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ELECTROCHEMICAL PROPERTIES OF PALLADIUM(0) COMPLEXES COORDINATED BY QUINONE DERIVATIVES

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Summary

The polarographic and cyclic voltammetric behavior of quinone derivatives (Q) and their palladium(0) complexes, $(Q)_1$ or $2Pd(PPh_3)_2$, has been studied. All free quinone derivatives except 5,8,9,10-tetrahydro-1,4-naphthoquinone (THNQ) showed two reversible waves, and all palladium(0) complexes showed irreversible waves. The reduction half-wave potentials for free quinone derivatives lie in the following order: 7,7,8,8-tetracyanoquinodimethane (TCNQ) > *p*-benzoquinone (BQ) > 5,8-dihydro-1,4-naphthoquinone (DHNQ) > 1,4-naphthoquinone (NQ) > THNQ. The reduction potentials for quinone derivatives shifted toward the negative on coordination to palladium(0). The extent of the shifts depended on the electron-withdrawing ability of the free quinone derivatives. On the other hand, the oxidation potentials for the central palladium(0) in their complexes showed more positive values in comparison with the potential for $Pd(PPh_3)_4$. However, the oxidation potentials were almost constant for all complexes of the quinone derivatives. On the basis of these facts, the phenomena of charge transfer in the complexes are discussed.

Introduction

The electrochemical behavior of free quinones is perhaps studied most thoroughly in organic redox couples [1]. However, very few electrochemical

studies on metal complexes of quinones have been reported. As a very rare example, Nesmeyanov and his coworkers reported the polarographic reduction behavior of quinone π -complexes of nickel [2]. Interestingly, on the basis of a comparison of the half-wave potentials and data on their chemical behavior, they showed that these compounds can be arranged in the following order with respect to their ability to undergo reduction: bis(duroquinone)nickel(0) > duroquinone > (1,5-cyclooctadiene)duroquinonenickel(0). However, they did not report the oxidation behavior of these compounds.

Previously, we reported the preparation of palladium(0) complexes containing a ligand which has both an electron-donating olefin site and an electron-withdrawing quinone or dihydro-quinone site in a ligand molecule, i.e. DHNQ or THNQ [3]. These quinones are of particular interest since they contain a quinone (or dihydro-quinone) site and a dihydro- (or tetrahydro-)benzene-type olefin site in a ligand molecule. Therefore, DHNQ has both oxidation and reduction sites within one structure.

In this paper, we describe a comparison of the reduction potentials for free quinone derivatives with those for quinone derivatives coordinated to palladium(0). In addition, the oxidation behavior of the central palladium(0) in the quinone complexes is reported for the first time from cyclic voltammetric measurement using a platinum electrode. From the results obtained on the electrochemical behavior of the free quinone derivatives and their complexes, the phenomena of charge transfer by complexation and the mechanisms of electrode reactions of the complexes are discussed.

Results and discussion

1. The electrochemistry of free quinone derivatives

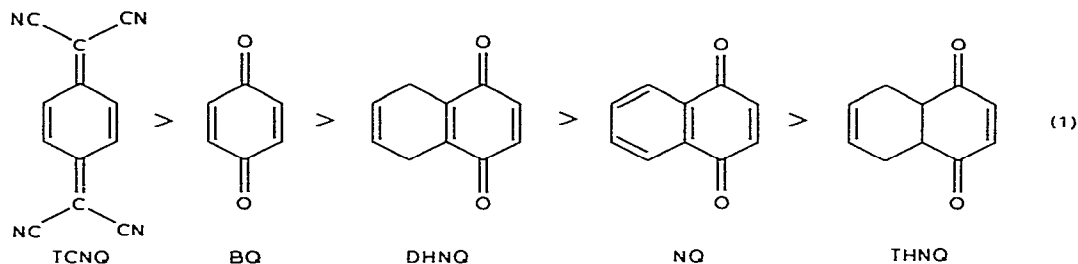
The half-wave potentials for TCNQ, BQ, and NQ have been already reported [1,4]. Taking into account the differences in measurement conditions, our results were almost in agreement with those reported. Further, the half-wave potentials for DHNQ and THNQ were measured for comparison with the three above. Table 1 summarizes the reduction half-wave potentials for the free quinone derivatives obtained by direct current polarography. As was expected, THNQ showed a more negative reduction potential than the others and irreversibility resulting from the nonquinone structure. On the other hand, DHNQ indicated an interesting behavior. The reduction potential for DHNQ held a position between those for BQ and NQ, contrary to the expectation that it lies between those for NQ and THNQ because of their analogous structures.

TABLE 1

THE REDUCTION HALF-WAVE POTENTIALS FOR THE FREE QUINONE DERIVATIVES BY DIRECT CURRENT POLAROGRAPHY

Quinone derivatives	TCNQ	BQ	DHNQ	NQ	THNQ
$E^1(1/2)$ (V)	0.37	-0.32	-0.43	-0.50	-1.02
$E^2(1/2)$ (V)	-0.16	-0.96	-1.03	-1.05	<-2.40
Reversibility	rev.	rev.	rev.	rev.	irrev.

Such an order (eq. 1) of the reduction potentials differs from that of the ligand exchange reactions for palladium(0) complexes coordinated by the corresponding quinone derivatives as ligands [3]. The difference may be caused by the steric influence in ligand exchange reactions.



2. The electrochemistry of palladium(0) complexes coordinated by quinone derivatives

The electrochemical behavior of palladium(0) complexes was complicated by the phenomenon of dissociation in a dilute solution. The dissociation was detected in the polarograms and the cyclic voltammograms. In addition, the dissociation was observed in the infrared spectra. For example, (NQ)Pd(PPh₃)₂ shows a frequency of the $\nu(\text{C}=\text{O})$ band at 1638 cm⁻¹, while free NQ shows it at 1677 cm⁻¹. When the solution, which had been measured by polarographic method, was investigated by IR, it showed the $\nu(\text{C}=\text{O})$ band at 1677 cm⁻¹ as well as at 1638 cm⁻¹. Therefore, the electrochemical analyses of the complexes were measured under such conditions that the dissociation was minimized.

2.1. The influence of solvent, temperature, and electrode on the dissociation.

First, the influence of solvent and temperature on the dissociation in acetonitrile

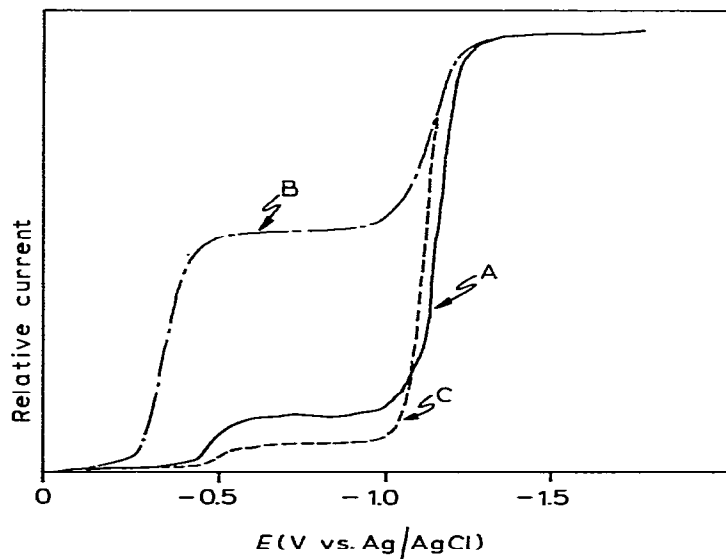


Fig. 1. Polarograms for (1,4-naphthoquinone)Pd(PPh₃)₂. A: in acetonitrile at 25°C; B: in dimethyl sulfoxide at 25°C; C: in acetonitrile at 0°C.

was less than that in dimethyl sulfoxide (A and B in Fig. 1). This may be described in terms of the donor number (acetonitrile 14.1, dimethyl sulfoxide 29.8 [5]). Solvents of higher donor properties will have higher coordinating ability and will promote the dissociation. The influence of temperature on the dissociation was also investigated. The dissociation of the complexes at 0°C was less than at 25°C (A and C in Fig. 1). Secondary, the influence of the electrode on the dissociation was investigated. The dissociation was extremely dependent on the electrode used [6]. In the measurements with the mercury electrode the phenomenon of dissociation was clearly observed, even in acetonitrile at 0°C. This fact probably indicates an interaction between the complexes and the mercury electrode. On the other hand, in the measurement with the platinum electrode, all the complexes except $(\text{TCNQ})_2\text{Pd}(\text{PPh}_3)_2$ did not dissociate, even at 25°C. Accordingly, the electrochemical behavior was generally investigated with the platinum electrode in acetonitrile at 25°C.

2.2. *Charge transfer in palladium(0) complexes and the reversibility.* Table 2 shows the reduction peak potentials for complexed quinone derivatives, the oxidation peak potentials for complexed palladium(0), and the reduction half-wave potentials for free quinone derivatives as a reference. The cyclic voltammogram for $(\text{DHNQ})\text{Pd}(\text{PPh}_3)_2$ is shown as an example in Fig. 2, together with those for DHNQ and $\text{Pd}(\text{PPh}_3)_4$ for comparison [7].

Shown in Fig. 2, the first reduction peak (a) for DHNQ coordinated to palladium(0) appeared at -1.05 V, and the corresponding reoxidation peak (a') for the radical anion of DHNQ coordinated to palladium(0) was ill-defined; this indicates an irreversible electrode reaction. The second reduction peak for DHNQ coordinated to palladium(0) was not present. The incorporation of an electron into the complex may result in the dissociation of the complex to $\text{Pd}(\text{PPh}_3)_2$ and the radical anion of DHNQ. Since the potential of the peak (a) is more negative than the reduction potential of the radical anion of DHNQ, it is reduced immediately to the dianion of DHNQ. Accordingly, the peak (a) probably includes the reduction of the radical anion. In fact, only when the complex was reduced at potentials more cathodic than -1.05 V, did two oxidation peaks (b and c), which correspond to the oxidation of the radical anion and the dianion of free DHNQ, appear. The peak (b) was ill defined due to the influence of the peak (a). When the scan rate of CV was decreased, peaks (b)

TABLE 2
THE REDOX POTENTIALS FOR $(\text{PPh}_3)_2\text{Pd}(\text{L})$ BY CYCLIC VOLTAMMETRY

Ligand (L)		TCNQ ^a	BQ	DHNQ	NQ	THNQ
Free ^c	$E^{1(1/2)}$ (V) ^b	0.35	-0.34	-0.47	-0.51	(-1.05) ^e
Complex ^c	$E_p(\text{red})$ (V)	-0.42	-1.01	-1.05	-1.10	-1.44
	$E_p(\text{ox})$ (V) ^d	0.90	0.92	0.90	0.89	0.89
	$ \Delta E $ (V) ^f	0.77	0.67	0.58	0.59	(0.39)

^a $(\text{PPh}_3)_2\text{Pd}(\text{L})_2$. ^b Half-wave potentials for ligand L. ^c Scan rate = 100 mV/sec. ^d $E_p(\text{ox})$ for $\text{Pd}(\text{PPh}_3)_4 = 0.09$ V. ^e The first peak potential for irreversible system. ^f $|\Delta E| = |E_p(\text{red}) - E^{1(1/2)}|$ for free ligand.

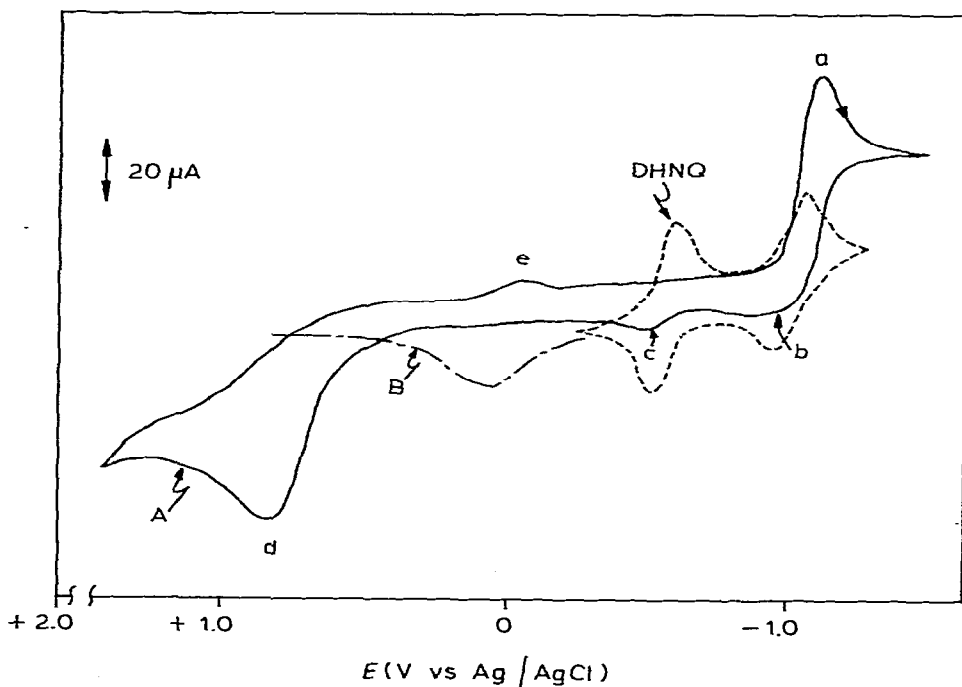
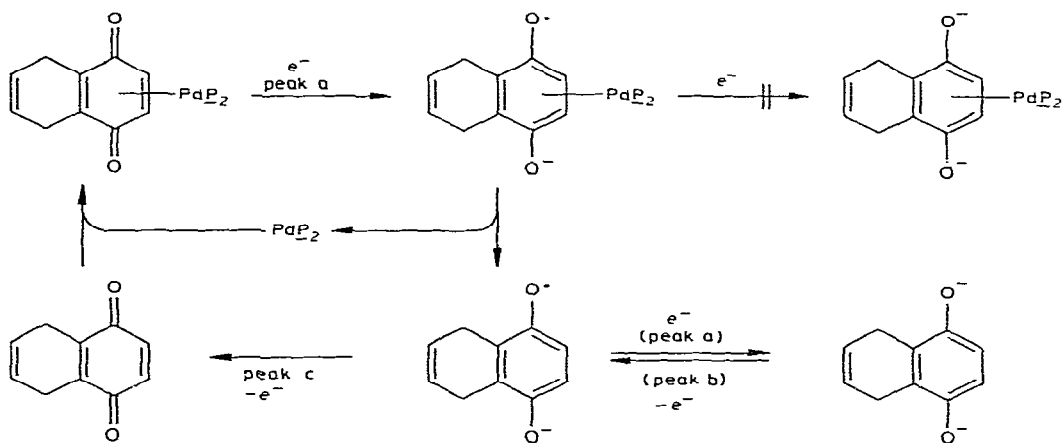


Fig. 2. Cyclic voltammograms for (5,8-dihydro-1,4-naphthoquinone) $\text{Pd}(\text{PPh}_3)_2$ [A], 5,8-dihydro-1,4-naphthoquinone [DHNQ] and $\text{Pd}(\text{PPh}_3)_4$ [B]. Concentration: $10^{-3} M$ for [A] and [DHNQ], $10^{-4} M$ for [B]. Scan rate: 100 mV/sec. With platinum electrode in 0.1 M $\text{NEt}_4\text{PF}_6/\text{CH}_3\text{CN}$ at 25°C .

and (c) were not enlarged. The free DHNQ, which was formed by the oxidation of the radical anion, will coordinate to $\text{Pd}(\text{PPh}_3)_2$ again to regenerate (DHNQ)- $\text{Pd}(\text{PPh}_3)_2$, as is demonstrated by the presence of peak (d) mentioned below.

SCHEME 1



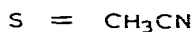
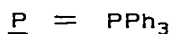
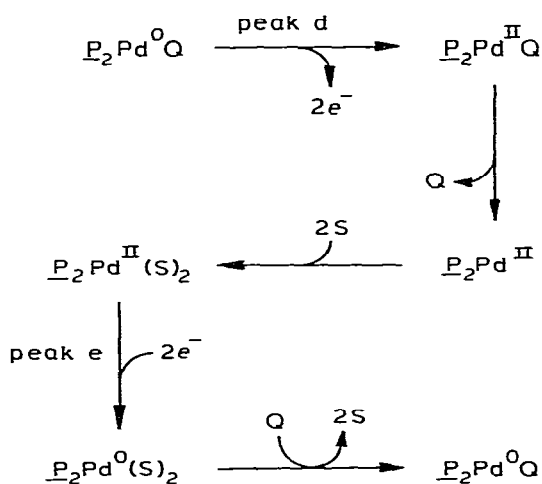
DHNQ

$\underline{P} = \text{PPh}_3$

The facts support the idea that the dissociation of the complex, which is caused by accepting an electron, must lead to irreversibility. From these results, we propose a tentative scheme for electrode reaction of the quinone derivatives (DHNQ) coordinated to palladium(0) as given in Scheme 1.

On the other hand, the oxidation peak (d) for the central palladium(0), which appeared at similar potentials for all the complexes measured, was present at 0.90 V, and the corresponding reduction peak was ill-defined, showing the irreversibility of the electrode reaction. A certain reduction peak (e) always appeared at -0.02 V regardless of the ligand in the complexes, when the complexes were oxidized at potentials more anodic than ca. 0.90 V. The peak (e) may correspond to the reduction of $[\text{Pd}(\text{PPh}_3)_2(\text{CH}_3\text{CN})_2]^{2+}$ which is probably formed by a two-electron oxidation [7] and the subsequent replacement of one quinone ligand in the complex by two solvent molecules. The resulting complex, $\text{Pd}(\text{PPh}_3)_2(\text{CH}_3\text{CN})_2$, reacts with free DHNQ to regenerate (DHNQ)- $\text{Pd}(\text{PPh}_3)_2$. The reduction of $[\text{Pd}(\text{PPh}_3)_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$, prepared to substantiate the assignment of the peak (e) by another method, gave a peak at the same potential. A peak which corresponds to the oxidation of a dihydrobenzene-type site in the complex (DHNQ) $\text{Pd}(\text{PPh}_3)_2$ was not observed in the potential range of our measurements (1.8 V to -1.8 V). Based on these observations, a reaction scheme for palladium(0) coordinated by the quinone derivatives is tentatively proposed as follows (Scheme 2).

SCHEME 2



From these results, it was confirmed that the reduction potentials for quinone derivatives shifted toward the negative, and the oxidation potentials for com-

plexed palladium(0) shifted toward the positive on complexation. The shifts undoubtedly correspond to charge transfer from the central palladium metal to the quinone derivative ligand.

As shown in Table 2, the shifts of reduction potentials for quinone derivatives, $|\Delta E|$, caused by the coordination to palladium(0), indicated a similar dependence on the electron-withdrawing ability of the free quinone derivatives. That is to say, as the electron-withdrawing ability of the acceptors is higher, the quinone derivatives coordinated to palladium(0) are more difficult to reduce. However, the oxidation potentials of the central palladium(0) were almost constant for all complexes of the quinone derivatives. This phenomenon may show that the triphenylphosphine ligands compensate for the reduction in electron density on palladium(0) by the electron-accepting quinone derivatives. To sum up, in these palladium(0) complexes electron density is transferred between ligands via the central palladium atom, and the electron density on the palladium is almost constant regardless of the electron-withdrawing ability of the free quinone derivatives.

Experimental

Chemicals and solvents

All compounds for electrochemical studies were prepared by the literature methods [3,8] and were used after purification by recrystallization or sublimation. $(\text{TCNQ})_2\text{Pd}(\text{PPh}_3)_2$ was prepared by a similar method to that in the literature [3]. TCNQ was used as a ligand in place of quinones. TCNQ (97.8 mg, 0.479 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (553 mg, 0.479 mmol) were dissolved in benzene (20 ml) under argon at room temperature. The mixture was stirred for 24 h at room temperature to precipitate a dark purple powder, which was filtered, washed with benzene and diethyl ether, and dried in vacuo. The product was recrystallized from toluene to yield dark purple crystals of $(\text{TCNQ})_2\text{Pd}(\text{PPh}_3)_2$ (179 mg, 72% yield). Decomp. 211–214°C; IR(CHCl_3) 2204 ($\text{C}\equiv\text{N}$) and 1600 cm^{-1} ($\text{C}=\text{C}$); Found: C, 69.23; H, 3.98. $\text{C}_{60}\text{H}_{38}\text{N}_8\text{P}_2\text{Pd}$ calcd.: C, 69.34; H, 3.69%. $[\text{Pd}(\text{PPh}_3)_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$ was also prepared by the method similar to the literature one [9]. The procedure was based on the higher coordinating ability of triphenylphosphine than that of acetonitrile. Palladium chloride (177 mg, 1.00 mmol) and triphenylphosphine (525 mg, 2.00 mmol) were dissolved in acetonitrile (10 ml) under argon at room temperature to yield a yellow suspension. Silver tetrafluoroborate (389 mg, 2.00 mmol) in acetonitrile (5 ml) was added to the suspension and the mixture was stirred for 18 h at room temperature to afford a yellow solution. The solvent was evaporated, and dried in vacuo. The yellow powder of $[\text{Pd}(\text{PPh}_3)_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$ was obtained (640 mg, 73% yield). Decomp. 102–106°C; Found: C, 54.66; H, 4.44. $\text{B}_2\text{C}_{40}\text{F}_8\text{H}_{36}\text{N}_2\text{P}_2\text{Pd}$ calcd.: C, 54.18; H, 4.09%. Tetraethylammonium hexafluorophosphate (NEt_4PF_6) as supporting electrolyte was prepared by the literature method [10]. The solvents were purified before use. Dimethyl sulfoxide was purified by drying over potassium hydroxide, and distilling at reduced pressure. Acetonitrile was dried over calcium hydride and then phosphorus pentoxide, and distilled repeatedly [11].

Apparatus

The infrared spectra were recorded on a Jasco IRA-3 spectrometer. The polarograms were recorded on a Yanagimoto Polarograph model P8-D, and the cyclic voltamograms were recorded on Hokuto Denko IHB-107A, HA101, and Watanabe X-Y recorder WX441.

Electrochemistry

Unless otherwise stated, the experiments were performed in acetonitrile or dimethyl sulfoxide at a temperature of 25 or 0 (± 1) °C under a nitrogen atmosphere. The concentration of the supporting electrolyte was 0.1 M and that of the electroactive species was 10^{-3} or 10^{-4} M. The working electrode was the dropping mercury electrode (flow rate: 1.19 mg/sec in dimethyl sulfoxide or 1.38 mg/sec in acetonitrile, height of mercury: 70 cm) or the stationary platinum electrode. Ag/AgCl (saturated lithium chloride in acetonitrile or dimethyl sulfoxide) was used as a reference electrode (the experimental errors were ± 0.01 V). In the cyclic voltammetry, the scan rate was 100 mV/sec.

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