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Electron Transfer Activation in the Oxidative Addition of Iodine to Rhodium(I) Complexes

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The kinetics of the oxidative addition of iodine to the following isocyaniderhodium(I) monomers and dimers in MeCN has been examined; $[Rh(RNC)_4]^+$, $[Rh(RNC)_2(PPh_3)_2]^+$, $[Rh_2(dppm)_2(RNC)_4]^{2+}$, and $[Rh_2(dicp)_4]^{2+}$ (R=alkyl, aryl; dppm=bis(diphenylphosphino)methane; dicp=1,3-diisocyanopropane). The reaction proceeds *via* two consecutive steps which consist of the formation of the initial adduct followed by the intramolecular isomerization to yield the final *trans*-adduct. The kinetic results for the first step of the oxidative addition reactions suggest that there exist three kinds of intermediates formed between the Rh(I) complex and iodine with 1:1, 1:2, and 2:1 stoichiometry prior to the formation of the initial adduct. This mechanism coincides with that for the electron transfer reactions between the Rh(I) complexes and inorganic oxidants such as $[Fe(N\text{-}N)_3]^{3+}$ (N-N=1,10-phenanthroline and 2,2′-bipyridine). The values of the rate constants for the first step of the oxidative addition of iodine to dppm- or dicp-bridged Rh(I) dimers are found to agree with those for the electron transfer reactions between the same reactants by using linear free energy relationships. The possibility of electron transfer activation as the rate determining step in the oxidative addition to Rh(I) complexes is discussed.

Coordinatively unsaturated d^8 metal complexes are converted into octahedral d^6 metal complexes by the oxidative addition of polar or highly polarizable addenda such as alkyl halides RX and halogens X_2.[1,2] Despite extensive studies on the mechanism of the oxidative additions from the importance of their key role in various metal catalyzed processes,[1–3] there has been no simple generalization to predict the reactivities of the metal complexes. Such a situation in organo-transition metal chemistry is in a marked contrast to organic reaction systems, where reactivities of organic substrates have been summarized as a number of linear free energy relationships such as the Taft σ^* constant in electrophilic additions of X_2 to olefins and the Brown σ^+ constant in electrophilic aromatic substitutions with X_2.[4] These constants represent donor properties of substituents of the organic substrates, providing quantitative prediction on the change of reactivities of the substrates with different substituents.[5]

Our aim in this study is to understand the change of the reactivities of d^8 metal complexes in the oxidative addition reactions in terms of the donor properties of d^8 metal complexes with various ligands. The system we chose for study is the oxidative addition of iodine to Rh(I) (d^8) complexes.[6,7] Rhodium(I) complexes were selected since we have previously reported the electrochemistry of Rh(I) complexes as well as the electron transfer reactions with inorganic oxidants[8,9] which revealed the donor properties of the Rh(I) complexes. Thus, the kinetic study on the oxidative addition reactions of the same series of Rh(I) complexes with iodine allows the direct comparison of the reactivities as well as the mechanisms for the oxidative addition reactions with those for the electron transfer reactions of the Rh(I) complexes.

Experimental

Materials. Tetrakis(isocyanide)- and bis(isocyanide)-bis(triphenylphosphine)rhodium(I) perchlorates used in this study were prepared as described previously ($[Rh(RNC)_4]^+$: R=*p*-MeC_6H_4, 2,4,6-$Me_3C_6H_2$, Ph, $PhCH_2$, *t*-Bu, C_6H_{11}; $[Rh(RNC)_2(PPh_3)_2]^+$:R=*p*-$MeOC_6H_4$, 2,4,6-$Me_3C_6H_2$).[8,10) Ligand-bridged complexes of Rh(I) dimer of the $[Rh_2(dppm)_2(RNC)_4](ClO_4)_2$ (dppm=bis(diphenylphosphino)methane; R=Ph, *p*-$MeOC_6H_4$, *t*-Bu, $PhCH_2$)[11] were prepared by the addition of dppm to a solution of the corresponding $[Rh(RNC)_4](ClO_4)$ in acetone by the procedure analogous to the literature.[7a,9] Another ligand-bridged complex of Rh(I) dimer, $[Rh_2(dicp)_4]Cl_2$ (dicp=1,3-diisocyanopropane),[12] was prepared by the reaction of dicp with $[Rh(cyclooctadiene)Cl]_2$[13] in chloroform. Since the chloride salt formed in the reaction is sparingly soluble in acetonitrile, the tetraphenylborate salt which is soluble in acetonitrile was prepared by methathesis in methanol. Iodine was sublimed three times prior to use. Acetonitrile used as a solvent for kinetic and electrochemical measurements was purified by a standard procedure.[14]

Kinetic Measurements. Acetonitrile solutions of the Rh(I) complexes as well as those of iodine were freshly prepared before use. The reactions of Rh(I) complexes with iodine were carried out at 298 K in the presence of a large excess of either Rh(I) complexes or iodine. Rates of the reactions were measured by monitoring the change of the absorbance (at 360 nm) due to the reaction by using a Union RA-103 stopped-flow spectrophotometer. The ionic strength of the reaction medium was adjusted to 0.1 with *n*-Bu_4NClO_4. The change of the absorbance at 360 nm was expressed as two consecutive pseudo-first-order steps with significantly different half-lives, *e.g.*, the half-life of the first step was 1.2×10^3 times shorter than the second step for the reaction of $[Rh(2,4,6\text{-}Me_3C_6H_2NC)_4]^+$ (2.43×10^{-4} mol dm^{-3}) with iodine (2.72×10^{-3} mol dm^{-3}) in MeCN at 298 K. The two steps were then well separated by changing the monitoring time scale; the first and the second steps were monitored for 50 ms—1 s and 200—1000 s, respectively. The pseudo-first-order rate constants $k^{(1)}$ and $k^{(2)}$ for the first and the second steps were determined from Eqs. 2 and 3, respectively, by the least squares curve fit, using a microcomputer Union System 77;

$$A^{(1)} = A_\infty^{(1)} + (A_0^{(1)} - A_\infty^{(1)}) \exp(-k^{(1)}t) \tag{2}$$

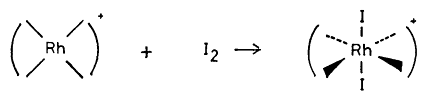
$$A^{(2)} = A_\infty^{(2)} + (A_0^{(2)} - A_\infty^{(2)}) \exp(-k^{(2)}t) \tag{3}$$

where $A^{(1)}$ and $A^{(2)}$ are the absorbances at 360 nm for the first and second steps, respectively, in the two different time scales, $A_0{}^{(1)}$ and $A_0{}^{(2)}$ are the initial absorbances, and $A_\infty{}^{(1)}$ and $A_\infty{}^{(2)}$ are the final absorbances due to the products in the first and second steps, respectively. It should be noted that $A_\infty{}^{(1)}=A_0{}^{(2)}$. It was confirmed that the pseudo-first-order rate constants $k^{(1)}$ and $k^{(2)}$ were independent of the monitoring wavelengths in the range 340—450 nm.

Cyclic Voltammetry. The cyclic voltammograms (CV) of Rh(I) complexes were obtained as described previously.[9)] The CV of iodine in MeCN containing 0.1 mol dm^{-3} n-Bu_4NClO_4 as a supporting electrolyte was measured on a Hokuto Denko Model HA-301 potentiostat/galvanostat at 298 K, using a platinum microelectrode and a Ag/Ag$^+$ ($AgNO_3$ 0.1 mol dm^{-3}) reference electrode. A reversible CV wave was observed at $E_{1/2}=0.34$ V *vs.* Ag/Ag$^+$ with the peak separation of 0.1 V, which corresponds to the two electron processes; $I_2 \overset{2e}{\rightleftharpoons} 2I^-$.

Results and Discussion

Kinetics and Mechanism of Oxidative Addition of Rh(I) Complexes with Iodine. The final products of the oxidative addition of I_2 to Rh(I) complexes have well been established as the *trans*-adducts (Eq. 4).[6,7)] Typical decay curves of the absorbance at 360 nm after mixing $[Rh(2,4,6\text{-}Me_3C_6H_2NC)_4]^+$ and excess I_2 in MeCN at 298 K are shown in Fig. 1, which indicates that the reaction proceeds *via* two consecutive pseudo-first-order steps with different half-lives of 44 ms and 53 s. The reaction rates in the two steps differ from each other sufficiently to allow the determination of both rate constants separately. As shown in Table 1, the pseudo-first-order rate constant $k^{(2)}$ for the second step is independent of the I_2 concentration, while $k^{(1)}$ for the first step varies with the I_2 concentration. Thus, the second step is suggested as an intramolecular process. Since the final product is the *trans*-adduct, the two consecutive steps may consist of the formation of the initial *cis*-adduct followed by the isomerization to the *trans*-adduct (Eqs. 5 and 6). Such an intramolecular *cis-trans* isomerization has been reported also for transition metal complexes of $[Rh(I)_2(dtc)L_2]$ (dtc=S_2CNMe_2, L=2,4,6-$Me_3C_6H_2NC$),[6a)] $[Cr(CO)_4(C(OMe)Me)(PR_3)]$ (R=C_2H_5, C_6H_{11}),[15)] $[Ru(CO)_4(SiCl_3)_2]$,[16)] and $[Os(CO)_4(SiMe_3)_2]$.[16)]



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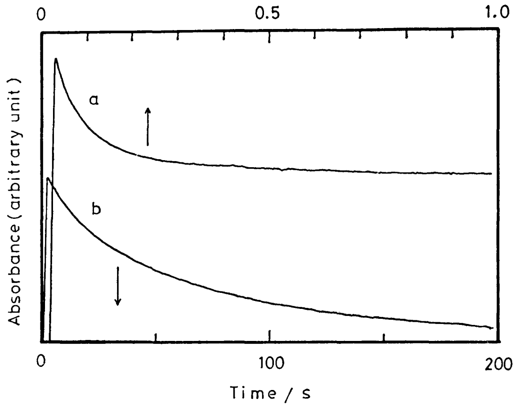


Fig. 1. Decay curves of the absorbance at 360 nm for the reaction of $[Rh(2,4,6\text{-}Me_3C_6H_2NC)_4]^+$ (2.4×10^{-4} mol dm^{-3}) with I_2 (2.7×10^{-3} mol dm^{-3}) in MeCN containing 0.1 mol dm^{-3} n-Bu_4NClO_4 at 298 K; a) monitored for 1 s, b) monitored for 200 s.

Table 1. Observed rate constants for the two consecutive steps for the reactions of Rh(I) complexes with excess I_2 in MeCN at 298 K

$[Rh(2,4,6\text{-}Me_3C_6H_2NC)_4]^+$ (mol dm^{-3})	I_2 (mol dm^{-3})	$k^{(1)}$ / s^{-1}	$k^{(2)}$ / s^{-1}
1.1×10^{-5}	1.2×10^{-4}	1.2	1.3×10^{-2}
1.8×10^{-5}	2.0×10^{-4}	2.0	1.3×10^{-2}
3.1×10^{-5}	3.3×10^{-4}	2.4	1.3×10^{-2}
5.1×10^{-5}	5.5×10^{-4}	3.6	1.2×10^{-2}
8.8×10^{-5}	5.9×10^{-4}	2.7	1.3×10^{-2}
8.8×10^{-5}	9.8×10^{-4}	5.1	1.3×10^{-2}
1.5×10^{-4}	1.6×10^{-3}	7.3	1.4×10^{-2}
$[Rh(PhCH_2NC)_4]^+$ (mol dm^{-3})			
5.7×10^{-5}	6.9×10^{-4}	1.7	1.0×10^{-2}
9.5×10^{-5}	1.2×10^{-3}	2.6	1.0×10^{-2}
1.6×10^{-4}	1.9×10^{-3}	3.5	1.0×10^{-2}
2.7×10^{-4}	3.2×10^{-3}	5.3	8.9×10^{-3}

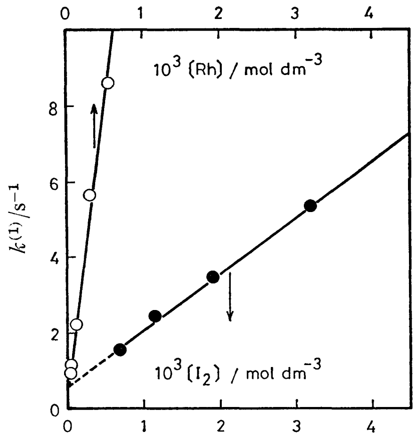
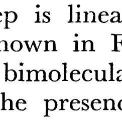


Fig. 2. Kinetics of the oxidative addition of $[Rh(PhCH_2NC)_4]^+$ with I_2; the pseudo-first-order rate constant $k^{(1)}$ for the first step as a function of large excess I_2 (●) or $[Rh(PhCH_2NC)_4]^+$ (○) in MeCN at 298 K.

$$[RhL_4]^+ + I_2 \xrightarrow{k^{(1)}} [RhL_4(I)_2]^+ \qquad (5)$$

$[RhL_4(I)_2]^+ \xrightarrow{k^{(2)}}$


(6)

On the other hand, the pseudo-first-order rate constant $k^{(1)}$ for the first step is linearly dependent on the I_2 concentration as shown in Fig. 2. Thus, the first step may involve a bimolecular process. However, the $k^{(1)}$ values in the presence of large excess Rh(I) complex differ significantly from those in the presence of large excess I_2 when they are compared at the same concentrations as seen in Fig. 2, where the reaction of $[Rh(PhCH_2NC)_4]^+$ with I_2 is illustrated as a typical example. Such different $k^{(1)}$ values suggest that the reactive species are different, depending upon the conditions where either I_2 or the Rh(I) complex is present in large excess. Since the extrapolated $k^{(1)}$ values to the zero concentration in both cases, *i.e.*, the intercepts in Fig. 2, are the same,

TABLE 2. RATE CONSTANTS FOR THE REACTIONS OF Rh(I) COMPLEXES WITH I_2 AND INORGANIC OXIDANTS IN MeCN AT 298 K[a)]

No.	Rh(I) Monomer	I_2		$[Fe(phen)_3]^{3+}$ b)		$[Co(bpy)_3]^{3+}$ c)	
		k_1 / s^{-1}	k_2K_2 / $mol^{-1}\,dm^3\,s^{-1}$	k_1' / s^{-1}	$k_2'K_2'$ / $mol^{-1}\,dm^3\,s^{-1}$	k_1' / s^{-1}	$k_1'K_2'$ / $mol^{-1}\,dm^3\,s^{-1}$
1	$[Rh(p\text{-}MeC_6H_4NC)_4]^+$	8.1×10^{-1}	1.3×10^3	4.6×10	8.5×10^5		
2	$[Rh(2,4,6\text{-}Me_3C_6H_2NC)_4]^+$	6.3×10^{-1}	5.5×10^3	2.0×10	4.3×10^5	1.0×10^{-6}	1.9×10^{-4}
3	$[Rh(PhNC)_4]^+$	9.3×10^{-1}	3.4×10^3	3.2×10	6.1×10^5		
4	$[Rh(PhCH_2NC)_4]^+$	8.5×10^{-1}	1.4×10^3	4.6×10	1.5×10^6		
5	$[Rh(t\text{-}BuNC)_4]^+$	2.8×10^{-1}	1.1×10^3	4.0×10	8.0×10^5	1.5×10^{-6}	1.9×10^{-4}
6	$[Rh(C_6H_{11}NC)_4]^+$	1.3	1.5×10^3	7.2×10	8.1×10^5		
7	$[Rh(p\text{-}MeOC_6H_4NC)_2(PPh_3)_2]^+$	2.3	1.3×10^3	4.0×10	3.5×10^5		
8	$[Rh(2,4,6\text{-}Me_3C_6H_2NC)_2(PPh_3)_2]^+$	2.1	1.7×10^3	6.5	1.4×10^5		
	Rh(I) Dimer						
9	$[Rh_2(dppm)_2(t\text{-}BuNC)_4]^{2+}$	6.8×10	4.4×10^5				
10	$[Rh_2(dppm)_2(p\text{-}MeC_6H_4NC)_4]^{2+}$	5.7×10	1.5×10^5			5.5×10^{-2}	4.4×10
11	$]Rh_2(dppm)_2(PhCH_2NC)_4]^{2+}$	1.1×10^2	2.7×10^5			6.3×10^{-2}	6.2
12	$[Rh_2(dppm)_2(PhNC)_4]^{2+}$	3.9×10^2	1.1×10^5			8.2×10^{-2}	1.1×10
13	$[Rh_2(dicp)_4]^{2+}$	4.8×10^2	5.8×10^5				

a) Containing 0.1 mol dm^{-3} n-Bu_4NClO_4. b) From Ref. 8. c) From Ref. 9.

$$[RhL_4]^+ + I_2 \overset{K_1}{\rightleftharpoons} ([RhL_4]^+\ I_2) \xrightarrow{k_1} [RhL_4(I)_2]^+ \quad (7)$$

I_2 in excess

$$([RhL_4]^+I_2) + I_2 \overset{K_2}{\rightleftharpoons} ([RhL_4]^+\ 2I_2) \xrightarrow{k_2} [RhL_4(I)_2]^+ + I_2 \quad (8)$$

$[RhL_4]^+$ in excess

$$([RhL_4]^+\ I_2) + [RhL_4]^+ \overset{K_3}{\rightleftharpoons} (2[RhL_4]^+\ I_2) \xrightarrow{k_3} [RhL_4(I)_2]^+ + [RhL_4]^+ \quad (9)$$

Scheme 1.

it is suggested that there exist three kinds of intermediates, one of which is common for both cases. Thus, the kinetics for the first step may best be interpreted by assuming three kinds of complexes formed between the Rh(I) cation and I_2 with 1:1, 1:2, and 2:1 stoichiometry (Scheme 1). According to Scheme 1, the pseudo-first-order rate constants $k_I^{(1)}$ and $k_{RR}^{(1)}$ for the first step are expressed by Eqs. 10 and 11 in the presence of excess I_2 and $[RhL_4]^+$, respectively, when a steady state approximation is applied to the three complexes with 1:1, 1:2, and 2:1 mole ratios. When $K_1[I_2]$, $K_1[Rh] \gg 1$ and $K_2[I_2]$, $K_3[Rh] \ll 1$, Eqs. 10 and 11 are reduced to Eqs. 12 and 13, respectively.

$$k_I^{(1)} = \frac{k_1K_1[I_2] + k_2K_1K_2[I_2]^2}{1 + K_1[I_2] + K_1K_2[I_2]^2} \quad (10)$$

$$k_{RR}^{(1)} = \frac{k_1K_1[Rh] + k_3K_1K_3[Rh]^2}{1 + K_1[Rh] + K_1K_3[Rh]^2} \quad (11)$$

Thus, the intercept of the plots of $k_I^{(1)}$ vs. $[I_2]$ and $k_{RR}^{(1)}$ vs. [Rh] in Fig. 2 gives the k_1 value and the slopes of $k_I^{(1)}$ and $k_{RR}^{(1)}$ yield the k_2K_2 and k_3K_3 values, respectively. The same kinetic formulation as Eq. 12 was applied to dppm- and dicp-bridged Rh(I)

$$k_I^{(1)} = k_1 + k_2K_2[I_2] \quad (12)$$

$$k_{RR}^{(1)} = k_1 + k_3K_3[Rh] \quad (13)$$

dimers, $[Rh_2(dppm)_2(RNC)_4]^{2+}$ and $[Rh_2(dicp)_4]^{2+}$, as well as other $[RhL_4]^+$ monomers. The k_1 and k_2K_2 values for reactions of these complexes in the presence of excess I_2 are listed in Table 2.

Mechanistic Comparison for Reactions of Rh(I) Complexes between the Oxidative Addition of Iodine and the Electron Transfer with Inorganic Oxidants. The Rh(I) complexes employed in this study are readily oxidized by inorganic oxidants such as $[Fe(N\text{-}N)_3]^{3+}$ (N-N= 1,10-phenanthroline and 2,2′-bipyridine) and $[Co(bpy)_3]^{3+}$ (bpy=2,2′-bipyridine) (Eq. 14);[8,9)]

$$[RhL_4]^+ + Ox \longrightarrow [RhL_4]^{2+} + Ox^- \quad (14)$$

where Ox represents the inorganic oxidants. Based on the kinetic study the following scheme has previously been presented for the electron transfer reactions between the Rh(I) complexes and inorganic oxidants;[8,9)]

$$[RhL_4]^+ + Ox \overset{K_1'}{\rightleftharpoons} ([RhL_4]^+\ Ox) \xrightarrow[\text{e.t.}]{k_1'} \quad (15)$$

$$([RhL_4]^+\ Ox) + Ox \overset{K_2'}{\rightleftharpoons} ([RhL_4]^+\ 2Ox) \xrightarrow[\text{e.t.}]{k_2'} \quad (16)$$

$$([RhL_4]^+\ Ox) + [RhL_4]^+ \overset{K_3'}{\rightleftharpoons} (2[RhL_4]^+\ Ox) \xrightarrow[\text{e.t.}]{k_3'} \quad (17)$$

Scheme 2.

where e.t. represents the electron transfer reaction in Eq. 14. It is noteworthy that Scheme 1 for the oxidative addition of Rh(I) complexes with I_2 is equivalent to Scheme 2 for the electron transfer reactions of the same Rh(I) complexes with inorganic oxidants, as characterized by three kinds of complexes formed between the Rh(I) cation and I_2 or Ox with 1:1, 1:2, and 2:1 stoichiometry. Such complex formation may occur through the d_{z^2} HOMO orbital of the Rh(I) complex[17)] since a given Rh(I) complex can interact with I_2, Ox, or another Rh(I) complex at both sides of the square-planar Rh(I) complex. The

TABLE 3. THE $E^{\mathrm{p}}_{\mathrm{ox}}-E^{0}_{\mathrm{red}}$ VALUES FOR REDOX PAIRS BETWEEN Rh(I) COMPLEXES AND I_2 AS WELL AS INORGANIC OXIDANTS ($[\mathrm{Fe(phen)_3}]^{3+}$ AND $[\mathrm{Co(bpy)_3}]^{3+}$)[a]

	$(E^{\mathrm{p}}_{\mathrm{ox}}-E^{0}_{\mathrm{red}})$/V		
	I_2	$[\mathrm{Fe(phen)_3}]^{3+}$	$[\mathrm{Co(bpy)_3}]^{3+}$
$[\mathrm{Rh}(p\text{-}\mathrm{MeC_6H_4NC})_4]^+$	0.72	0.33	1.09
$[\mathrm{Rh}(2,4,6\text{-}\mathrm{Me_3C_6H_2NC})_4]^+$	0.80	0.41	1.17
$[\mathrm{Rh(PhNC)_4}]^+$	0.84	0.45	1.21
$[\mathrm{Rh(PhCH_2NC)_4}]^+$	0.73	0.34	1.10
$[\mathrm{Rh}(t\text{-}\mathrm{BuNC})_4]^+$	0.86	0.47	1.23
$[\mathrm{Rh(C_6H_{11}NC)_4}]^+$	0.75	0.36	1.21
$[\mathrm{Rh_2(dppm)_2}(t\text{-}\mathrm{BuNC})_4]^{2+}$	0.29	−0.10	0.66
$[\mathrm{Rh_2(dppm)_2(PhCH_2NC)_4}]^{2+}$	0.28	−0.11	0.65
$[\mathrm{Rh_2(dppm)_2(PhNC)_4}]^{2+}$	0.34	−0.05	0.71
$[\mathrm{Rh_2(dicp)_4}]^{2+}$	0.22	−0.17	0.59

a) The $E^{\mathrm{p}}_{\mathrm{ox}}$ values of Rh(I) complexes and the E^{0}_{red} values of inorganic oxidants were taken from Refs. 9 and 8, respectively.

kinetic formulation for the electron transfer reactions (Eqs. 18 and 19)[8] also is equivalent to that for the first step for the oxidative addition reactions (Eqs. 12 and 13);

$$k'_{\mathrm{ox}} = k'_1 + k'_2K'_2[\mathrm{Ox}] \qquad (18)$$

$$k'_{\mathrm{Rh}} = k'_1 + k'_3K'_3[\mathrm{Rh}] \qquad (19)$$

where k'_{ox} and k'_{Rh} are the pseudo-first-order rate constants in the presence of excess oxidant and Rh(I) complex, respectively. The k'_1 and $k'_2K'_2$ values for the electron transfer reactions of the Rh(I) complexes with the inorganic oxidants have been determined previously from the intercepts and the slopes of the plots between k'_{ox} and [Ox] by the same manner as described above,[8] and relisted in Table 2 for comparison.

In addition to the similarity in the reaction scheme between the oxidative addition (Scheme 1) and the electron transfer reactions (Scheme 2), there can be seen similarities in the reactivity patterns of the Rh(I) complexes as well. In both oxidative additions and electron transfer reactions, the k_1 and k_2K_2 values as well as the k'_1 and $k'_2K'_2$ values for ligand bridged Rh(I) dimers $[\mathrm{Rh_2(dppm)_2(RNC)_4}]^{2+}$ and $[\mathrm{Rh_2(dicp)_4}]^{2+}$ are significantly larger than those for Rh(I) monomers $[\mathrm{Rh(RNC)_4}]^+$. Moreover, the rate constants for Rh(I) monomers as well as Rh(I) dimers are approximately constant in both reactions, independent of the ligands. Such similarities in the reactivity patterns of Rh(I) complexes as well as the reaction scheme between the oxidative additions and the electron transfer reactions indicate that the activation process for the oxidative addition is analogous to that for the electron transfer shown in Eq. 20,

$$([\mathrm{RhL_4}]^+\ I_2) \xrightarrow{\text{e.t.}} ([\mathrm{RhL_4}]^{2+}\ I_2^-)^{\ddagger} \qquad (20)$$

where the double dagger represents the activated complex. Attachment of electron to I_2 is known to cause the dissociation of the I–I bond since the ground state energy of I_2 is 1.5 eV higher than the dissociation limit for I_2^- (Eq. 21).[18] Thus, electron transfer from

$$I_2 \xrightarrow{e} I\cdot + I^- \qquad (21)$$

$[\mathrm{RhL_4}]^+$ to I_2 would result in the facile dissociation of I–I bond, followed by the geminate recombination between the $[\mathrm{RhL_4}]^{2+}$ and I· radicals to yield the adduct as the first step (Eq. 22). In the next section,

$$([\mathrm{RhL_4}]^{2+}I_2^-)^{\ddagger} \longrightarrow [\mathrm{RhL_4(I)_2}]^+ \qquad (22)$$

the rate constants for the oxidative additions of Rh(I) complexes with I_2 are compared with those of the posturated electron transfer reactions (Eq. 20) in a quantitative manner with the aid of linear free energy relationships.

Quantitative Comparison of Rate Constants between the Oxidative Additions and the Electron Transfer Reactions of Rh(I) Complexes. Previously, we have established a linear free energy relationship (LFER) for the electron transfer reactions of Rh(I) complexes with inorganic oxidants (Eq. 14), which can be expressed as Eq. 23,[9,19]

$$\log k'_1 = -8.6(E^{\mathrm{p}}_{\mathrm{ox}}-E^{0}_{\mathrm{red}}) + \mathrm{Const.} \qquad (23)$$

where k'_1 stands for the rate constant (Eq. 15), $E^{\mathrm{p}}_{\mathrm{ox}}$ is the anodic current peak potential in the cyclic voltammogram of the Rh(I) complex at a constant sweep rate (100 mV s^{-1}), and E^{0}_{red} is the standard reduction potential of the oxidant. Thus, the rate constant for the electron transfer reaction from the Rh(I) complex to I_2 (Eq. 20) may be evaluated by substituting the reduction potential of I_2 into Eq. 23. The reduction potential may be approximated by the $E_{1/2}$ value of I_2 obtained in the Experimental section, since the peak separation (0.1 V) is close to that for one electron reversible process (0.06 V).[20,21] The $E^{\mathrm{p}}_{\mathrm{ox}}-E^{0}_{\mathrm{red}}$ values for the redox pairs between the Rh(I) complexes and I_2 as well as the representative inorganic oxidants are listed in Table 3.

The plot of Eq. 23 is shown by open circles in Fig. 3a, where the plot of the log k_1 values for the oxidative additions of Rh(I) complexes with I_2 against the $E^{\mathrm{p}}_{\mathrm{ox}}-E^{0}_{\mathrm{red}}$ values (Table 3) also is given by closed circles. The log k_1 values for the Rh(I) dimers (Nos. 9, 11—13) agree well with the solid line which represents the rate constant when electron transfer reactions between the cationic Rh(I) complexes and I_2 would occur (Eq. 20). The k_2K_2 values for the same

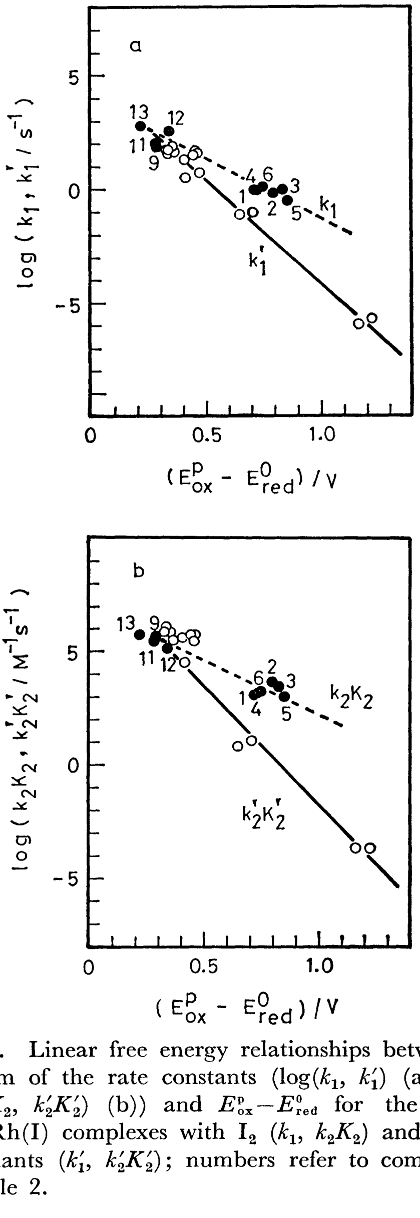


Fig. 3. Linear free energy relationships between logarithm of the rate constants ($\log(k_1, k_1')$ (a) and $\log(k_2K_2, k_2'K_2')$ (b)) and $E^p_{ox}-E^0_{red}$ for the reactions of Rh(I) complexes with I_2 (k_1, k_2K_2) and inorganic oxidants (k_1', $k_2'K_2'$); numbers refer to compounds in Table 2.

Rh(I) dimers also are in agreement with those for the electron transfer rate constant $k_2'K_2'$ drawn by the solid line in Fig. 3b, which barrs fortuitous coincidences. Such agreement of the absolute values of k_1 as well as k_2K_2 for the oxidative additions of I_2 to the Rh(I) dimers with those for the electron transfer reactions strongly suggests that the activation process in the first step of the oxidative additions is electron transfer from the Rh(I) complexes to I_2 as shown in Eq. 20.

The k_1 and k_2K_2 values decrease with increasing the $E^p_{ox}-E^0_{red}$ values as shown by the dotted lines in Figs. 3a and 3b. The differences between the Rh(I) dimers (Nos. 9, 11—13) and the Rh(I) monomers (Nos. 1—6) are remarkable both in k_1 and in k_2K_2. These values for the Rh(I) monomers, however, lie somewhat above the solid lines which represent the electron transfer rate constants. Accordingly the slopes of the linear free energy relationships for the oxidative additions are smaller than those for the electron transfer reactions. The linear free energy relationships in Figs. 3a and 3b themselves are not a definitive proof for the occurrence of complete electron transfer in the activation process of the oxidative addition reactions of I_2 to the Rh(I) complexes since the reaction *via* an intermediate with greater or lesser charge-transfer character is expected to show similar trends.[22,23] The description of the activation process as the complete electron transfer in Eq. 20, however, enables us to evaluate the rate constants for the oxidative additions of the Rh(I) dimers with I_2 as the rate constants for the electron transfer reactions in the same systems as shown in Figs. 3a and 3b. Since the solid lines in Figs. 3a and 3b represent the electron transfer rate constants, the larger rate constants for the oxidative additions of the Rh(I) monomers with I_2 than expected from the solid lines in Figs. 3a and 3b may be regarded as arising from the stronger interaction of the Rh(I) monomers with I_2 in the transition state of electron transfer in Eq. 20 than that with the inorganic oxidants.

A similar electron transfer mechanism has been presented by Tsou and Kochi[24] for the oxidative addition of aryl halides to tetrakis(triethylphosphine)-nickel, in which the second-order rate constant (log k) were linearly related to the polarographic $E_{1/2}$ values of aryl halides. Our study has shown that there exists a mechanistic similarity between the oxidative addition of Rh(I) complexes with I_2 and the electron transfer reactions with inorganic oxidants $[Fe(N\text{-}N)_3]^{3+}$ and $[Co(bpy)_3]^{3+}$, and that the absolute values of the rate constants for the oxidative additions can be approximated by the rate constants for the electron transfer reactions from the Rh(I) complexes to I_2. The generalization of the electron transfer mechanism for the oxidative additions of Rh(I) complexes with I_2 described above or its utility to predict the rate constants for oxidative additions of other metal complexes with different substrates remains to be elaborated in further studies.

References

1) J. Halpern, *Acc. Chem. Res.*, **3**, 386 (1970); R. Cramer, *ibid.*, **1**, 186 (1968); R. Crabtree, *ibid.*, **12**, 331 (1979); L. Vaska, *ibid.*, **1**, 335 (1968); E. L. Muetterties and J. R. Bleeke, *ibid.*, **12**, 324 (1979); J. Halpern, *Inorg. Chim. Acta*, **50**, 11 (1981); R. D. W. Kemmit and M. A. R. Smith, *Inorg. React. Mech.*, **3**, 451 (1974).

2) J. K. Kochi, "Organometallic Mechanisms and Catalysis," Academic Press, New York, (1978).

3) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 4th ed, Wiley-Interscience, New York (1980), p. 1243, and references cited therein.

4) N. B. Chapman and J. Shorter, "Correlation Analysis in Chemistry," Plenum Press, New York, (1978); L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, **1**, 35 (1963); R. W. Taft, Jr., "Steric Effects in Organic Chemistry," ed by M. S. Newman, Wiley, New York (1956), p. 556; N. B. Chapman and J. Shorter, "Advances in Linear Free Energy Relationships," Plenem Press, London (1972).

5) S. Fukuzumi and J. K. Kochi, *J. Am. Chem. Soc.*, **103**, 2783, 7240 (1981).

6) a) R. Kuwae, T. Tanaka, and K. Kawakami, *Bull. Chem. Soc. Jpn.*, **52**, 437 (1979); b) R. Kuwae and T. Tanaka,

ibid., **52**, 1067 (1979).

7) a) A. L. Balch, *J. Am. Chem. Soc.*, **98**, 8049 (1976); b) N. S. Lewis, K. R. Mann, J. G. Gordon, II, and H. B. Gray, *ibid.*, **98**, 7461 (1976); c) J. T. Mague, M. O. Nutt, *Inorg. Chem.*, **16**, 1259 (1977).

8) S. Fukuzumi, N. Nishizawa, and T. Tanada, *Bull. Chem. Soc. Jpn.*, in press.

9) S. Fukuzumi, N. Nishizawa, and T. Tanaka, *Bull. Chem. Soc. Jpn.*, **55**, 2892 (1982).

10) T. Iinuma and T. Tanaka, *Inorg. Chim. Acta*, **49**, 79 (1981).

11) W. Hewertson and H. R. Watson, *J. Chem. Soc.*, **1962**, 1490.

12) W. P. Weber, G. W. Gokel, and I. K. Ugi, *Angew. Chem., Int. Ed. Engl.*, **11**, 530 (1972).

13) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, **1957**, 4735.

14) D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals," Pergamon Press, New York (1966).

15) H. Fischer, E. O. Fischer, and H. Werner, *J. Organomet. Chem.*, **73**, 331 (1974).

16) R. K. Pomeroy and W. A. G. Graham, *J. Am. Chem. Soc.*, **94**, 274 (1972).

17) H. Isci and W. R. Mason, *Inorg. Chem.*, **14**, 913 (1975).

18) A. D. McLean, O. Gropen, and S. Huzinaga, *J. Chem. Phys.*, **73**, 396 (1980); R. F. Barrow, D. F. Broyd, L. B. Pederson, and K. K. Yee, *Chem. Phys. Lett.*, **18**, 357 (1973).

19) The $E^{\mathrm{p}}_{\mathrm{ox}}-E^{0}_{\mathrm{red}}$ value can be taken as the free energy change of electron transfer reaction from the Rh(I) complex to the oxidant, $\Delta G^0+\mathrm{Const.}$[9)]

20) W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice Hall, Englewood Cliffs, N. J. (1952), p. 62.

21) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

22) I. E. Kochevar and P. J. Wagner, *J. Am. Chem. Soc.*, **94**, 3859 (1972); J. B. Gutteplan and S. G. Cohen, *ibid.*, **94**, 4040 (1972); B. M. Monroe, C. G. Lee, and N. J. Turro, *Mol. Photochem.*, **6**, 271 (1974); F. Wilkinson and A. Garner, *J. Chem. Soc., Faraday Trans. 2*, **73**, 222 (1977).

23) C. Walling, *J. Am. Chem. Soc.*, **102**, 6854 (1980).

24) T. T. Tsou and J. K. Kochi, *J. Am. Chem. Soc.*, **101**, 6319 (1979).