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Phase-Transfer Catalysts in Extraction Kinetics: Palladium Extraction by Dioctyl Sulfide and KELEX 100

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The rate of palladium extraction from acidic chloride solutions with dioctyl sulfide (R_2S) in chloroform containing tetraheptylammonium chloride (THA^+Cl^-) and with 7-(1-vinyl-3,3,5,5-tetramethylhexyl)-8-quinolinol (KELEX 100) (HL) in chloroform containing decyltrimethylammonium chloride ($DTMA^+Cl^-$) has been evaluated as a function of the quaternary ammonium salt (Q^+Cl^-), the extractant, the aqueous chloride concentrations, and the solution pH. The data are consistent with an extraction mechanism in which the kinetically active metal complex, $PdCl_3^-$, is transferred from the aqueous phase to the bulk organic phase as an ion pair of the type $Q^+PdCl_3^-$, where it reacts with the extractant (R_2S or HL). The rate-determining steps for extraction by R_2S or KELEX 100 are of the following type: $Q^+PdCl_3^-(o) + R_2S(o) \xrightarrow{k_1} Q^+PdCl_3(R_2S)^-(o)$; $Q^+PdCl_3^-(o) + HL(o) \xrightarrow{k_2} Q^+PdCl_2L^-(o) + H^+ + Cl^-$.

Introduction

Recently, this laboratory has launched a series of kinetic studies on palladium extraction with a variety of hydrophobic extractants such as 2-hydroxy-5-nonylbenzophenone oxime (LIX 65N),[1] R_2S,[2] KELEX 100,[3] and 1-(2-pyridylazo)-2-naphthol (PAN).[4] Slow extractions, with observed rate constant values of the order of 10^{-5} s^{-1}, were reported. A common extraction mechanism was advanced that involved the equilibrium transfer of the extractant from the organic phase into the aqueous phase, where sequential stepwise complex formation occurred, followed by extraction of the neutral, extractable species into the organic phase (Figure 1). The homogeneous aqueous bulk phase reaction

$$PdCl_3^- + R_2S \xrightarrow{k_3} PdCl_3(R_2S)^- \qquad (1)$$

appeared to be the rate-determining step on the basis of the following rate law that was found to describe the extraction kinetics:

$$-\frac{d[Pd]_T}{dt} = \frac{k_3\alpha_4[Pd]_T[R_2S]_o}{K_{DR}K_{f4}[Cl^-]} \qquad (2)$$

where k_3 = forward rate constant, α_4 = fraction of $PdCl_4^{2-}$, K_{f4} = formation constant of $PdCl_4^{2-}$, K_{DR} = distribution coefficient of the extractant, and subscript o represents organic phase concentration.

It is obvious that, because of the high hydrophobicity of the extractants used, a very low concentration of the reagent will be present in the aqueous phase, and consequently a slow extraction rate will be observed (Table I).

One way to improve the extraction rate would be to transfer some of the chloropalladate(II) complex as an ion pair with a suitable quaternary ammonium ion to the organic phase, which contains a high concentration of the extractant (Figure 2).

When a preliminary test of this concept indicated that palladium extraction by R_2S and KELEX 100 can be accelerated by the presence of several quaternary ammonium salts, we decided to conduct a systematic kinetic study in order to elucidate the mechanism of the improved extraction process.

Experimental Section

Reagents. Dioctyl sulfide and tetraheptylammonium bromide (THA^+Br^-) were obtained from Morton Thiokol, Inc. Tetrabutylammonium bromide (TBA^+Cl^-), decyltrimethylammonium bromide ($DTMA^+Br^-$), dodecyltrimethylammonium bromide ($DDTMA^+Br^-$), and tetradecyltrimethylammonium bromide ($TDTMA^+Br^-$) were obtained from Eastman Kodak Co. Tricaprylmethylammonium chloride ($TCMA^+Cl^-$) was obtained from General Mills Chemicals, Inc. THA^+Cl^-, TBA^+Cl^-, $DTMA^+Cl^-$, $DDTMA^+Cl^-$, and $TDTMA^+Cl^-$ were prepared by twice equilibrating equal volumes of 2×10^{-2} M of their corresponding bromide salts with 5 M sodium chloride. THA^+SCN^- was prepared by twice equilibrating equal volumes of 1×10^{-2} M THA^+Br^- with 2 M sodium thiocyanate solution. These quaternary ammonium salts were standardized by equilibrating 10 mL of approximately 5×10^{-5} M samples with an equal volume of 1×10^{-3} M bromothymol blue in aqueous solution at pH 8.02 and by measuring the absorbance of the Q^+–bromothymol blue ion pair at 410 nm (ϵ = 19000 M^{-1} cm^{-1}). All other reagents were of analytical grade. Chloroform was washed with water twice, stored in the dark, and kept no longer than 1 week. All aqueous metal solutions were prepared daily from a 1×10^{-3} M palladium stock solution prepared by dissolving a weighed quantity of palladium(II) chloride (99.9% purity, Johnson Mathey, Inc.) in 0.1 M hydrochloric acid solution and standardized by an indirect EDTA method.[5] Distilled deionized water was used throughout the study.

Table I. Contribution of the Distribution Coefficient of the Extractant to Rate of Palladium Extraction[a]

extractant	k_3, M^{-1} s^{-1}	K_{DR}	$[HL]_{aq}$, M	$-d[Pd]_T/dt$, M s^{-1}
PAN	1.86×10^4	2.51×10^5	3.98×10^{-8}	7.40×10^{-10}
R_2S	3.51×10^4	5.62×10^5	1.78×10^{-8}	6.24×10^{-10}
LIX 65N	3.74×10^3	3.98×10^4	2.51×10^{-7}	9.39×10^{-10}
KELEX 100	7.94×10^2	3.31×10^5	3.02×10^{-8}	2.40×10^{-11}

[a] Assuming that $[PdCl_3^-] = 1 \times 10^{-6}$ M and [extractant] = 1×10^{-2} M.

Apparatus. The automated extraction kinetics apparatus has been described elsewhere.[6] The course of the reaction was followed by monitoring the absorbance of the $PdCl_2(R_2S)_2$ complex (310 nm) and PdL_2 complex (460 nm) in chloroform. All pH measurements were made with an Orion Research 701A pH meter calibrated with pH 2.00, 4.00, and 7.00 standard buffer solutions.

Extraction Kinetics Procedure. A 50-mL sample of the organic phase is introduced into the thermostated flask, and the peristaltic pump is started. The organic phase passes through the flow cell in the Cary 219 spectrophotometer and returns to the flask. Thermal equilibration is indicated when the absorbance reading reaches a steady value (corrected to zero). Then, 50 mL of the thermally equilibrated phase is added to the flask, and the reaction is started by initiating stirring at 6500 rpm. (Tests with this system demonstrate that the reaction kinetics become independent of stirring rates above 3500 rpm.) Absorbance values at λ_{max} for the $PdCl_2(R_2S)_2$ complex were taken every second, while those of the $Pd(KELEX\ 100)_2$ complex were taken every 4 s. All studies were carried out under pseudo-first-order conditions in metal ion, i.e., ligand in great excess over Pd. The pseudo-first-order rate constant, k_{obs}, and the sum of the forward and reverse rate constants, $k_f + k_r$, were simply determined from

$$\ln (A_e/(A_e - A_t)) = (k_f + k_r)t = k_{obs}t \qquad (3)$$

where t is the sampling time and A_e and A_t correspond to the absorbance of the complex at equilibrium and at time t, respectively. Since, under

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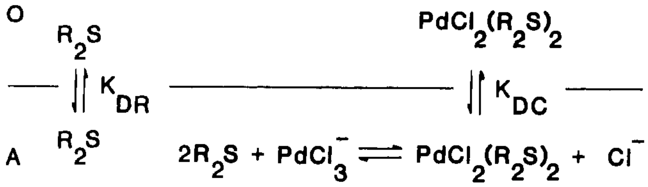

Figure 1. Mechanism of Pd extraction in absence of Q^+Cl^-.

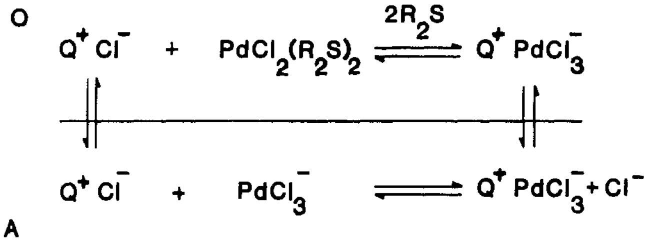

Figure 2. Mechanism of Pd extraction in presence of Q^+Cl^-.

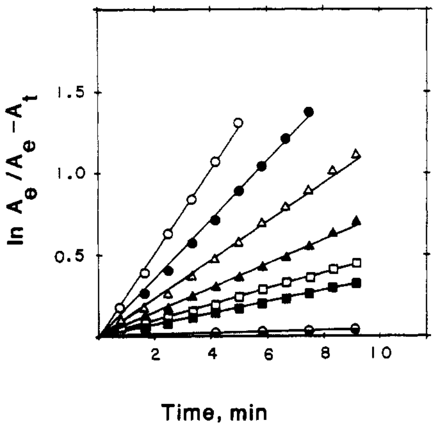

Figure 3. Effect of $[THA^+Cl^-]$ on the rate of Pd extraction. $[Pd]_T = 6 \times 10^{-5}$ M; $[Cl^-] = 1.0$ M.; $[R_2S]_0 = 2 \times 10^{-2}$ M. $[THA^+Cl^-]_0$ (M): (⊖) 0; (■) 2×10^{-4}; (□) 3×10^{-4}; (▲) 4×10^{-4}; (△) 6×10^{-4}; (●) 8×10^{-4}; (○) 1×10^{-3}.

Table II. Kinetics Data for Palladium Extraction by R_2S

A. Dependence on $[THA^+Cl^-]_0$
$[Pd]_T = 6 \times 10^{-5}$ M, $[R_2S]_0 = 2 \times 10^{-2}$ M,
$[Cl^-] = 1$ M, pH =2.00

$10^3[THA^+Cl^-]_0$, M	log k_{obs}	$10^3[THA^+Cl^-]_0$, M	log k_{obs}
0.2	-3.21	0.6	-2.67
0.3	-3.06	0.8	-2.50
0.4	-2.88	1.0	-2.42

slope of log k_{obs} vs log $[THA^+Cl^-]_0$: 1.18 ± 0.05

B. Dependence on $[Cl^-]$
$[Pd]_T = 6 \times 10^{-5}$ M, $[R_2S]_0 = 2 \times 10^{-2}$ M,
$[THA^+Cl^-]_0 = 8 \times 10^{-4}$ M, pH = 2.00,
Ionic Strength = 1.0 M with Na_2SO_4

$[Cl^-]$, M	log k_{obs}	$[Cl^-]$, M	log k_{obs}
0.35	-1.67	0.80	-2.30
0.40	-1.75	1.00	-2.50
0.60	-2.05		

slope of log k_{obs} vs log [Cl–]: −1.81 ± 0.07

our experimental conditions, extraction was essentially complete at equilibrium, $k_f \gg k_r$, so that k_{obs} is essentially a measure of k_f.

Results and Discussion

Gauging the effect of THA^+Cl^- concentration in the range 2×10^{-4}–1×10^{-3} M on the rate of palladium extraction from 1.0 M chloride solutions by R_2S by plotting ln $(A_e/(A_e - A_t))$ vs time results in straight lines passing through the origin (Figure 3), confirming that the extraction rate is first order with respect to the metal. These results also show that the extraction rate increases with quaternary salt concentration. A logarithmic plot of the observed rate constant (slopes in Figure 3) against the quaternary salt concentration yields a good linear relationship with a slope of 1.18 ± 0.05 (Table II).

The values of the observed rate constants at various chloride ion and R_2S concentrations were obtained similarly. The observed rate constants vary close to inverse second order with the chloride concentration (−1.81 ± 0.07) (Table II). The observed rate constants show variable dependence on R_2S concentration (Figure 4). The reaction order ranges from almost 1 (0.85 ± 0.04) to close to zero with increasing R_2S.

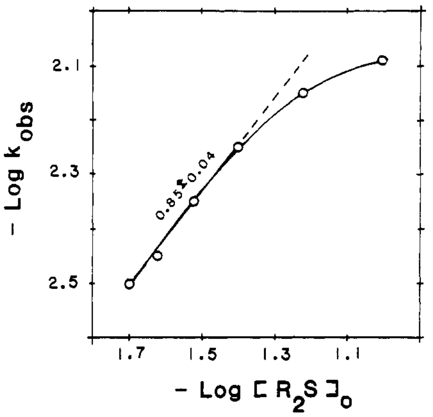

Figure 4. Palladium-extraction rate as a function of $[R_2S]_0$. $[Pd]_T = 6 \times 10^{-5}$ M; $[Cl^-] = 1.0$ M; $[THA^+Cl^-]_0 = 8 \times 10^{-4}$ M; pH = 2.00.

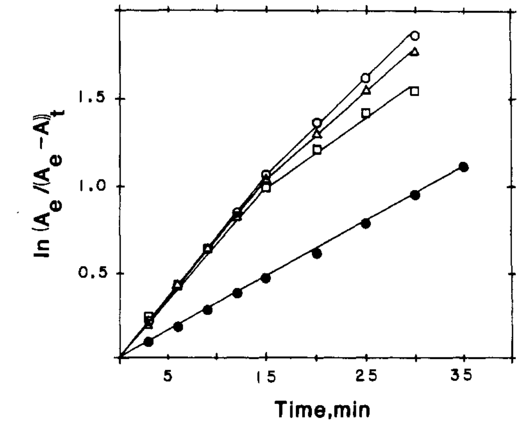

Figure 5. Effect of size of quaternary ammonium ion on Pd-extraction kinetics. $[Pd]_T = 1 \times 10^{-4}$ M; $[Cl^-] = 0.5$ M; ionic strength = 1.0 M with Na_2SO_4; $[HL]_0 = 5 \times 10^{-2}$ M; $[Q^+Cl^-]^0 = 1 \times 10^{-3}$ M; pH = 5.30. Q^+Cl^-: (○) $TCMA^+Cl^-$; (△) TBA^+Cl^-; (□) THA^+Cl^-; (●) $DTMA^+Cl^-$.

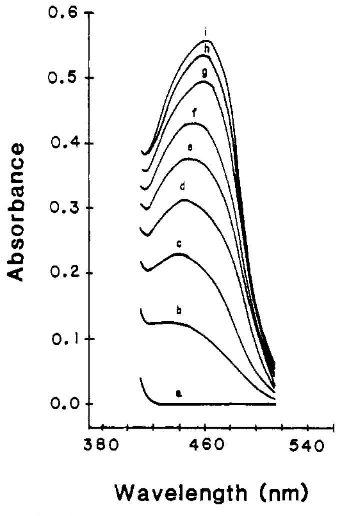

Figure 6. Change of Pd–KELEX 100 complex spectrum with time of extraction. $[Pd]_T = 1 \times 10^{-4}$ M; $[Cl^-] = 0.5$ M; ionic strength = 1.0 M with Na_2SO_4; $[HL]_0 = 5 \times 10^{-2}$ M. Time (min): (a) 0; (b) 3; (c) 6; (d) 9; (e) 12; (f) 15; (g) 20; (h) 25; (i) 30.

The kinetics of palladium extraction from chloride solutions by KELEX 100 in the presence of THA^+Cl^- were found to be complex. The plot of $\ln (A_e/(A_e - A_t))$ vs time (Figure 5) is linear for up to a 15-min extraction. At longer times, a transition to a lower slope occurs. The absorption spectra of the bulk organic phase recorded every 3 min after mixing the two phases show two absorbance bands (Figure 6). One absorption band with λ_{max} at 433 nm appearing at early stages of extraction is later shifted to λ_{max} at 460 nm, which corresponds to the final product, PdL_2. Therefore, the results in Figure 5 (□) can be explained by assuming that the overall reaction rate is controlled by slow formation of an intermediate species and its slow conversion to the final product.

Similar results were obtained when THA^+Cl^- was replaced by TBA^+Cl^- and $TCMA^+Cl^-$ (Figure 5 (△, ○)). However, when $DTMA^+Cl^-$ was used, the absorption spectra of the organic phase recorded every 3 min after mixing the two phases showed only the absorbance band of the final product, 460 nm. Furthermore, the extraction rate showed the same first-order dependence on the metal concentration for up to the 35 min studied (Figure 5 (●)). This may indicate that the extraction rate is only controlled by the formation of the intermediate species, while its conversion to the final product is a fast process.

The effect of $DTMA^+Cl^-$ concentrations in the range 7×10^{-4}–3×10^{-3} M on the rate of palladium extraction from 0.5 M chloride solutions at pH 5.30 when plotted as $\ln (A_e/(A_e - A_t))$ vs time showed straight lines passing through the origin. Furthermore, the plot of observed rate constant against $DTMA^+Cl^-$ concentration showed a linear relation with a slope of 1.18 ± 0.03 (Table III). In the presence of 1×10^{-3} M $DTMA^+Cl^-$, the extraction rate exhibited first-order dependence on the [HL] (0.90 ± 0.03), inverse second-order dependence on the $[Cl^-]$ (−1.80 ± 0.11), and independence of the solution pH (0.11 ± 0.05) (Table III). These results are consistent with those observed for palladium extraction by R_2S in the presence of THA^+Cl^- (Table II, Figure 4).

For both systems, the extraction mechanism can be described schematically as follows: (1) formation of an ion pair between the dissolved Q^+Cl^- and the kinetically active aqueous metal complex, $PdCl_3^-$, which has been reported to be involved in the rate-determining step of palladium extraction by R_2S[1] and KELEX 100[2] in the absence of Q^+Cl^-

$$\text{fast:}\quad Q^+\,Cl^-(o) \xrightleftharpoons{K_{DQCl}^{-1}K_{IPQCl}^{-1}} Q^+ + Cl^- \qquad (4)$$

$$\text{slow:}\quad PdCl_4^{2-} \xrightleftharpoons[k_{-1}]{k_1} PdCl_3^- + Cl^- \qquad (5)$$

$$\text{fast:}\quad Q^+ + PdCl_3^- \xrightleftharpoons{K_{IPQPdCl_3}} Q^+PdCl_3^- \qquad (6)$$

(2) the transfer of the ion pair into the bulk organic phase

$$\text{fast:}\quad Q^+PdCl_3^- \xrightleftharpoons{K_{DQPdCl_3}} Q^+PdCl_3^-(o) \qquad (7)$$

(3) reaction of the metal with the extractant in the organic phase
(i) for dioctyl sulfide

$$\text{slow:}\quad Q^+PdCl_3^-(o) + R_2S(o) \xrightleftharpoons[k_{-2}]{k_2} Q^+PdCl_3(R_2S)^-(o) \qquad (8)$$

$$\text{fast:}\quad Q^+PdCl_3(R_2S)^-(o) + R_2S(o) \rightleftharpoons PdCl_2(R_2S)_2(o) + Q^+Cl^-(o) \qquad (9)$$

(ii) for KELEX 100

$$\text{slow:}\quad Q^+PdCl_3^-(o) + HL(o) \xrightleftharpoons[k_{-3}]{k_3} Q^+PdCl_2L^-(o) + Cl^- + H^+ \qquad (10)$$

$$\text{fast:}\quad Q^+PdCl_2L^-(o) + HL(o) \rightleftharpoons PdL_2(o) + Q^+Cl^-(o) + H^+ + Cl^- \qquad (11)$$

where K_{DQCl} is the distribution constant of Q^+Cl^-, K_{DQPdCl_3} the distribution constant of $Q^+PdCl_3^-$, K_{IPQCl} the ion-pair formation constant of Q^+Cl^-, and $K_{IPQPdCl_3}$ the ion-pair formation constant of $Q^+PdCl_3^-$. Equation 8 or 10 was considered as the rate-determining step, and therefore

$$-\frac{d[Pd]_T}{dt} = k_2[Q^+PdCl_3^-]_o[R_2S]_o \qquad (12)$$

Table III. Kinetics Data for Palladium Extraction by KELEX 100

A. Dependence on $[DTMA^+Cl^-]_o$
$[Pd]_T = 1 \times 10^{-4}$ M, $[HL]_o = 5 \times 10^{-2}$ M,
$[Cl^-] = 0.5$ M, pH = 5.32,
Ionic Strength = 1.0 M with Na_2SO_4

$10^3[DTMA^+Cl^-]_o$, M	log k_{obs}	$10^3[DTMA^+Cl^-]_o$, M	log k_{obs}
0.7	−3.51	2.0	−2.96
1.0	−3.30	3.0	−2.75
1.5	−3.08		

slope of log k_{obs} vs log $[DTMA^+Cl^-]_o$: 1.18 ± 0.03

B. Dependence on $[HL]_o$
$[Pd]_T = 1 \times 10^{-4}$ M, $[DTMA^+Cl^-]_o = 1 \times 10^{-3}$ M,
$[Cl^-] = 0.5$ M, pH = 5.32,
Ionic Strength = 1.0 M with Na_2SO_4

$10^2[HL]_o$, M	log k_{obs}	$10^2[HL]_o$, M	log k_{obs}
1.0	−3.90	4.0	−3.38
1.5	−3.75	5.0	−3.30
2.5	−3.55	6.0	−3.18

slope of log k_{obs} vs log $[HL]_o$: 0.90 ± 0.03

C. Dependence on $[Cl^-]$
$[Pd]_T = 1 \times 10^{-1}$ M, $[DTMA^+Cl^-]_o = 1 \times 10^{-3}$ M,
$[HL]_o = 5 \times 10^{-2}$ M, pH = 5.30
Ionic Strength = 1.0 M with Na_2SO_4

$[Cl^-]$, M	log k_{obs}	$[Cl^-]$, M	log k_{obs}
0.5	−3.30	0.8	−3.66
0.6	−3.40	1.0	−3.82
0.7	−3.51		

log k_{obs} vs log $[Cl^-]$: −1.80 ± 0.11.

D. Dependence on pH
$[Pd]_T = 1 \times 10^{-4}$ M, $[DTMA^+Cl^-]_o = 1 \times 10^{-3}$ M,
$[HL]_o = 5 \times 10^{-2}$ M, $[Cl^-] = 0.5$ M,
Ionic Strength = 1.0 M with Na_2SO_4

pH	log k_{obs}	pH	log k_{obs}
5.31	−3.30	4.73	−3.31
5.10	−3.32	4.51	−3.41
4.91	−3.35		

log k_{obs} vs pH: 0.11 ± 0.05

On the assumption of a steady-state condition for the formation of $PdCl_3^-$ in the aqueous phase and its reaction with the extractant in the organic phase, the expression can be obtained for the concentration of the ion pair in the organic phase as

$$[Q^+PdCl_3^-]_o = \frac{k_1\alpha_4[Pd]_T[Q^+Cl^-]_o}{\dfrac{k_{-1}K_{DQCl}K_{IPQCl}}{K_{DQPdCl_3}K_{IPQPdCl_3}}[Cl^-]^2 + k_2[R_2S]_o[Q^+Cl^-]_o} \qquad (13)$$

and therefore

$$-\frac{d[Pd]_T}{dt} = \frac{k_1k_2\alpha_4[Pd]_T[Q^+Cl^-]_o[R_2S]_o}{K[Cl^-]^2 + k_2[R_2S]_o[Q^+Cl^-]_o} \qquad (14)$$

where $k_{-1}K_{DQCl}K_{IPQCl}/K_{DQPdCl_3}K_{IPQPdCl_3} = K$ and α_4 is the fraction of $PdCl_4^{2-}$ in the aqueous phase that is equal to $[PdCl_4^{2-}]/[Pd]_T$.

According to eq 14, the first-order dependence of the extraction rate on the ligand and the quaternary ammonium salt concentrations and the inverse second-order dependence on the aqueous chloride concentration, obtained for palladium extraction by dioctyl sulfide (Table II, Figure 4) and KELEX 100 (Table III), can be explained by assuming that $K[Cl^-]^2 \gg k_2[R_2S]_o[Q^+Cl^-]_o$. Furthermore, the transition from a region where the extraction is first-order dependent on $[R_2S]_o$ to a region where the extraction is almost independent of the reagent concentration (Figure 4) can be explained by assuming that, beyond 5×10^{-2} M, the term $k_2[R_2S]_o[Q^+Cl^-]_o$ becomes greater than $K[Cl^-]^2$. This transition in the extraction rate as a function of the reagent concentration was not observed in palladium extraction by KELEX 100 up to 6×10^{-2} M concentration. It may be related to the slower reaction rate with the metal in the organic phase and therefore lower k_2 values in eq 14. This is expected because, in the absence of Q^+Cl^-, the rate of palladium extraction by KELEX 100, 7.94×10^2 M^{-1} s^{-1},[2] is about 45-fold lower than that of R_2S, 3.51×10^4 M^{-1} s^{-1}.[1]

The slow addition of the first and the second KELEX 100 molecules to the metal ion (eq 10 and 11) may be considered as the two slow steps involved when THA$^+$Cl$^-$, TBA$^+$Cl$^-$, or TCMA$^+$Cl$^-$ was used as the phase-transfer catalyst. This is rather surprising because the addition of the second ligand molecule is usually considered to be a fast process and has been confirmed in palladium extraction by KELEX 100 in the absence of Q^+Cl^-.[2] Nevertheless, this has also been observed when DTMA$^+$Cl$^-$ was used with KELEX 100 (Table III), and even when THA$^+$Cl$^-$ was used with R_2S (Figure 4). This indicates that the molecular geometry and the nature of Q^+Cl^- and/or the extractant used may play an important role in the behavior of the quaternary ammonium salt as a phase-transfer catalyst.

The catalytic behavior of Q^+Cl^- has generated a dramatic improvement in palladium extraction by R_2S. For example, the presence of as little as 8×10^{-4} M THA$^+$Cl$^-$ caused a 100-fold enhancement in the observed rate [from 1.82×10^{-4} s^{-1}[1] to 1.78×10^{-2} s^{-1} (Table II)] of palladium extraction from 0.4 M chloride solutions at pH 2.00 with 2×10^{-2} M R_2S. A further improvement in the extraction rate was observed when the quaternary ammonium thiocyanate salt was used. The rate of palladium extraction from 1.0 M chloride solutions at pH 2.00 by 2×10^{-2} M R_2S increased from 1.1×10^{-4} to 6.5×10^{-3} s^{-1} (>60-fold) when 1×10^{-5} M THA$^+$Cl$^-$ was replaced by 1×10^{-5} M THA$^+$SCN$^-$.

An equivalent improvement in the rate of palladium extraction by KELEX 100 was also observed in the presence of quaternary ammonium salts. For example, in the presence of 3×10^{-3} M DTMA$^+$Cl$^-$, the observed rate of palladium extraction from 0.5 M chloride solutions at pH 5.32 with 5×10^{-2} M KELEX 100 increased from 1.32×10^{-5} (ref 2) to 1.78×10^{-3} s^{-1} (Table III). The extraction rate further improved when 5×10^{-4} M DTMA$^+$Cl$^-$ was replaced by an equivalent amount of larger quaternary ammonium ions (2.09×10^{-4} s^{-1} for DTMA$^+$Cl$^-$, 6.76×10^{-4} s^{-1} for DDTMA$^+$Cl$^-$, and 8.91×10^{-4} s^{-1} for TDTMA$^+$Cl$^-$). This is in accord with the expectation that extraction of the ion pair containing the $PdCl_3^-$ anion increases with increasing cation size.

Any effort to evaluate k_2 for eq 8 or 12 representing the reaction rates in the organic phase requires knowledge of the values of the extraction constants (K_DK_{IP}) of the ion pairs Q^+Cl^- and $Q^+PdCl_3^-$. In the absence of such data, it might still be useful to explore the consequence of the reasonable assumption that $K_{DQCl}K_{IPQCl}$ is 10^{-3} times as large as the corresponding extraction constant involving the larger less hydrated ion $PdCl_3^-$.

For $k_1/k_{-1} = 0.05$,[7] the rate data yield a value of k_2 of 3.75 ± 0.46 for R_2S and 0.059 ± 0.006 for KELEX 100. These rate constant values are much lower than those reported for the similar reaction in the aqueous phase (3.51×10^4 for R_2S,[2] 7.94×10^2 for KELEX 100[3]), which is reasonable for the lower dielectric constant if the mechanism is dissociative.

It is interesting to note that the ratio of the calculated rate constant value involving R_2S to that of KELEX 100 is 64, compared to the corresponding ratio for the reactions in the aqueous phase, 44. This clearly indicates that a comparable mechanism applies to both phases, which is consistent with the approach elaborated in this paper.

In conclusion, since the quaternary ammonium salts do not affect the composition or the extent of final extraction, they are truly catalysts. The role of quaternary ammonium salts in accelerating palladium extraction from chloride solutions by dioctyl sulfide and KELEX 100 in chloroform can be recognized as "phase-transfer" catalysis; i.e., the rate-determining step is governed by reaction of the extractant with the kinetically active aqueous metal complex in the organic phase, which contains a high concentration of the extractant. Quaternary ammonium salts can be characterized as a novel series of extraction catalysts and may have tremendous utility in process-scale metal recovery by extraction. Further studies in this area are underway in this laboratory.

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Registry No. R_2S, 2690-08-6; THA$^+$Cl$^-$, 10247-90-2; Kelex 100, 29171-27-5; THA$^+$SCN$^-$, 86108-30-7; TBA$^+$Cl$^-$, 1112-67-0; DTMA$^+$Cl$^-$, 2082-84-0; DDTMA$^+$Cl$^-$, 112-00-5; TDTMA$^+$Cl$^-$, 4574-04-3; TCMA$^+$Cl$^-$, 5137-55-3; Pd, 7440-05-3.

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