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Kinetics of the Oxidative Addition Reaction of Iodine to (Dimethyldithiocarbamato)bis(2,4,6-trimethylphenyl isocyanide)rhodium(I)

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The reaction of Rh(dtc)L_2 (dtc=$S_2CN(CH_3)_2$, L=2,4,6-$(CH_3)_3C_6H_2NC$) with an equimolar amount of iodine yields a *trans* adduct, RhI_2(dtc)L_2. The rate of this reaction was measured in benzene, employing a stopped-flow technique under pseudo-first-order conditions with excess iodine. The result indicates that the reaction proceeds *via* a charge transfer complex Rh(dtc)$L_2 \cdot I_2$, which is rearranged in two consecutive zero-order reactions with respect to the I_2 concentration; the rearrangement of Rh(dtc)$L_2 \cdot I_2$ to a *cis* adduct followed by isomerization to the *trans* adduct. This mechanism is supported from kinetic data for the reaction of Rh(acac)L_2 (acac=$CH_3COCHCOCH_3$) with I_2. It is also described that RhI(I_3)(dtc)L_2 and RhI(I_3)(acac)L_2 were obtained by reactions of Rh(dtc)L_2 and Rh(acac)L_2 with excess iodine, respectively.

Coordinatively unsaturated rhodium(I) complexes undergo oxidative addition reactions with various organic and inorganic molecules.[1,2] The interest in these reactions stems partly from their catalytic implications.[3] Recently, kinetic studies have been reported for the reactions of Rh(I) substrates with hydrogen,[4,5] oxygen,[5] organic halides,[5–7] and olefins.[5,8,9] However, little is known concerning the mechanism of the addition reactions of halogen, although various halogen adducts of Rh(I) have been isolated.[2,10–14]

This paper reports the kinetic study on the reactions of (dimethyldithiocarbamato)bis(2,4,6-trimethylphenyl isocyanide)rhodium(I), Rh(dtc)L_2, and (acetylacetonato)bis(2,4,6-trimethylphenyl isocyanide)rhodium(I), Rh(acac)L_2, with iodine giving *trans*-RhI_2(dtc)L_2 and -RhI_2(acac)L_2, respectively. The isolation of RhI(I_3)(dtc)L_2 and RhI(I_3)(acac)L_2 is also described.

Experimental

Materials. Rh(dtc)L_2[15] and Rh(acac)L_2[16] (L=2,4,6-$(CH_3)_3C_6H_2NC$, dtc=$S_2CN(CH_3)_2$, acac=$CH_3COCHCOCH_3$) were prepared as described previously. Iodine was sublimed three times. Benzene was purified by the usual method.[17]

Equimolar Reactions of Rh(dtc)L_2 and Rh(acac)L_2 with Iodine. Iodine (0.74 mmol) was added to a suspension of Rh(dtc)L_2 (0.74 mmol) in diethyl ether (70 ml), and the mixture was stirred for 10 h. The resulting precipitate was recrystallized from a mixture of benzene and cyclohexane to give reddish brown crystals of RhI_2(dtc)L_2 in a 69% yield. Found: C, 36.38; H, 3.63; N, 5.41%; mol wt, 798 in $CHCl_3$ at 37 °C. Calcd for $C_{23}H_{28}I_2N_3S_2Rh$: C, 36.00; H, 3.68; N, 5.48%; mol wt, 767.

The analogous acac complex, RhI_2(acac)L_2, was similarly obtained by the reaction of Rh(acac)L_2 with an equimolar amount of I_2 in a 68% yield. Found: C, 40.48; H, 3.97; N, 3.83%; mol wt, 754 in $CHCl_3$ at 37 °C. Calcd for $C_{25}H_{29}I_2N_2O_2Rh$: C, 40.24; H, 3.92; N, 3.75%; mol wt, 746.

Reaction of Rh(dtc)L_2 or Rh(acac)L_2 with Excess Iodine. To a suspension of Rh(dtc)L_2 (0.74 mmol) in diethyl ether (40 ml) was added large excess iodine (7.4 mmol), and the mixture was stirred for 15 h. The resulting precipitate was washed with diethyl ether to remove unreacted iodine and recrystallized from tetrahydrofuran (THF)–petroleum ether to give dark brown crystals of RhI_4(dtc)$L_2 \cdot 3/4$THF in a 64% yield. Found: C, 28.85; H, 3.13; N, 3.79%. Calcd for $C_{26}H_{34}I_4N_3O_{3/4}S_2Rh$: C, 29.04; H, 3.19; N, 3.91%. This compound was prepared also by the reaction of RhI_2(dtc)L_2 with excess iodine in diethyl ether, and recrystallized from THF–petroleum ether.

The corresponding acac complex, RhI_4(acac)L_2, was similarly obtained by the reaction of Rh(acac)L_2 with excess iodine in a 41% yield. Found: C, 29.84; H, 2.91; N, 2.87%. Calcd for $C_{25}H_{29}I_4N_2O_2Rh$: C, 30.03; H, 2.92; N, 2.80%.

Kinetic and Other Measurements. Kinetic runs were performed by using a Union RA-413 stopped-flow spectrophotometer equipped with a 0.2 cm quartz cell in a cell holder thermostated to ±0.2 °C, under pseudo-first-order conditions by mixing a benzene solution of the Rh(I) substrate (1.0×10^{-4} M) with excess iodine in benzene (1.0—4.0×10^{-3} M). The rate of reaction was measured by following the decay of absorbance at 370 nm with time. At least five reaction curves were accumulated by a Union System-71 kinetic data processor and an average curve was recorded on a National VP-6421A X-Y recorder.

Molecular weights, infrared, and ^{1}H NMR spectra were measured as described elsewhere.[18] Electronic spectra in benzene or toluene were recorded on a Hitachi 124 spectrophotometer.

Results and Discussion

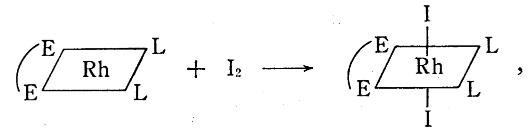
Characterization of Reaction Products. Table 1 shows relevant infrared frequencies (in $CHCl_3$) and ^{1}H NMR chemical shifts (in $CDCl_3$) of the four adducts obtained here. The 1:1 adducts exhibit two ν(N≡C) bands, whose frequencies are higher than those of the Rh(I) substrates, confirming the occurrence of oxidative addition reactions[10,12,13] with the retention of mutual *cis* positions of the two isocyanide ligands. The ^{1}H

TABLE 1. ν(N≡C) FREQUENCIES (in $CHCl_3$, cm^{-1}) AND ^{1}H NMR CHEMICAL SHIFTS (in $CDCl_3$, ppm) OF THE ADDUCTS

Adduct	ν(N≡C)$^{a)}$	δ(dtc- or acac-Me)	δ(2,6-Me)	δ(4-Me)	δ(3,5-H)
RhI_2(dtc)L_2	2187, 2203	3.32	2.51	2.30	6.88
RhI_2(acac)L_2	2199, 2215	2.11	2.52	2.32	6.92
RhI_4(dtc)$L_2 \cdot$ 3/4THF	2181, 2197	3.36	2.50	2.33	6.97
RhI_4(acac)L_2	2200, 2215	2.12	2.51	2.32	6.95

a) Rh(dtc)L_2: 2057 and 2120 cm^{-1}, Rh(acac)L_2: 2082 and 2147 cm^{-1}.

NMR spectrum of $RhI_2(dtc)L_2$ shows only a signal for the dtc-methyl and the isocyanide protons, respectively (Table 1), suggesting that both of the two dtc-methyl groups and the two isocyanide ligands are magnetically equivalent, respectively. These results imply that $RhI_2(dtc)L_2$ assumes an octahedral geometry, in which dtc and two isocyanides are located in an equatorial plane with the two iodide ligands in axial positions. The same geometry is suggested for $RhI_2(acac)L_2$ on the basis of infrared and ^1H NMR spectra. The ^1H NMR spectrum of a benzene-d_6 solution containing equimolar amounts (5.0×10^{-2} M) of $Rh(dtc)L_2$ or $Rh(acac)L_2$ and I_2 showed no signal other than those assignable to $RhI_2(dtc)L_2$ or $RhI_2(acac)L_2$. Thus, the stoichiometry for the addition reaction of equimolar iodine to the rhodium substrate is expressed by



where E–E stands for dtc (E=S) or acac (E=O).

The $RhI_4(dtc)L_2$ and $RhI_4(acac)L_2$ complexes may be formulated as $RhI(I_3)(dtc)L_2$ and $RhI(I_3)(acac)L_2$ respectively, both of which involve a triiodide anion, since trivalent rhodium is known to assume a hexa-coordinated geometry. Coordination of I_3^- to metal ions has been proposed for some Pt(II)[19,20] and Fe(III)[21] complexes.

Kinetics and Mechanism. As shown in Fig. 1, benzene solutions of $Rh(dtc)L_2$ and I_2 exhibit absorption maxima at 352 (ε 14000) and 500 nm (ε 1200) in the electronic spectra, respectively. Immediately after mixing of these solutions, however, appeared an absorption maximum at 370 nm, which decreased with a half-life of about 3 ms, as shown in Fig. 2. This Figure was obtained by plotting $A_t - A_\infty$ at nine different wavelengths in the 340—400 nm range against time, where A_t and A_∞ are absorbances at a given wavelength at the time "t" and at the end of reaction. This result indicates the formation of a transient intermediate during the dead time of the instrument, followed by its rapid degradation. The mixing of $Rh(acac)L_2$ with excess I_2 in benzene also gave a similar short-lived absorption maximum at 360 nm (half-life; about 4 ms at 25.1 °C). In view of the fact that the absorption maxima observed in the two reaction systems do not coincide in wavelength with each other, those bands may not be associated with a common chemical species, such as the I_3^- anion, although this anion formed by mixing $(n\text{-}C_4H_9)_4NI$ with I_2 in benzene[22] exhibited an absorption maximum at 367 nm. Alternatively, the 370 nm band which occurred in the $Rh(dtc)L_2$–I_2 system may be assigned to the charge transfer (CT) transition from the dtc-sulfur atom to the I_2 molecule, by analogy with the fact that both $(CH_3)_2Sn\{S_2CN(C_2H_5)_2\}_2$[23] and $Zn\{S_2CN(n\text{-}C_4H_9)_2\}_2$[24] react with I_2 to yield short-lived absorptions at 385 and 360 nm, respectively, assignable to CT transitions of the same

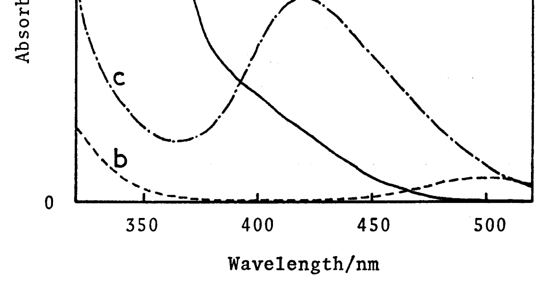


Fig. 1. Electronic spectra of $Rh(dtc)L_2$ (**a**), I_2 (**b**), and *trans*-$RhI_2(dtc)L_2$ (**c**) in benzene (1.0×10^{-4} M) at 25.1 °C; cell length 1.0 cm.

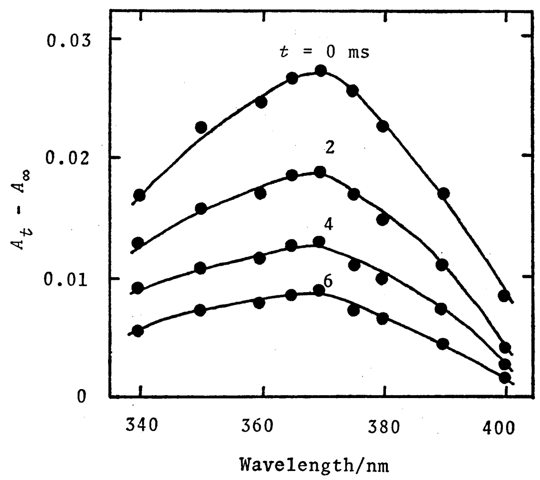


Fig. 2. Decay of the absorption band with time after mixing $Rh(dtc)L_2$ (1.0×10^{-4} M) with I_2 (1.0×10^{-3} M) in benzene at 10.0 °C.

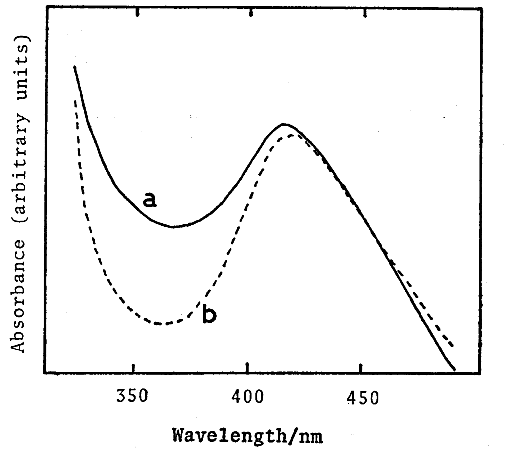


Fig. 3. Electronic spectra of toluene solutions containing equimolar quantities of $Rh(dtc)L_2$ and I_2 at −60 °C; **a** and **b** are those of the solutions prepared at −60 °C and at room temperature, respectively.

type. Similarly, the 360 nm band observed in the $\mathrm{Rh(acac)L_2}$–$\mathrm{I_2}$ system may be due to the CT transition from the acac-oxygen to $\mathrm{I_2}$. This is supported from the fact that ethanol, *N*,*N*-dimethylformamide, and related oxygen-containing compounds have been reported to form CT complexes with iodine; the CT bands were observed around 250 nm.[25]

Figure 3 shows the electronic spectra of two toluene solutions both containing equimolar quantities of $\mathrm{Rh(dtc)L_2}$ and $\mathrm{I_2}$ at −60 °C; one was prepared at −60 °C (solution **a**) and the other at room temperature followed by cooling (solution **b**). No absorption maximum is observed around 370 nm for these solutions, indicating that the CT complex had already decomposed even at −60 °C. It is to be noted, however, that the absorbance in the 370 nm region is different between the spectra of solution **a** and **b**, despite the similarity in those spectra. In addition, the same spectrum as solution **b** was observed in solution **a** which was allowed to stand at room temperature for several minutes, followed by cooling down to −60 °C. The spectrum of solution **b** can be ascribed to *trans*-$\mathrm{RhI_2(dtc)L_2}$, because it showed no change at all even in prolonged standing at room temperature. Thus, the spectrum of solution **a** may arise from another intermediate frozen at −60 °C. No direct evidence has been obtained for the configuration of the intermediate, because in nonpolar solvents such as toluene $\mathrm{Rh(dtc)L_2}$ is not soluble at low temperatures enough to measure the ^{1}H NMR and infrared spectra. The intermediate is presumably assigned to *cis*-$\mathrm{RhI_2(dtc)L_2}$. A similar *cis* addition was reported to occur in the reaction of hydrogen with some Vaska-type complexes, $\mathrm{IrX(CO)\{P(C_6H_5)_3\}_2}$ (X=halide).[26]

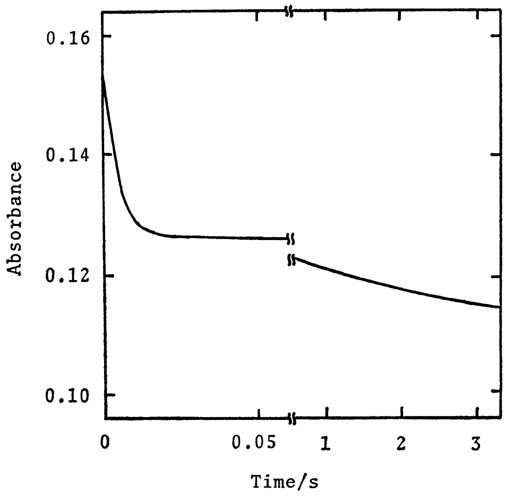


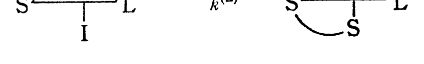
Fig. 4. Decay of the absorbance at 370 nm with time for the reaction of $\mathrm{Rh(dtc)L_2}$ (1.0×10^{-4} M) with $\mathrm{I_2}$ (1.0×10^{-3} M) in benzene at 10.0 °C.

TABLE 2. OBSERVED RATE CONSTANTS[a)] FOR THE TWO CONSECUTIVE PROCESSES IN THE REACTIONS OF $\mathrm{Rh(dtc)L_2}$ (1.0×10^{-4} M) WITH EXCESS $\mathrm{I_2}$ AT VARIOUS TEMPERATURES

Temp / °C	$[\mathrm{I_2}]/[\mathrm{Rh(dtc)L_2}]$	$k^{(1)}_{\mathrm{obsd}}$ / $\mathrm{s^{-1}}$	$10^3\,k^{(2)}_{\mathrm{obsd}}$ / $\mathrm{s^{-1}}$
10.0	10	206±1	216±1
	20	212±1	183±1
	30	213±1	223±1
	40	216±1	183±0
		(212±3)	(201±14)
14.5	10	331±2	318±2
	20	317±2	303±2
	30	318±2	278±1
	40	304±2	280±1
		(318±7)	(295±13)
20.1	10	543±4	579±4
	20	568±4	524±4
	30	544±4	551±3
	40	528±3	531±3
		(546±11)	(546±17)
25.1	10	785±8	1095±9
	20	779±14	1103±5
	30	722±7	1020±9
	40	746±4	1083±11
		(758±20)	(1075±25)

a) Average values in parentheses. $k^{(1)}_{\mathrm{obsd}}$ and $10^3\,k^{(2)}_{\mathrm{obsd}}$ are 197±1 and 83.2±0.6, respectively, for the reaction of $\mathrm{Rh(acac)L_2}$ (1.0×10^{-4} M) with $\mathrm{I_2}$ (1.0×10^{-3} M) at 25.1 °C.

The two intermediates in the present reaction were confirmed to exist also from kinetic measurements. A typical decay curve of the absorbance at 370 nm after mixing $\mathrm{Rh(dtc)L_2}$ and excess $\mathrm{I_2}$ in benzene at 10.0 °C is depicted in Fig. 4, which indicates the reaction proceeds *via* two consecutive processes with the half-lives of about 3 ms and 3 s, respectively. These two processes were followed by a much slower one in which the *trans*-$\mathrm{RhI_2(dtc)L_2}$ further reacted with excess $\mathrm{I_2}$ to give $\mathrm{RhI(I_3)(dtc)L_2}$. The last process, however, has not been kinetically analyzed, because there was little change in absorbance. The reaction rate in the two initial processes is different from each other sufficiently enough to allow the graphical determination of rate constants.[27] Plots of $\ln(A_t-A_\infty)$ *vs.* time for each process were found to be linear. Pseudo-first-order rate constants, $k^{(1)}_{\mathrm{obsd}}$ and $k^{(2)}_{\mathrm{obsd}}$ were obtained by the least-squares method. The results are shown in Table 2; the $k^{(1)}_{\mathrm{obsd}}$ and $k^{(2)}_{\mathrm{obsd}}$ are both essentially independent of the concentration of $\mathrm{I_2}$ at a given temperature. Thus, the equimolar reaction of $\mathrm{Rh(dtc)L_2}$ with $\mathrm{I_2}$ is suggested to proceed *via* the CT complex, $\mathrm{Rh(dtc)L_2\cdot I_2}$, which undergoes a rapid rearrangement probably to give *cis*-$\mathrm{RhI_2(dtc)L_2}$, followed by isomerization to the *trans* adduct, as shown in the following scheme. The isomeri-



zation of the *cis* adduct to the *trans* one may be a site exchange between the equatorial iodide ligand and the axial dtc-sulfur atom *via* a rhombic twist or by a metal-sulfur bond rupture mechanism. According to this reaction scheme, $k_{\text{obsd}}^{(1)}$ can be expressed by Eq. 1.

$$k_{\text{obsd}}^{(1)} = \frac{Kk^{(1)}[\mathrm{I_2}]}{1+K[\mathrm{I_2}]} \tag{1}$$

When $K[\mathrm{I_2}]$ is much greater than unity, $k_{\text{obsd}}^{(1)}$ can be reduced to $k^{(1)}$. This is consistent with the present result that $k_{\text{obsd}}^{(1)}$ is little dependent on the I_2 concentration. Since the *cis-trans* isomerization proceeds intramolecularly, the scheme also predicts $k_{\text{obsd}}^{(2)}$ being independent of $[\mathrm{I_2}]$, which is in agreement with the results obtained. Activation parameters obtained by the Arrhenius plots for the two processes are: $\Delta H_{298}^{\ddagger(1)}=57.7\pm2.0$ kJ mol^{-1}, $\Delta S_{298}^{\ddagger(1)}=4.0\pm6.9$ J mol^{-1} K^{-1} for the decomposition of CT complex, and $\Delta H_{298}^{\ddagger(2)}=75.5\pm3.9$ kJ mol^{-1}, $\Delta S_{298}^{\ddagger(1)}=8.0\pm9.9$ J mol^{-1} K^{-1} for the *cis–trans* isomerization. The small positive values of $\Delta S_{298}^{\ddagger(1)}$ and $\Delta S_{298}^{\ddagger(2)}$ are consistent with the two proposed intramolecular processes. In addition, the $\Delta H_{298}^{\ddagger(2)}$ value is comparable to the activation enthalpies (75 to 104 kJ mol^{-1}) of *cis-trans* isomerizations of $\mathrm{Cr(CO)_4\{C(OCH_3)CH_3\}(PR_3)}$ ($\mathrm{R{=}C_2H_5, C_6H_{11}}$),[28] $\mathrm{Ru(CO)_4(SiCl_3)_2}$,[29] and $\mathrm{Os(CO)_4\{Si(CH_3)_3\}_2}$,[29] which have been proposed to proceed *via* intramolecular manners, supporting the formation of the *cis* isomer as a short-lived species as suggested above.

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