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PHOTO-INDUCED OXIDATIVE ADDITION OF BUTYL IODIDE TO A DIMERIC RHODIUM(I) COMPLEX. AN ELECTRON TRANSFER CHAIN MECHANISM

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Irradiation of an acetonitrile solution of $[Rh_2(dicp)_4]^{2+}$ (dicp = 1,3-diisocyanopropane) in the presence of butyl iodide by the visible light at 553 nm produces the adduct, $[Rh_2(dicp)_4(n\text{-}Bu)(I)]^{2+}$, in a high quantum yield, e.g., $\Phi = 25.2$. A photo-induced electron transfer chain mechanism is presented based on the effects of electron acceptors (*p*-dinitrobenzene, *p*-benzoquinone, and chloranil) and radical scavengers (oxygen and isopentyl nitrite) on the photochemical reaction.

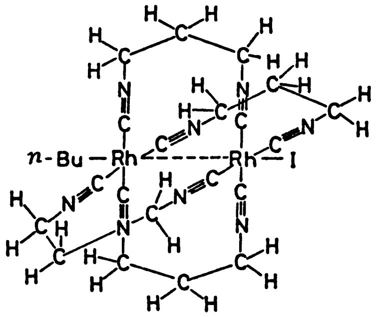
Oxidative additions of transition metal complexes prompted photochemically have recently merited a special attention as offerring possibilities for photochemical energy storage.[1] However, there has been no photochemical study of oxidative additions of simple substrates such as alkyl halides to transition metal complexes. We wish to report herein that a dimeric Rh(I) complex, $[Rh_2(dicp)_4]^{2+}$ (dicp = 1,3-diisocyanopropane), undergoes a photo-induced oxidative addition with butyl iodide (*n*-BuI) by 553 nm irradiation in high quantum yields, $\Phi >> 1$, under the conditions that the thermal reaction is negligible, indicating that the reaction is a chain process.

The tetraphenylborate salt of the dimeric $[Rh_2(dicp)_4]^{2+}$ cation was prepared according to the literature.[2] The lowest energy band of the electronic absorption spectrum in CH_3CN appears at 553 nm, which is assigned to the fully allowed $1a_{2u}$ $(d_{z^2}) \rightarrow 2a_{1g}(p_z, \pi^*\ dicp)$ transition.[2,3] When a CH_3CN solution of $[Rh_2(dicp)_4]^{2+}$ and *n*-BuI was irradiated under nitrogen atmosphere by the visible light (a Ushio Model U1-501C Xenon lamp) through a filter transmitting the light λ > 550 nm (a Toshiba glass filter O-55), the intense violet color faded in 30 s to give a yellow solution. The color change corresponds to the oxidative addition of *n*-BuI to $[Rh_2(dicp)_4]^{2+}$ (Eq. 1). The same reaction occurs thermally also in the dark

$$[Rh_2(dicp)_4]^{2+} + n\text{-BuI} \xrightarrow[>550\ nm]{h\nu} [Rh_2(dicp)_4(n\text{-Bu})(I)]^{2+} \qquad (1)$$

for longer reaction time.$^{4)}$ The thermal reaction, however, was negligible under the conditions where the photochemical experiments were carried out.

The product of the photochemical reaction was isolated as brown crystals of a tetraphenylborate salt by slow addition of diethyl ether. The infrared spectrum of the product in a KBr pellet shows two $\nu(C\equiv N)$ bands at 2200 and 2220 cm^{-1}, both of which are higher than the $\nu(C\equiv N)$ frequency (2172 cm^{-1}) of $[Rh_2(dicp)_4]^{2+}$. This is consistent with the structural formulation as shown below. The *trans*-$[Rh_2(dicp)_4(n\text{-}Bu)(I)]^{2+}$ cation in CH_3CN exhibits an intense absorption band at 407 nm ($\varepsilon = 5.09 \times 10^5$ $mol^{-1}dm^2$), which is assigned to $\sigma \rightarrow \sigma^*$ transition.



The quantum yield at 553 nm for the photochemical reaction (Eq. 1) was determined with a standard actinometer (potassium hexacyanoferrate(II))$^{5)}$ and a Nikon G-250 monochromator. The rate of the photo-

Table 1. Quantum yields of the photo-induced oxidative addition of *n*-BuI to $[Rh_2(dicp)_4]^{2+}$ (7.6×10^{-4} mol dm^{-3}) in CH_3CN under 553 nm irradiation.[a]

Additive/mol dm^{-3}	[*n*-BuI] /mol dm^{-3}	Φ
none	4.38×10^{-2}	6.8
none	8.76×10^{-2}	14.0
none	1.75×10^{-1}	25.2
p-dinitrobenzene		
5.23×10^{-2}	1.75×10^{-1}	1.0
1.11×10^{-1}	1.75×10^{-1}	0.87
p-benzoquinone		
4.63×10^{-2}	1.75×10^{-1}	3.7
chloranil		
2.56×10^{-2}	1.75×10^{-1}	7.5
oxygen[b]	1.75×10^{-1}	3.2
isopentyl nitrite		
1.49×10^{-2}	1.75×10^{-1}	15.6

[a] Under a nitrogen atmospheric pressure unless otherwise noted. [b] Under an oxygen atmospheric pressure.

chemical reaction in Eq. 1 under 553 nm irradiation was followed by the decay of the absorbance of $[Rh_2(dicp)_4]^{2+}$ at 553 nm ($\varepsilon = 1.45 \times 10^5\ mol^{-1}dm^2$).[3] The quantum yields thus evaluated under various conditions are listed in Table 1, which reveals increasing the quantum yield Φ with the *n*-BuI concentration when the reactions are carried out under nitrogen atmosphere, and a high quantum yield, $\Phi = 25.2$, is obtained for 1.75×10^{-1} mol dm^{-3} *n*-BuI without additives. Such a high quantum yield strongly indicates that the photo-induced oxidative addition of $[Rh_2(dicp)_4]^{2+}$ with *n*-BuI is a chain process.

The quantum yields in the presence of 5.23×10^{-2} and 1.11×10^{-1} mol dm^{-3} *p*-dinitrobenzene ($\Phi = 1.0$ and 0.87, respectively) which is a powerful one electron acceptor[6] are drastically reduced from that in the absence of *p*-dinitrobenzene with the same concentration of *n*-BuI ($\Phi = 25.2$). The reductions in the quantum yield are observed in the presence of other electron acceptors such as *p*-benzoquinone and chloranil as well (Table 1). Thus, it is suggested that the initiation step for the photochemical chain reaction is electron transfer from $[Rh_2(dicp)_4]^{2+}$ to *n*-BuI as shown in Eqs. 2 and 3,

$$\text{Initiation}\quad [Rh_2(dicp)_4]^{2+*} + n\text{-BuI} \xrightarrow{\text{e.t.}} [Rh_2(dicp)_4]^{3+\cdot} + n\text{-BuI}^{\cdot-} \qquad (2)$$

$$n\text{-BuI}^{\cdot-} \xrightarrow{\text{fast}} n\text{-Bu}\cdot + I^- \qquad (3)$$

where e.t. stands for electron transfer. Attachment of an electron to *n*-BuI is known to be dissociative to yield butyl radical (Eq. 3).[7] The electron acceptors may intervene the initiation step by taking away electrons from $[Rh_2(dicp)_4]^{2+*}$ before the reaction with *n*-BuI as well as from the radical anion of *n*-BuI before loss of iodide takes place and thereby prevent the formation of butyl radical.

The formation of butyl radical is further confirmed by the effect of oxygen on the photochemical reaction. The quantum yield under oxygen atmosphere is significantly reduced from that under nitrogen at the same concentration of *n*-BuI (Table 1). Thus, oxygen which is a typical radical scavenger also inhibits the photochemical reaction appreciably. The G.C. analysis of the products after the photochemical reaction of $[Rh_2(dicp)_4]^{2+}$ (8.30×10^{-4} mol dm^{-3}) with *n*-BuI (1.75×10^{-1} mol dm^{-3}) under the irradiation ($\lambda > 550$ nm) showed the formation of equimolar amounts of butanol and butyraldehyde (26 % based on the Rh concentration). This result confirms the formation of butyl radical in the initiation step (Eqs. 2 and 3), followed by the radical trap with oxygen to form butylperoxyl radical, and the known bimolecular reaction of the peroxyl radicals to yield equimolar amounts of butanol and butyraldehyde as shown in Eqs. 4 and 5.[8)] A coupling

$$C_4H_9\cdot + O_2 \longrightarrow C_4H_9O_2\cdot \quad (4) \qquad 2\,C_4H_9O_2\cdot \longrightarrow C_4H_9OH + C_3H_7CHO + O_2 \quad (5)$$

product, $[Rh_4(dicp)_8(I)_2]^{4+}$ (λ_{max} = 631 nm and $\varepsilon = 8.71 \times 10^5\ mol^{-1}dm^2$),[9)] also was formed (33 %) by the termination reaction (Eq. 6) of the Rh(II) radicals formed in the initiation step.[10)] The addition of isopentyl nitrite which also is a radical scavenger[11)] reduces the quantum yield although less effective than oxygen.

$$2\,[Rh_2(dicp)_4(I)]^{2\dot{+}} \longrightarrow [Rh_4(dicp)_8(I)_2]^{4+} \qquad (6)$$

Based on the above results, the chain propagation step where butyl radical is a chain carrier is suggested as follows.

$$\text{Propagation} \quad n\text{-Bu}\cdot + [Rh_2(dicp)_4]^{2+} \longrightarrow [Rh_2(dicp)_4(n\text{-Bu})]^{2\dot{+}} \qquad (7)$$

$$[Rh_2(dicp)_4(n\text{-Bu})]^{2\dot{+}} + n\text{-BuI} \longrightarrow [Rh_2(dicp)_4(n\text{-Bu})(I)]^{2+} + n\text{-Bu}\cdot \qquad (8)$$

A further detailed study on the mechanism of the photo-induced oxidative addition is now under progress.

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9) The same species is formed in the iodinolysis of $[Rh_2(dicp)_4]^{2+}$ and converted to $[Rh_2(dicp)_4(I)_2]^{2+}$ by the 631 nm irradiation in the presence of iodine.
10) $[Rh_4(dicp)_8(I)_2]^{4+}$ was converted to $[Rh_2(dicp)_4(I)_2]^{2+}$ by the further irradiation (λ > 550 nm).[9)]
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