, respectively.

By analyzing the experimental results using Eqs. (10) and (11), the values of the constants shown in Table 2 were obtained. In the analysis, the values of k_1 , K_{HR} , S_{HR} and k_{HR} obtained in the previous papers^{3,4)} were used. It is found from Table 2 that the reactivity of chloro-thiocyno-palladium complexes with DDTA is roughly in the following order:

As mentioned previously,³⁾ these results are explained by the trans-effect of thiocyanate ion, which is softer than chloride ion. $\text{PdCl}_2(\text{SCN})_2^{2-}$ is considered to have the highest reactivity because that species tends to take cis-conformation.⁵⁾

Conclusion

The extraction rate of palladium with didodecylmonothiophosphoric acid from acidic thiocyanate solution was measured and an enhancement in the

rate was observed. By assuming the interfacial reaction model, the reaction rate constants of the chloro-thiocyano-palladium complexes with the extractant were obtained. These results could be explained by the trans-effect of thiocyanate ion.

Nomenclature

C	= concentration	[mol/m ³]
f_i	= distribution fraction of complexes ($i=0-4$)	[-]
J_0	= initial extraction rate of palladium	[mol/(m ² ·s)]
K_{HR}	= adsorption equilibrium constant of extractant	[m ³ /mol]
K_{SCN}	= protonation constant of thiocyanate ion	[m ³ /mol]
k_1	= reaction rate constant	[m ³ /(mol·s)]
k_{si}	= reaction rate constant ($i=1-3$)	[m ³ /(mol·s)]
k_{HR}	= mass transfer coefficient of extractant	[m/s]
k_{Pd}	= mass transfer coefficient of palladium	[m/s]
r	= reaction rate	[mol/(m ² ·s)]
S_{HR}	= interfacial area occupied by unit mole of extractant	[m ² /mol]
β_i	= stability constant of complexes ($i=1-4$)	[-]
θ_o	= fraction of active vacant site at interface	[-]
[]	= concentration	[mol/m ³]

<Subscripts>

ad	= adsorption state
Cl	= chloride ion
H	= hydrogen ion
HR	= extractant
i	= adjacent to interface
org	= organic phase
Pd	= palladium
SCN	= thiocyanate ion
0	= initial value

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