October, 1975] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(10), 2825—2828 (1975) 2825

The Polarographic Reduction of [Pd(oxine)$_2$] and [Pd(acac)$_2$] in a *N*,*N*-Dimethylformamide Solution

Michio Hirota and Shizuo Fujiwara

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113

(Received May 7, 1975)

Palladium(I) species were produced by the polarographic reduction of palladium(II)-oxinate and -acetylacetonate complexes in a *N*,*N*-dimethylformamide solution. These species were unstable and decomposed into electro-inactive species through an irreversible following chemical reaction. The rate constants were obtained from the fundamental and second harmonic AC polarograms, which were obtained at two different frequencies of the AC potential, 55.8 and 173.6 Hz, at 22.5 °C as $5.5 \pm 1.0\ s^{-1}$ for the oxinate complex and as $50 \pm 10\ s^{-1}$ for the acetylacetonate complex.

Many palladium(II) complexes are irreversibly reduced to a palladium amalgam at a dropping mercury electrode in an aqueous solution.[1] However, it has been found that Pd(I) is detected as a product of the following chemical reaction in the case of $[Pd(CN)_4]^{2-}$.[2]

Such a lower-valence state has been proven to be produced in an aprotic dipolar solvent by the polarographic reduction of bipyridine complexes of iron, cobalt, and other metal ions.[3,4] The palladium *o*-phenylenediamine complex can also exist as a low-valent species in an acetonitrile solution.[5] These results seem to suggest that the π-bonding nature between the central ion and the ligand stabilizes the lower-valence state and that Pd(I) may be observed in the polarographic reduction of the oxinate and acetylacetonate complexes of palladium.

In this study, the polarographic reduction of the palladium(II)-oxinate and -acetylacetonate complexes was studied in a *N*, *N*-dimethylformamide(DMF) solution. Low-valent species(Pd(I)) were detected as unstable intermediates. The life-times of the intermediates were obtained quantitatively by the fundamental and second harmonic AC polarography.

Experimental

Material. The palladium(II) complexes were prepared according to the usual method and were recrystallized. The DMF was treated with K_2CO_3 and distilled. The tetraethylammonium perchlorate (TEAP) was recrystallized five times from water.

Measurements. The DC polarogram was taken with a Yanagimoto Polarograph, Model P-8. The oscillo- and AC polarograms were taken with apparatuses constructed in this laboratory. The details of the measurements were the same as those given in previous papers.[6,7] An H-type cell was used with a reference electrode (saturated calomel electrode(SCE), Yanagimoto Model MRP). The flow rate of the mercury was 0.67 mg/s at the mercury column height of 40 cm in a 1 M KCl solution at an open circuit. All the measurements were carried out at (22.5 ± 0.5) °C. All the potentials were referred to the SCE.

The calculations of the simulation curves were based on the expanding plane model.[8,9] The following chemical reactions were assumed to be irreversible (See Results and Discussion). A computer simulation was performed with a HITAC 8700/8800 system, the Computer Center, the University of Tokyo, using the FORTRAN program of Smith.[8,9]

Results and Discussion

DC Polarography. The oxinate complex, [Pd(oxine)$_2$], was reduced through two waves (first at -1.39 V and second at -1.8 V). The first wave gave a diffusion controlled current. The second wave was very drawn out. The acetylacetonate complex, [Pd(acac)$_2$], was reduced through one wave at -1.17 V. This wave was also diffusion controlled and corresponded to the reduction of Pd(II) to a palladium amalgam.[10]

Oscillopolarography. The oscillopolarograms of these complexes are shown in Fig. 1-(A, B).

In the system of [Pd(oxine)$_2$]-0.5 M TEAP, the (1) and (5) waves correspond to the two waves of the DC polarogram. The (2) wave is the reoxidation wave of the reduced product of the (1) wave. This wave refers to the presence of the low-valent species. If the first reduced form is the palladium amalgam, it is difficult for the palladium to be reoxidized before the dissolution of mercury starts.[11] The (5) wave is irreversible. Hence, it is attributed to the reduction to the palladium amalgam. The (1), (2), and

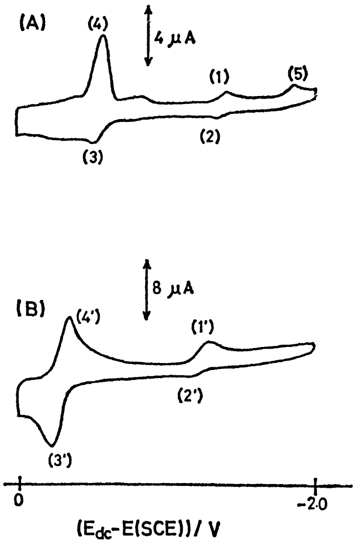

Fig. 1. The oscillopolarogram of Pd(II) complexes in N,N-dimethylformamide.
[TEAP]=0.5 M, sweep rate=34.8 V/s
h=40 cm, $T = (22.5 \pm 0.5)$ °C
(A) [Pd(oxine)$_2$]=0.27 mM
(B) [Pd(acac)$_2$]=1.28 mM.

(5) waves suggest that [Pd(oxine)$_2$] is first reduced to the Pd(I) species and then to the amalgam.

In the system of [Pd(acac)$_2$]-0.5 M TEAP, the (1′) wave corresponds to the wave of the DC polarogram. The reoxidation wave (2′) suggests that a low-valent species (Pd(I) or Pd(0)) is present. The (3′) and (4′) waves did not appear when the sweep range was reduced so that the reduction of [Pd(acac)$_2$] did not occur. Therefore, these waves are assumed probably to be due to the oxidation and reduction of mercury by the free acetylacetonate anion,[10] which has been liberated by the reduction of [Pd(acac)$_2$].

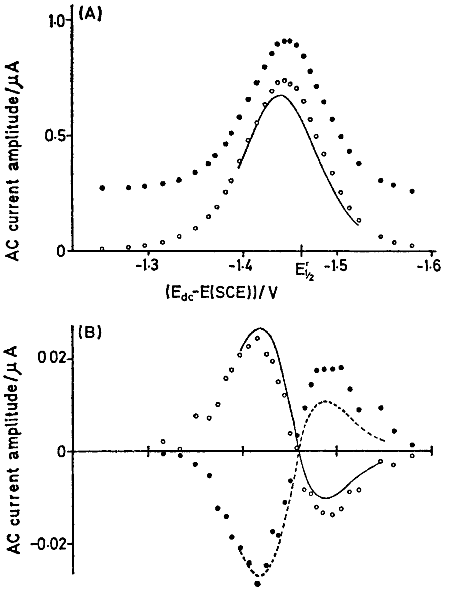

Fig. 2. The AC polarogram of [Pd(oxine)$_2$].
[Pd(oxine)$_2$] = 0.50 mM, [TEAP] = 0.5 M
(A): Fundamental harmonic AC polarogram.
(B): Second harmonic AC polarogram.
○: In-phase component, ●: quadrature component.
Simulation curves;
—— in-phase component, --- quadrature component
$n=1$, frequency = 55.8 Hz, $\Delta E = 5$ mV, $D_o = D_r = 1.28 \times 10^{-5}$ cm^2/s, $k_s = \infty$, $k_f = 5.5$/s, $A = 0.015$ cm^2, $T = (22.5 \pm 0.5)$ °C.

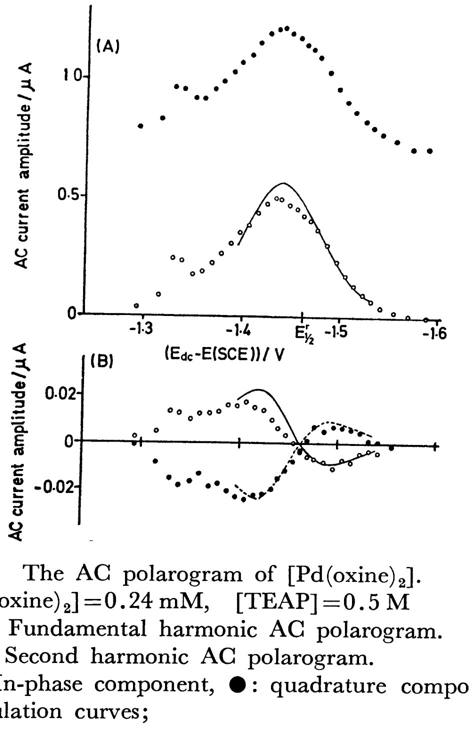

Fig. 3. The AC polarogram of [Pd(oxine)$_2$].
[Pd(oxine)$_2$] = 0.24 mM, [TEAP] = 0.5 M
(A): Fundamental harmonic AC polarogram.
(B): Second harmonic AC polarogram.
○: In-phase component, ●: quadrature component.
Simulation curves;
—— in-phase component, --- quadrature component
same parameters as Fig. 2, except frequency = 173.6 Hz.

In the system of [Pd(oxine)$_2$]-0.5 M TEAP, the (3) and (4) waves appeared only when the reduction of [Pd(oxine)$_2$] occurred. When only the (1) wave appeared, these waves were also observed, but were as small as one-third of those in Fig. 1. These wave forms were different from the normal redox wave. This is probably because of the adsorption of the species which participate in the redox reaction of mercury by the oxinate anion.

AC Polarography. Figures 2 and 3 show the AC polarograms of [Pd(oxine)$_2$] corresponding to the first wave of the DC polarogram. Though the phase angles of the fundamental and second harmonic AC polarograms were almost consistent with that of the reversible electrode reaction, the amplitudes were considerably smaller than that expected from the diffusion coefficient, which was calculated from the DC polarogram. The peak potential(E_p) of the fundamental harmonic AC polarogram was not equal to the zero-current potential (E_{min}) of the second harmonic AC polarogram. These features are typical of a reversible electrode reaction coupled with a following chemical reaction. As was seen in the preceding paragraph, the following chemical reaction was a decomposition reaction and was assumed to be irreversible. In the case of an irreversible following chemical reaction, the presence of the zero-current potential and the small cathodic peak height compared with the anodic one in the second harmonic AC polarogram indicate that the following chemical reaction is slow and so is inoperative in the AC polarographic sense. Figures 2 and 3 correspond to this case. This conclusion coincides with the fact that the cotangent of the phase angle of the second harmonic AC polarogram was almost equal to -1.[9] From the half-width of the fundamental harmonic AC polarogram, the number of electrons transferred(n) was found to be one. Therefore, the life-time of the Pd(I) species is assumed to be long in the AC polarographic sense. From the computer simulation, which was carried out at two frequencies, the rate constant of the following chemical reaction was estimated to be 5.5 ± 1.0 s^{-1}; *i.e.*, the life-time was about 0.18 s.

Figures 4 and 5 show the AC polarograms of [Pd(acac)$_2$]. In the fundamental harmonic AC polarogram, another small peak was observed at -1.65 V. These results seem to suggest that [Pd(acac)$_2$] is also reduced through two steps. The observed second wave was irreversible; hence, it was attributed to the reduction to the amalgam. The Pd(I) species was also detected in this system. The two waves were so close together that the DC polarogram apparently showed only one wave. The first AC wave was also typical of an electrode reaction coupled with a following chemical reaction. When the rate constant of

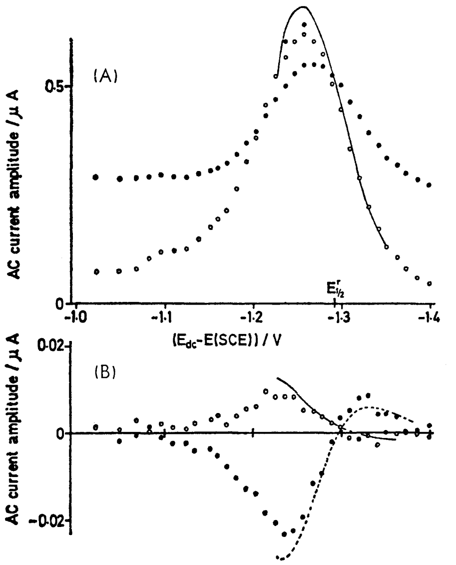

Fig. 4. The AC polarogram of [Pd(acac)$_2$].
[Pd(acac)$_2$] = 1.12 mM, [TEAP] = 0.5 M.
(A): Fundamental harmonic AC polarogram.
(B): Second harmonic AC polarogram.
○: In-phase component, ●: quadrature component.
Simulation curves;
—— in-phase component, --- quadrature component
$n=1$, frequency = 55.8 Hz, $\Delta E=5$ mV, $D_o=D_r=1.52\times10^{-5}$ cm^2/s, $k_s=7\times10^{-2}$ cm/s, $\alpha=0.50$, $k_f=50$/s, $A=0.015$ cm^2, $T=(22.5\pm0.5)$ °C.

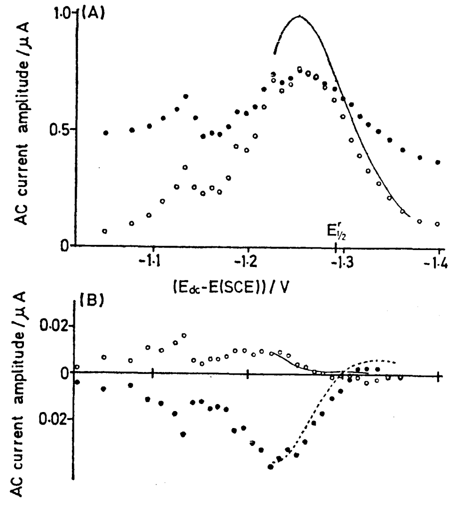

Fig. 5. The AC polarogram of [Pd(acac)$_2$].
[Pd(acac)$_2$] = 1.06 mM, [TEAP] = 0.5 M.
(A): Fundamental harmonic AC polarogram.
(B): Second harmonic AC polarogram.
○: In-phase component, ●: quadrature component.
Simulation curves;
—— in-phase component, --- quadrature component
same parameters as Fig. 4, except frequency = 173.6 Hz.

the following chemical reaction increases and/or that of the charge transfer reaction decreases, the phase angle of the second harmonic AC polarogram deviates from the value of a reversible electrode reaction, and the cathodic peak of the second harmonic AC polarogram becomes remarkably small. The system of

Table 1. Polarographic data of Pd(II)-0.5 M TEAP System

	$E^r_{1/2}$ or Pd(II)/Pd(I) (*vs.* SCE)	k_s ($\alpha=0.5$)	k_f of Pd(I)
[Pd(oxine)$_2$]	-1.46_2 V	>1 cm/s	(5.5±1.0)/s
[Pd(acac)$_2$]	-1.29_2 V	(0.07±0.03) cm/s	(50±10)/s

$T=(22.5\pm0.5)$°C, k_s; the standard rate constant of a charge transfer reaction, k_f; the rate constant of a following chemical reaction.

[Pd(acac)$_2$] corresponds to this case. From the computer simulation assuming an irreversible following chemical reaction and assuming that the transfer coefficient of the charge transfer reaction(α) was 0.5, it was found that n was 1 and that the rate constant of the following chemical reaction and the standard rate constant of the charge transfer reaction were 50±10 s^{-1} and 0.07±0.03 cm/s respectively; *i.e.*, the lifetime of the Pd(I) species was about 0.020 s. The parameters of these complexes can be summarized as is shown in Table 1.

In conclusion, these complexes were first reduced to mono-valent species. These complexes may have the same configuration as the starting complexes. These mono-valent species were unstable, decomposed, and liberated the ligands. These mono-valent species were also reduced irreversibly to palladium amalgams, and liberated the ligands.

The k_s of the Pd(II)/Pd(I) couple was larger in the [Pd(oxine)$_2$] system than in the [Pd(acac)$_2$] system. The rate constant of the decomposition was slower in the [Pd(oxine)$_2$] system than in the [Pd(acac)$_2$] system. These results show that the bi-valent species is reduced to the mono-valent species more easily in the oxinate complex than in the acetylacetonate complex, and that the mono-valent species is more stabilized as the oxinate complex than as the acetylacetonate complex.

From the ESR study of γ-ray irradiated Pd(I) complexes,[12] the covalency of the palladium-ligand σ bond has been found larger in [Pd(I)(oxine)$_2$]$^-$ than in [Pd(I)(acac)$_2$]$^-$. Therefore, the stabilization of Pd(I) may be due to the delocalization of the highest occupied energy level of Pd(I) complexes.

The product of the decomposition reaction is unknown. However, from the second harmonic AC polarogram, the regeneration of Pd(II) species can not be considered.[13] As there seems to be no species which can stabilize the mono-valent species, the decomposition reaction may be the reduction to palladium metal. In both systems with the higher frequency of the AC potential, humps were observed in the second harmonic AC polarogram. These are probably due to the adsorption of the complex preceding the reduction. In the data analysis for the following chemical reaction, this effect was neglected. In the simulation program, the diffusion coefficients of the first reduced form and the product of the following chemical reaction are assumed to be equal to each other. This condition was not applicable in these systems. However, this discrepancy was assumed not to be very serious. The effect of a spherical diffusion was also not considered.

References

1) M. Hirota, Y. Umezawa, M. Nakamura, and S. Fujiwara, *J. Inorg. Nucl. Chem.*, **33**, 2617 (1971).

2) M. Hirota and S. Fujiwara, *ibid.*, **35**, 3883 (1973).

3) N. Tanaka and Y. Sato, *Electrochim. Acta*, **13**, 333 (1968).

4) N. Tanaka and Y. Sato, This Bulletin, **41**, 1021, 2059 (1968).

5) A. L. Balch and R. H. Holm, *J. Amer. Chem. Soc.*, **88**, 5201 (1966).

6) T. Kugo, Y. Umezawa, and S. Fujiwara, *Chem. Instr.*, **2**, 189 (1969).

7) M. Hirota, Y. Umezawa, H. Kojima, and S. Fujiwara, This Bulletin, **47**, 2486 (1974).

8) T. G. McCord, H. L. Hung, and D. E. Smith, *J. Electroanal. Chem.*, **21**, 5 (1969).

9) T. G. McCord and D. E. Smith, *Anal. Chem.*, **41**, 1423 (1969).

10) R. W. Murray and L. K. Hiller, Jr. *ibid.*, **39**, 1221 (1967).

11) E. P. Parry and K. B. Oldham, *ibid.*, **40**, 1031 (1968).

12) M. Nakamura and S. Fujiwara, *J. Coord. Chem.*, **1**, 221 (1971).

13) K. R. Bullock and D. E. Smith, *Anal. Chem.*, **46**, 1567 (1974).