known to be unstable in contact with acidic aqueous media, was assumed to be that of a secondary palladium dithizonate, probably $Pd(ClO_4)Dz$. In view of the failure of Pd to appear in the aqueous phase following the reaction, this seemed to be a reasonable assumption. A tentative description of the reaction then is

$$2Pd(Dz)_2(o) + Hg^{2+} + 2ClO_4^- \overset{K}{\rightleftharpoons} 2Pd(ClO_4)Dz(o) + Hg(Dz)_2(o) \quad (1)$$

From the absorbance measurements at various wavelengths, which permitted the construction of a difference spectrum corresponding to $Pd(ClO_4)Dz$ and the stoichiometric relationships inherent in eq 1, concentrations of each of the reactants and products were calculated and used to evaluate the equilibrium constant K (eq 2). The results shown in Table II provide strong evidence in the relatively invariant K values under different experimental conditions in one solvent system as well as a rational progression of K values in different solvent systems that generally reflects their "polarity".

$$K = \frac{[Pd(ClO_4)Dz]_o^2[Hg(Dz)_2]_o}{[Pd(Dz)_2]_o^2[Hg^{2+}][ClO_4^-]^2} \quad (2)$$

The absence of a reaction when $HgCl_2$ was used in place of $Hg(ClO_4)_2$ can be understood in terms of the adverse effect of strong chloride complexation ($\log \beta_4 = 15.2^{11}$) on the Hg activity and, therefore, on the extent of the reaction in eq 1.

Equation 2 can be considered to be a composite of the formation of $Hg(Dz)_2$ ($K_{ex}(Hg(Dz)_2)$) and that of $Pd(ClO_4)Dz$ ($K_{ex}(Pd\ ClO_4)Dz)$), from which the formation of $Pd(Dz)_2$ ($K_{ex}(Pd(Dz)_2)$) is subtracted, or

$$K_3 = [K_{ex}(Pd(ClO_4)Dz)^2][K_{ex}(Hg(Dz)_2)]/K_{ex}(Pd(Dz)_2)^2 \quad (3)$$

With use of the K_3 value obtained here of $K = 10^{-2.79}$, $K_{ex}(Hg(Dz)_2) = 10^{27.0}$,[7] and the corrected value from ref 6 of $K_{ex}(Pd(Dz)_2) = 10^{25.1}$, the secondary chelate $Pd(ClO_4)Dz$ formation constant can be calculated as $10^{10.2}$. This is far larger than might be expected on the basis of the reasonable assumption that the coordination of the second dithizonate ligand to Pd is not too much weaker than the first. Frequently the formation constants of successive chelating ligands are within a factor of 10–100 of each other. Even if one were to assume that the formation constant of Pd–ClO_4 is as high as 10^3, there would have to be a minimum factor of 10^{12} between the stepwise formation constants of $Pd(Dz)_2$. Certainly, this interesting chelate system merits further study.

The reaction of $Pd(Dz)_2$ in organic solvents with $AgClO_4$ resembles that with $Hg(ClO_4)_2$ in that a color change (from green to violet) was observed in the organic layer while no Pd was detected in the aqueous phase. It differs in that no primary dithizonate complex is formed (no increase in absorbance at 460 nm, characteristic of the primary silver dithizonate). The secondary silver dithizonate is described as violet colored but also as very insoluble in most organic solvents. Although our results did not allow us to fully explain this reaction now, we considered it of sufficient interest to report here.

From a practical point of view, these reactions suggest that back-extractions of Pd from extracted chelates such as the dithizonates are more difficult than anticipated earlier. In order to utilize ligands that form highly stable Pd chelates, further study of chelate reactivity is required.

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Registry No. $Pd(Dz)_2$, 12213-17-1; $Hg(Dz)_2$, 14783-59-6; $Hg(ClO_4)_2$, 7616-83-3; $AgClO_4$, 7783-93-9.

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Solvent Extraction Equilibria and Kinetics in the Palladium(II)-Hydrochloric Acid-7-(1-Vinyl-3,3,5,5-tetramethylhexyl)-8-quinolinol System

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Investigation of the extraction equilibria of palladium by chloroform solutions of 7-(1-vinyl-3,3,5,5-tetramethylhexyl)-8-quinolinol (Kelex 100, HL) from aqueous chloride solutions demonstrated that the extracted species is the simple chelate PdL_2, which, according to the kinetic study, is formed through stepwise replacement of pairs of coordinated chloride ions by the protonated ligand. Measurement of distribution ratios of Kelex 100 between chloroform and aqueous hydrochloric acid yielded values of the distribution constant of the neutral ligand, which is the predominant organic-phase species even up to 2.0 M HCl, as well as that of the ion pair H_2L^+,Cl^-. The metal chelate extraction constant and the rate of the aqueous-phase reaction $PdCl_2L^- + H_2L^+ \rightleftharpoons PdL_2 + 2H^+ + 2Cl^-$ were determined.

In spite of the widespread use of organic chelating agents for the analysis of the platinum-group metals, very little fundamental information of the reactions, i.e. the kinetic and thermodynamic parameters, has been reported. Palladium extraction by chelating agents can usually be accomplished even from acidic media, under conditions where most metals cannot be extracted. This provides high selectivity in the recovery and purification of palladium. Usually the time required for the achievement of equilibrium is so long, however, as to constitute a practical disadvantage. In this laboratory we are undertaking systematic mechanistic studies of chelation extractions of palladium[1] in order to learn more of the intrinsic nature of such reactions and how to develop systems of optimal characteristics.

Palladium extraction by 8-quinolinol (oxine), an amphoteric chelating agent widely used in analytical chemistry, has been shown to occur in the range pH 0–10.[2] The study of the extraction of Pd by 7-(1-vinyl-3,3,5,5-tetramethylhexyl)-8-

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quinolinol (Kelex 100), a 7-dodecenyl-substituted derivative of oxine, is interesting not only because it would provide basic information required for a hydrometallurgical separation, but the comparison with oxine itself would shed light on useful structure–behavior influences. Kelex 100 possesses a K_{DR} that is 3 orders of magnitude larger and a rather smaller K_a value than does oxine.[3] By its high hydrophobicity and the consequent lower aqueous-phase concentrations, Kelex 100 offers an opportunity to study the mechanism of palladium extraction in acidic systems, not possible with oxine because its low hydrophobicity results in very high extraction rates. In this work the acid–base and distribution equilibria of Kelex 100 as well as both equilibrium and kinetic aspects of palladium extraction by Kelex 100 from hydrochloric acid media have been studied.

Experimental Section

Reagents. 7-(1-Vinyl-3,3,5,5-tetramethylhexyl)-8-quinolinol (Kelex 100, HL) was kindly supplied by Sherex Chemical Co. and purified by washing with 1 M hydrochloric acid. Chloroform (AR grade) was washed twice by deionized water just before use. Palladium chloride was obtained from AESAR Johnson Matthey Inc. with 99.9% purity. All other reagents were AR grade.

Analyses. The concentration of Kelex 100 in $CHCl_3$ was determined indirectly by the measurement of the absorbance at 430 nm for the Cu–Kelex 100 chelate, which was formed quantitatively by the equilibration of equal volumes of a Kelex 100 solution in $CHCl_3$ and 0.1 M $CuSO_4$ solution for 1 h. The molar absorbance, ϵ, of Cu–Kelex 100 chelate in $CHCl_3$ was determined to be 2.26×10^3 within the range of $(1–5) \times 10^{-4}$ M Kelex 100 solution in $CHCl_3$. The determination of palladium in the aqueous phase was carried out by a spectrophotometric method using dithizone as reagent at 637 nm.[4]

Apparatus. A Burrell wrist-action shaker was employed for both the equilibrium and kinetic studies. A Perkin-Elmer 552 spectrophotometer and a Varian Cary 219 spectrophotometer were used for the measurement of absorbance and absorption spectra, respectively.

Procedure for Determination of Distribution Ratio, D_R, of Kelex 100 between $CHCl_3$ and Acidic Solution. An aqueous phase of 600 mL maintained at an ionic strength of 2.0 M (HCl + NaCl) with an HCl concentration between 0.5 and 2.0 M, presaturated with $CHCl_3$, was equilibrated with 20 mL of 0.100 M Kelex 100 in $CHCl_3$ for 4 h in the shaker. After phase separation, a 500-mL aliquot of the aqueous phase was placed in a separation funnel, neutralized by dropwise addition of 10 M NaOH to a pH between 5 and 6, and back-extracted with 20.0 mL of $CHCl_3$. The concentration of Kelex 100 obtained from the absorbance at 430 nm, A, of the copper chelate was used to calculate the value of D_R:

$$D_R = \frac{C_{HL}(o)}{C_{HL}} = \frac{0.100 \times 2.26 \times 10^3 \times 500}{20A}$$

Procedure for Palladium Extraction Equilibrium. The distribution ratio of palladium between equal phase volumes, D_{Pd}, was determined as a function of palladium, ligand, hydrogen ion, and chloride ion concentrations. The procedure was similar to that previously described[1] except for the shaking time. Since it was found that shaking times of more than 5 days at high chloride concentration were needed to ensure the achievement of equilibrium, a 1 week equilibrium time was employed in all the experiments.

Procedure for Palladium Extraction Kinetics. The procedure was described previously.[1] A shaking speed of 280 oscillations/min was found to be sufficiently vigorous to ensure the extraction being carried out in the "plateau" region, i.e. where increasing the shaking speed gave no further change on the rate of extraction. The experimental conditions were adjusted as to be sufficiently far from the equilibrium state that the initial rate involved only the forward reaction, i.e., that the reverse reaction could be ignored. Since the palladium concentration is linearly related to the absorbance, A, this was used in all calculations. Thus, the pseudo-first-order forward rate constants, k_f, were determined from

$$\ln (A_0/A_t) = k_o t$$

where A_0 and A_t correspond to the absorbance of palladium ion at time zero and at time t, respectively, and k_o is the observed rate constant, which involves k_f and other parameters.

Results and Discussion

I. Reagent Distribution. The dissociation of the phenolic proton of Kelex 100 could be ignored in acidic media since its pK_a value is high (10.40).[3] The following equilibria can occur in the system:

$$HL + H^+ \xrightleftharpoons{K_a^{-1}} H_2L^+ \tag{1}$$

$$H_2L^+ + Cl^- \xrightleftharpoons{K_{IP}} H_2L^+,Cl^- \tag{2}$$

$$HL \xrightleftharpoons{K_{DR}} HL(o) \tag{3}$$

$$H_2L^+,Cl \xrightleftharpoons{K_{DR(IP)}} H_2L^+,Cl^-(o) \tag{4}$$

where (o) refers to organic-phase species.

The distribution ratio of Kelex 100, D_R, can be written as

$$D_R = \frac{[HL]_0 + [H_2LCl]_0}{[HL] + [H_2L^+] + [H_2LCl]} \tag{5}$$

which, with the aid of the equilibrium expressions defined by eq 1–4, gives

$$D_R = \frac{K_{DR}K_aK_{IP}^{-1} + K_{DR(IP)}[H^+][Cl^-]}{K_aK_{IP}^{-1} + K_{IP}[H^+] + [H^+][Cl^-]} \tag{6}$$

It is reasonable to assume that the formation of the ion pair H_2L^+,Cl^- is usually very small in the aqueous phase, so that the second term in the denominator of eq 6 may be ignored. Then eq 6 simplifies to

$$D_R = \frac{K_{DR}K_aK_{IP}^{-1} + K_{DR(IP)}[H^+][Cl^-]}{K_aK_{IP}^{-1} + [H^+][Cl^-]} \tag{7}$$

which can be rearranged to give

$$D_R = K_{DR(IP)} + K_aK_{IP}^{-1}(K_{DR} - D_R)[H^+][Cl^-] \tag{8}$$

From the values of D_R at constant ionic strength (2.0 M HCl + NaCl) determined over a range of concentrations of hydrogen ion (0.5–2.0 M), and with use of the value of K_{DR} as $10^{5.53}$,[3] the dependence of D_R on $(K_{DR} - D_R)[H^+]^{-1}[Cl^-]^{-1}$ was shown to be linear, indicating the validity of eq 8 (Table I). From the slope of this line by the least-squares method from the data the value of $K_aK_{IP}^{-1}$ was found to be 0.102 ± 0.003 ($10^{-0.99\pm0.01}$). If the K_a of Kelex 100 in the aqueous phase is taken to be $10^{-4.05}$, expected to be 1 order of magnitude smaller than in 1:1 dioxane–water, $10^{-3.05}$,[3] the value of K_{IP} can be calculated to be $10^{-3.06}$, demonstrating the reasonableness of the assumption made above to simplify eq 6 to eq 7. The value of $K_{DR(IP)}$, the intercept of this equation, 340 ± 620, is not very reliably determined by this experiment.

As soon as a $CHCl_3$ solution of Kelex 100 is contacted with aqueous HCl, the organic phase immediately turns yellow, with an intensity depending on the acid concentration. Further, the absorption spectra of the chloroform solutions of Kelex 100 following equilibration are consistent with the formation of a weak chloride ion pair with the protonated reagent. When the acidity of the aqueous phase, which was 2.0 M in chloride, was increased, a broad peak at 390 nm appeared in the spectrum of the organic phase, whose absorbance increased with increasing acidity. This peak did not appear when sulfate was substituted for chloride. Both the extraction and spectrophotometric data indicate that the ion pair is present as a small fraction (about 4% in 2 M HCl) of the neutral ligand in chloroform.

II. Palladium Distribution. The equilibrium distribution of palladium was measured over a palladium concentration

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(3) S. Bag and H. Freiser, *Anal. Chim. Acta*, **135**, 319 (1982).

(4) Z. Marczenko, "Spectrophotometric Determination of Elements", Ellis Horwood Ltd., Chichester, England, 1976, p 415.

Table I. Distribution Data for Kelex 100 between Chloroform and Acidic Solution at 2.0 M Ionic Strength (HCl + NaCl) and 25 °C[a]

[HCl], M	0.5	1.0	1.2	1.5	1.7	2.0
distribn ratio, D_R	3.09×10^4	1.70×10^4	1.44×10^4	1.11×10^4	1.04×10^4	7.75×10^3
$[H^+][Cl^-]$	1.0	2.0	2.4	3.0	3.4	4.0
$(K_{DR} - D_R)/[H^+][Cl^-]$	3.02×10^5	1.58×10^5	1.33×10^5	1.07×10^5	9.49×10^4	8.13×10^4

[a] Slope and intercept for D_R vs. $(K_{DR} - D_R)/[H^+][Cl^-]$ are 0.102 ± 0.003 and 338 ± 621, respectively.

Table II. Equilibrium Data for Palladium Extraction with Kelex 100

A. Dependence on [Pd] ($[HL]_0 = 1.0 \times 10^{-2}$ M, [HCl] = 2.0 M)

$[Pd]_T$, M	$\log D_{Pd}$	$\log K_{ex}'$	$\log K_{ex}$
5.0×10^{-5}	0.0522	5.86	17.36
7.0×10^{-5}	0.0323	5.84	17.34
1.0×10^{-4}	0.0907	5.90	17.40
1.5×10^{-4}	0.0116	5.82	17.32
2.0×10^{-4}	−0.0348	5.77	17.27
		av 5.84 ± 0.03	av 17.34 ± 0.03

slope for $\log D_{Pd}$ vs. log [Pd] −0.13 ± 0.08

B. Dependence on $[HL]_0$ ($[Pd]_T = 5.0 \times 10^{-5}$ M, [HCl] = 1.0 M, [NaCl] = 1.0 M)

$[HL]_0$, M	$\log D_{Pd}$	$\log K_{ex}'$	$\log K_{ex}$
2.0×10^{-3}	0.326	5.91	17.41
3.0×10^{-3}	0.838	5.97	17.47
5.0×10^{-3}	1.40	5.75	17.25
7.0×10^{-3}	3.72	5.88	17.38
1.0×10^{-2}	6.54	5.82	17.32
1.5×10^{-2}	16.13	5.86	17.36
2.0×10^{-2}	35.47	5.95	17.45
		av 5.88 ± 0.06	av 17.38 ± 0.06

slope for $\log D_{Pd}$ vs. $\log [HL]_0$ 1.97 ± 0.09

C. Dependence on $[H^+]$ ($[HL]_0 = 1.0 \times 10^{-2}$ M, $[Pd]_T = 1.0 \times 10^{-4}$ M, $[Cl^-] = 2.0$ M (HCl + NaCl))

$[H^+]$, M	$\log D_{Pd}$	$\log K_{ex}'$	$\log K_{ex}$
0.30	1.803	5.96	17.46
0.50	1.439	6.04	17.54
0.70	1.051	5.94	17.44
1.0	0.801	6.01	17.51
1.2	0.573	5.93	17.43
1.5	0.358	5.91	17.41
2.0	0.0907	5.90	17.39
		av 5.95 ± 0.03	av 17.45 ± 0.03

slope for $\log D_{Pd}$ vs $\log [H^+]$ −2.11 ± 0.07

D. Dependence on $[Cl^-]$ ($[HL]_0 = 1.0 \times 10^{-2}$ M, $[Pd]_T = 1.0 \times 10^{-4}$ M, $[H^+] = 2.0$ M (HCl + H_2SO_4[a]))

$[Cl^-]$, M	$\log D_{Pd}$	$\log K_{ex}'$	$\log K_{ex}$
0.50	2.26	5.66	17.16
0.70	1.79	5.77	17.27
1.0	1.07	5.67	17.17
1.5	0.459	5.76	17.26
2.0	0.0907	5.90	17.39
		av 5.75 ± 0.07	av 17.25 ± 0.07

slope for $\log D_{Pd}$ vs. $\log [Cl^-]$ −3.70 ± 0.05

[a] Where H_2SO_4 is considered as a monobasic acid.

range from 5×10^{-5} to 2×10^{-4} M, a Kelex 100 range from 2×10^{-3} to 2×10^{-2} M, a hydrogen ion range from 0.3 to 2.0 M, and a chloride ion range from 0.5 to 2.0 M. From the dependence of D_{Pd}, the distribution ratio, on these several parameters, summarized in Table II, the overall extraction reaction can be expressed by the equation

$$PdCl_4^{2-} + 2HL(o) \xrightleftharpoons{K_{ex}''} PdL_2(o) + 2H^+ + 4Cl^- \tag{9}$$

or, since the formation of $PdCl_4^{2-}$ from Pd^{2+} can be accounted for by using available equilibrium data

$$Pd^{2+} + 2HL(o) \xrightleftharpoons{K_{ex}} PdL_2(o) + 2H^+ \tag{10}$$

Values of K_{ex}' and K_{ex} were calculated with the help of eq 11 and 12 In our study, since $[Cl^-] \geq 0.5$ M, the tetrachloropalladate is the predominant Pd species. Hence, in the aqueous phase

$$\log K_{ex}'' = \log D_{Pd} + 2 \log [H^+] - 2 \log [HL]_0 + 4 \log [Cl^-] \tag{11}$$

$$\log K_{ex} = \log D_{Pd} + 2 \log [H^+] - 2 \log [HL]_0 - \log \alpha_0 \tag{12}$$

$$\alpha_0 = [Pd^{2+}]/[Pd]_T \simeq (\beta_3[Cl^-]^3 + \beta_4[Cl^-]^4)^{-1}$$

With the use of the value of the formation constants of chloro–palladium complexes β_3 as $10^{10.2}$ and β_4 as $10^{11.5}$,[5] K_{ex} was estimated to be $10^{17.36\pm0.06}$, which is far greater than that corresponding to Cu–Kelex 100, $10^{1.09}$,[3] Ni–Kelex 100, $10^{-6.34}$,[6] and UO_2–Kelex 100, $10^{2.56}$.[7] K_{ex}' was calculated to be as $10^{5.86\pm0.06}$, which involves the predominant species, $PdCl_4^{2-}$, as the reactant. Even with use of K_{ex}', a more realistic comparison with the K_{ex} values for the other metals mentioned above, since they do not form chloro complexes, palladium extraction by Kelex 100 is still the most stable one. In comparison with the extraction of Pd from chloride media by 2-hydroxy-5-nonylbenzophenone oxime (LIX65N) (K_{ex} as $10^{16.30}$ and K_{ex}' as $10^{4.78}$),[1] Kelex 100 is seen to be a stronger extractant.

III. Palladium Extraction Kinetics. The dependence of the observed rate constant, $\log k_0$, on $\log [H^+]$, $\log [HL]_0$, and $\log [Cl^-]$ was found to be linear, with sloped close to 0 (0.14), 2 (2.15), and −2 (−1.77), respectively, giving rise to the empirical rate expression

$$-\frac{d[Pd]_T}{dt} = k'\frac{[Pd][HL]_0^2}{[Cl^-]^2} \tag{13}$$

The observed second-order dependence in ligand is unusual for palladium reactions although it has been observed with the reaction of copper(II), with LIX65N as well as other chelating agents.[8] The kinetics data are consistent with the extraction mechanism

$$HL(o) \rightleftharpoons HL \text{ rapid} \tag{3}$$

$$HL + H^+ \rightleftharpoons H_2L^+ \quad \text{rapid} \tag{1}$$

$$PdCl_4^{2-} + H_2L^+ \xrightleftharpoons{K_1} PdCl_2L^- + 2H + 2Cl^- \quad \text{rapid} \tag{14}$$

$$PdCl_2L^- + H_2L^+ \xrightarrow{k_f} PdL_2 + 2H^+ + 2Cl^- \quad \text{slow} \tag{15}$$

$$PdL_2 \xrightleftharpoons{K_{DC}} PdL_2(o) \quad \text{rapid} \tag{16}$$

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(5) R. M. Smith and A. E. Martell, "Critical Stability Constants", Plenum Press, New York, 1975.

(6) K. Haraguchi and H. Freiser, *Inorg. Chem.*, **22**, 1187–90, (1983).

(7) L. Zhu and H. Freiser, *Anal. Chim. Acta*, **146**, 237–41 (1983).

(8) S. P. Carter and H. Freiser, *Anal. Chem.*, **52**, 511 (1980).

Table III. Kinetics Data for Palladium Extraction with Kelex 100

A. Dependence on $[\mathrm{HL}]_0$ ($[\mathrm{Pd}]_\mathrm{T} = 1.0 \times 10^{-4}$ M, [HCl] = 1 M, $[\mathrm{H_2SO_4}] = 1$ M)

$[\mathrm{HL}]_0$, M	log $[\mathrm{HL}]_0$	k_0	log k_0	$[\mathrm{HL}]_0$, M	log $[\mathrm{HL}]_0$	k_0	log k_0
5.0×10^{-3}	−2.301	1.15×10^{-5}	−4.939	2.0×10^{-2}	−1.699	2.17×10^{-4}	−3.664
1.0×10^{-2}	−2.000	3.52×10^{-5}	−4.453	3.0×10^{-2}	−1.523	4.92×10^{-4}	−3.308
1.5×10^{-2}	−1.824	9.93×10^{-5}	−4.005				

slope for log k_0 vs. log $[\mathrm{HL}]_0$ 2.15 ± 0.13

B. Dependence on $[\mathrm{H^+}]$ ($[\mathrm{HL}]_0 = 2.0 \times 10^{-2}$ M, $[\mathrm{Pd}]_\mathrm{T} = 1.0 \times 10^{-4}$ M, $[\mathrm{Cl^-}] = 2.0$ M (HCl + NaCl))

$[\mathrm{H^+}]$, M	log $[\mathrm{H^+}]$	k_0	log l_0	$[\mathrm{H^+}]$ M	log $[\mathrm{H^+}]$	k_0	log k_0
0.10	−1.000	2.87×10^{-5}	−4.542	0.50	−0.301	3.76×10^{-5}	−4.425
0.20	−0.699	3.08×10^{-5}	−4.511	1.00	0	3.87×10^{-5}	−4.412
0.30	−0.523	3.71×10^{-5}	−4.431				

slope for log k_0 vs. log $[\mathrm{H^+}]$ 0.14 ± 0.04

C. Dependence on $[\mathrm{Cl^-}]$ ($[\mathrm{HL}]_0 = 2.0 \times 10^{-2}$ M, $[\mathrm{Pd}]_\mathrm{T} = 1.0 \times 10^{-4}$ M, $\Sigma[\mathrm{H^+}] = 2.0$ M (HCl + $\mathrm{H_2SO_4}$))

$[\mathrm{Cl^-}]$, M	log $[\mathrm{Cl^-}]$	k_0	log k_0	α_4	$\alpha_4[\mathrm{Cl^-}]^{-2}$
0.20	−0.699	2.82×10^{-3}	−2.550	0.836	20.9
0.30	−0.523	1.44×10^{-3}	−2.842	0.877	9.74
0.50	−0.301	5.52×10^{-4}	−3.258	0.923	3.69
0.70	−0.155	3.79×10^{-4}	−3.421	0.942	1.92
1.00	0	2.17×10^{-4}	−3.664	0.949	0.949
1.20	0.0792	1.11×10^{-4}	−3.955	0.966	0.671
1.50	0.176	7.30×10^{-5}	−4.147	0.972	0.432

where $\alpha_4 \simeq \beta_4[\mathrm{Cl^-}]\,(\beta_3 + \beta_4[\mathrm{Cl^-}])$, log $\beta_3 = 10.2$, log $\beta_4 = 11.5$;[5] slope for log k_0 vs. log $[\mathrm{Cl^-}]$ −1.77 ± 0.09, slope for k_0 vs. $\alpha_4[\mathrm{Cl^-}]^2$ (1.337 ± 0.029) × 10^{-4}

For step 15, the rate-determining step (rds), the rate expression is

$$-\frac{\mathrm{d}[\mathrm{Pd}]_\mathrm{T}}{\mathrm{d}t} = k_\mathrm{f}[\mathrm{PdCl_2L^-}][\mathrm{H_2L^+}] \qquad (17)$$

which, by appropriate substitution, becomes

$$-\frac{\mathrm{d}[\mathrm{Pd}]_\mathrm{T}}{\mathrm{d}t} = k_\mathrm{f}K_1'K_\mathrm{a}^{-2}K_\mathrm{DR}^{-2}[\mathrm{Pd}]_\mathrm{T}[\mathrm{HL}]_0^{2}[\mathrm{Cl^-}]^{-2}\alpha_4 \qquad (18)$$

where $\alpha_4 = [\mathrm{PdCl_4^{2-}}]/[\mathrm{Pd}]_\mathrm{T} \simeq \beta_4[\mathrm{Cl^-}]/(\beta_3 + \beta_4[\mathrm{Cl^-}])$ and β_i represents the formation constants of $\mathrm{PdCl}_i^{(2-i)+}$ (log β_3 = 10.2, log β_4 = 11.5 (5)).

In order to calculate rate constant k_f from the experimental data with use of eq 18, only K_1 must be estimated. The equilibrium constant for the overall chelating reaction, i.e., the sum of eq 14 and 15 (whose equilibrium constants are represented by K_1' and K_2')

$$\mathrm{PdCl_4^{2-}} + 2\mathrm{H_2L^+} \overset{K'}{\rightleftharpoons} \mathrm{PdL_2} + 4\mathrm{H^+} + 4\mathrm{Cl^-} \qquad (19)$$

can be estimated by

$$K' = K_1'K_2' = K_\mathrm{ex}'K_\mathrm{DR}^{2}K_\mathrm{a}^{2}K_\mathrm{DC}^{-1} = 10^{-0.1} \qquad (20)$$

where K_DC is estimated as $10^{9.0}$ by comparison with the value for the copper-Kelex 100 chelate.[3,11] We may take K_1' as 1 from the estimated value of K'. With the use of these values in eq 17 the rate data as shown in Table IIIC yield the k_f value 3.63×10^2 $\mathrm{M^{-1}\,s^{-1}}$. This value is consonant with those generally observed in the substitution reactions of the complexes of divalent palladium.[9,10]

Improved kinetic behavior should be obtainable by decreasing the concentration of chloride ion and increasing the concentration of ligand as seen from eq 18. The reasons for the difference in the mechanisms of palladium extraction between Kelex 100 and LIX65N are not yet understood. Further studies with different types of extractants are under way.

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Registry No. Kelex 100, 29171-27-5; palladium, 7440-05-3.

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(9) F. R. Hartley, "The Chemistry of Platinum and Palladium", Applied Science Publishers Ltd., London, 1973, p 292.

(10) R. G. Wilkins, "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes", Allyn and Bacon, Boston, 1974, p 234.

(11) The value of K_DC for Cu-Kelex 100 was published as $10^{9.6}$ through erroneous calculation in ref 3 and should be $10^{9.0}$.