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An Electron Transfer Chain Mechanism for Photoinduced Oxidative Addition of Alkyl Iodide to a Dimeric Rhodium(I) Complex under Low Energy Irradiation (553 nm)

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A dimeric Rh^I complex, $[Rh_2(dicp)_4]^{2+}$ (dicp=1,3-diisocyanopropane) was found to undergo a photoinduced oxidative addition with butyl iodide and isopropyl iodide in MeCN by 553 nm irradiation in high quantum yields, $\Phi=25.2$ and 22.6, respectively. Electron acceptors (*p*-dinitrobenzene, *p*-benzoquinone, and chloranil) and radical scavengers (oxygen and isopentyl nitrite) act as inhibitors for the photoinduced oxidative addition, providing unambiguous evidence for a chain character of this reaction. The fluorescence quenching of $[Rh_2(dicp)_4]^{2+}$ by the electron acceptors as well as butyl iodide has also been examined. Based on the kinetics of the photochemical reactions in the absence or the presence of electron acceptors and radical scavengers, an electron transfer chain mechanism has been proposed. The formation of butyl radicals in the photoinitiation step was confirmed by the trap with oxygen to yield equimolar amounts of 1-butanol and butyraldehyde. The nature of the excited state of $[Rh_2(dicp)_4]^{2+*}$($^1A_{2u}$ or $^3A_{2u}$) involved in the photoinitiation step has also been discussed.

Oxidative additions of transition metal complexes with low-lying metal to ligand charge transfer (MLCT) excited states have recently merited a special attention as offering a possibility for photochemical energy storage.[1] There has, however, been reported only a few photochemical study on the oxidative additions of simple substrates such as alkyl halides and protic acids to transition metal complexes.[2] On the other hand, the thermal oxidative addition of organic halides to transition metal complexes have intensively been studied.[3] Although there is no simple generalization about the mechanisms of oxidative additions, some addition reactions of organic halides to transition metal complexes have been suggested to proceed *via* a radical chain process where the initiation step involves transfer of one electron rather than two electrons.[4] If such a radical chain process is initiated by light, the oxidative addition may be prompted photochemically with high quantum yields.

We have previously reported that a dimeric Rh^I complex, $[Rh_2(dicp)_4]^{2+}$ (dicp=1,3-diisocyanopropane), is an excellent one electron donor in the reactions with inorganic oxidants such as $[Fe(N\text{–}N)_3]^{3+}$ (N–N=2,2′-bipyridine and 1,10-phenanthroline).[5] The donor ability of $[Rh_2(dicp)_4]^{2+}$ would be further enhanced in the MLCT excited states, $[Rh_2(dicp)_4]^{2+*}$ ($^1A_{2u}$ or $^3A_{2u}$) formed by the irradiation of the lowest energy band which appears at 553 nm in MeCN.[6,7]

In this paper, we wish to report a photoinduced oxidative addition of butyl iodide (*n*-BuI) and isopropyl iodide (*i*-PrI) toward $[Rh_2(dicp)_4]^{2+*}$ by low energy irradiation (553 nm) under nitrogen atmosphere with exceptionally high quantum yields, $\Phi=25.2$ and 22.6, respectively. The reaction mechanism is discussed based on the kinetics of the photochemical reactions in the absence or the presence of electron acceptors (*p*-dinitrobenzene, *p*-benzoquinone, and chloranil) as well as radical scavengers (oxygen and isopentyl nitrite). Electron transfer quenching of the fluorescence of $[Rh_2(dicp)_4]^{2+*}$ by the electron acceptors has also been examined to obtain the rate constants for the electron transfer reactions between $[Rh_2(dicp)_4]^{2+*}$ and the electron acceptors. A preliminary report of the present study has appeared.[8]

Experimental

Materials. Preparation of $[Rh_2(dicp)_4](BPh_4)_2$ (dicp=1,3-diisocyanopropane) was described previously.[5,8] Commercially available *n*-BuI and *i*-PrI were purified by distillation. Electron acceptors (chloranil, *p*-benzoquinone, *p*-dinitrobenzene, *m*-dinitrobenzene, methyl *p*-nitrobenzoate, *m*-nitrobenzaldehyde, *p*-chloronitrobenzene, nitrobenzene, diethyl fumarate, and benzophenone) and a radical scavenger (isopentyl nitrite) also obtained commercially were purified by the standard methods.[9] Acetonitrile used as a solvent was purified by distillation over P_2O_5 three times before use.

Photoinduced Addition of n*-BuI to $[Rh_2(dicp)_4]^{2+}$ under Nitrogen Atmosphere.* Butyl iodide (7.9 mmol) was dissolved in a MeCN solution (45 cm^3) of $[Rh_2(dicp)_4](BPh_4)_2$ (31 μmol) under nitrogen atmosphere in the dark. When the solution was irradiated by the visible light (an Ushio Model Ul-501C Xenon lamp) through a Toshiba glass filter O-55 transmitting the light $\lambda>550$ nm, the intensive violet color of the solution faded in a few minutes to turn yellow. The resulting solution was concentrated to one third volume under reduced pressure, followed by the slow addition of diethyl ether. A precipitate appeared was collected by filtration and recrystallized from MeCN to give brown crystals of $[Rh_2(dicp)_4(n\text{-Bu})(I)](BPh_4)_2$ in a 80% yield. Found C, 59.27; H, 4.95; N, 7.93%.[10] Calcd for $C_{72}H_{73}N_8B_2IRh_2$: C, 61.56; H, 5.24; N, 7.98%. ν(C≡N): 2200 and 2220 cm^{-1} (KBr pellet).

Photochemical Reaction of $[Rh_2(dicp)_4]^{2+}$ with n*-BuI under Oxygen Atmosphere.* Upon 1 min irradiation by the visible light ($\lambda>550$ nm) under oxygen atmosphere, a violet MeCN solution (*ca.* 1 cm^3) containing $[Rh_2(dicp)_4]^{2+}$ (0.83 μmol) and *n*-BuI (0.175 mmol) turned into deep green with concomitant disappearance of the absorption band of $[Rh_2(dicp)_4]^{2+}$ at 553 nm. The resulting solution contained equimolar amounts of 1-butanol and butyraldehyde (26% yield) as determined by GLC. The other products were obtained as a mixture of $[Rh_2(dicp)_4(n\text{-Bu})(I)]^{2+}$ (67%) and $[Rh_4(dicp)_8(I)_2]^{4+}$ (16%), the composition of which was determined from their absorbances at λ_{max}; 407 nm ($\varepsilon=5.09\times10^5$ mol^{-1} dm^2) and 631 nm ($\varepsilon=8.71\times10^5$ mol^{-1} dm^2),[11] respectively.

Quantum Yield Determination. The visible light from an Ushio Model Ul-501C Xenon lamp was monochromatized with a Nikon G-250 monochromator. The incident light intensity at 553 nm was determined as 7.08×10^{-9} einsteins min^{-1} by the use of a standard actinometer (potassium hexacyanoferrate(II))[12] under the same conditions as the photochemical experiments. Quantum yields Φ for the photoinduced oxidative addition of *n*-BuI and *i*-PrI to $[Rh_2(dicp)_4]^{2+}$ were then calculated by the equation $\Phi = R/In$, where R is the photochemical reaction rate determined from the disappearance of the 553 nm band due to $[Rh_2(dicp)_4]^{2+}$ and In is the light intensity absorbed by the reactants. In the absence of electron acceptors and radical scavengers, the quantum yields exhibited some decreasing dependence on the percent conversion and the initial values were taken by extrapolating the plots of Φ *vs.* time.

Fluorescence Quenching by Electron Acceptors. Fluorescence measurements were carried out using a Hitachi 650-10S fluorescence spectrophotometer. Relative fluorescence intensities of $[Rh_2(dicp)_4]^{2+*}$ at 656 nm were measured for MeCN solutions containing $[Rh_2(dicp)_4]^{2+}$ (2.7×10^{-4}—8.0×10^{-4} mol dm^{-3}) and a quencher at various concentrations. The absorption band due to $[Rh_2(dicp)_4]^{2+}$ ($\lambda_{max} = 553$ nm) was not changed by the addition of quenchers with high concentrations ($> 1 \times 10^{-1}$ mol dm^{-3}) except for chloranil and *p*-benzoquinone. In these cases, the presence of quenchers in high concentrations caused the slight red shift (≈ 10 nm) of the $[Rh_2(dicp)_4]^{2+}$ band, and thus the lower concentrations ($\ll 1 \times 10^{-1}$ mol dm^{-3}) were used for the experiments of the fluorescence quenching in order to avoid the possible formation of the complexes with the ground state of $[Rh_2(dicp)_4]^{2+}$. Under such experimental conditions, the excitation wavelength agrees with the absorption maximum of $[Rh_2(dicp)_4]^{2+}$ where the quenchers used in this study have neither absorption nor emission. There was no change in the shape but intensity of the fluorescence spectrum of $[Rh_2(dicp)_4]^{2+*}$ by the addition of quenchers. The minimum slit width (1 mm) of the excitation light was chosen for the fluorescence quenching with *n*-BuI in order to avoid the facile photochemical reaction. The Stern-Volmer relationship (Eq. 1) between I_f^0/I_f and [Q] was obtained for each quencher,

$$I_f^0/I_f = 1 + K_q[Q], \tag{1}$$

where I_f^0 and I_f are relative fluorescence intensities in the absence and presence of a quencher, respectively, K_q is the quenching constant, and Q stands for the quencher. The quenching rate constant k_q was obtained by the relation $k_q = K_q\tau^{-1}$, where τ is the emission lifetime of $[Rh_2(dicp)_4]^{2+*}$ ($\tau = 1.3$ ns[7]).

Results and Discussion

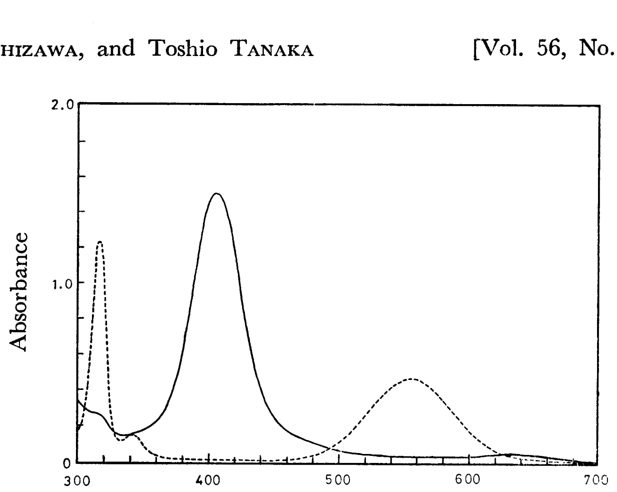


Fig. 1. Electronic absorption spectra of $[Rh_2(dicp)_4]^{2+}$ (3.23×10^{-4} mol dm^{-3}) in MeCN containing *n*-BuI (1.75×10^{-1} mol dm^{-3}) before irradiation (----) and after 1 min irradiation by the 553 nm light (——) under nitrogen atmosphere; 1 mm quartz cell.

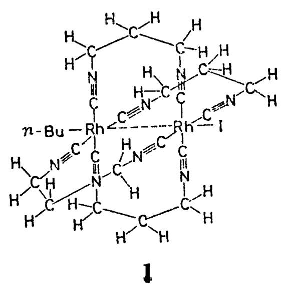
Photoinduced Oxidative Addition of n-*BuI to* $[Rh_2(dicp)_4]^{2+}$. Figure 1 shows the electronic absorption spectra of a MeCN solution containing $[Rh_2(dicp)_4]^{2+}$ (3.24×10^{-4} mol dm^{-3}) and *n*-BuI (1.75×10^{-1} mol dm^{-3}) before and after irradiation by the visible light through a filter transmitting the light $\lambda >$ 550 nm under nitrogen atmosphere. Since neither the shape nor intensity of the lowest energy band at 553 nm assigned to ${}^1A_{1g} \rightarrow {}^1A_{2u}$ transition of $[Rh_2(dicp)_4]^{2+}$ [6,7] has been changed by the addition of *n*-BuI which has no absorption band in the visible region, there seems to be no ground state complex formed between $[Rh_2(dicp)_4]^{2+}$ and *n*-BuI. The intense violet color ($\lambda_{max} = 553$ nm) of the solution, however, faded upon irradiation for 1 min. The resulting yellow solution contains the oxidative adduct, $[Rh_2(dicp)_4](n\text{-}Bu)(I)]^{2+}$ ($\lambda_{max} = 407$ nm), as a main product and a small amount of $[Rh_4(dicp)_8(I)_2]^{4+}$ ($\lambda_{max} =$ 631 nm, 4.6×10^{-6} mol dm^{-3})[11] as well as octane (4.9×10^{-6} mol dm^{-3}) detected by GLC. No butane has been detected. Thus, the photochemical reaction of $[Rh_2(dicp)_4]^{2+}$ with *n*-BuI under nitrogen atmosphere involves a main path and a side path, as expressed by Eqs. 2 and 3, respectively. The thermal reaction of

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

$$2[Rh_2(dicp)_4]^{2+} + 2n\text{-}BuI \xrightarrow[>550\,\mathrm{nm}]{h\nu} [Rh_4(dicp)_8(I)_2]^{4+} + Bu\text{-}Bu \tag{3}$$

$[Rh_2(dicp)_4]^{2+}$ with *n*-BuI has been negligible in the extent under the conditions where the photochemical experiment was carried out since the rate of the thermal reaction was at least 10^3 times slower than that of the photochemical reaction.

The oxidative adduct in Eq. 2 was isolated as brown crystals of the tetraphenylborate salt, $[Rh_2(dicp)_4(n\text{-}Bu)(I)](BPh_4)_2$. The infrared spectrum of the adduct in a KBr pellet showed two ν(C≡N) bands at 2200 and 2220 cm^{-1}, both of which are higher than the single ν(C≡N) frequency of $[Rh_2(dicp)_4](BPh_4)_2$ (2172 cm^{-1}) and lower than that of $[Rh_2(dicp)_4(I)_2]^{2+}$ (2227 cm^{-1}).[6] This is consistent with the structural formulation as *trans*-$[Rh_2(dicp)_4(n\text{-}Bu)(I)](BPh_4)_2$ (**1**). The $[Rh_2(dicp)_4(n\text{-}Bu)(I)]^{2+}$ cation in MeCN exhibits an intense absorption band at 407 nm ($\varepsilon = 5.09 \times 10^5$ mol^{-1}



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dm^2, Fig. 1), which is assigned to $\sigma \rightarrow \sigma^*$ transition in the Rh$^{\mathrm{II}}$–Rh$^{\mathrm{II}}$ single bonded species as in the case of the MeI adduct, $[\mathrm{Rh_2(dicp)_4(Me)(I)}]^{2+}$.[6)]

The $[\mathrm{Rh_2(dicp)_4}]^{2+}$ cation reacted with *i*-PrI as well under irradiation at 553 nm, yielding $[\mathrm{Rh_2(dicp)_4}(i\text{-Pr})(\mathrm{I})]^{2+}$ ($\lambda_{\max}$=414 nm, ε=6.16×10^5 mol^{-1} dm^2). The photochemical reaction of $[\mathrm{Rh_2(dicp)_4}]^{2+}$ with MeI, however, could not be examined since the thermal oxidative addition of MeI to $[\mathrm{Rh_2(dicp)_4}]^{2+}$ occurred appreciably upon mixing the reactants in the dark.[6)]

Quantum Yields for the Photochemical Reaction of $[Rh_2(dicp)_4]^{2+}$ *with n-BuI.* Quantum yield Φ for the photochemical reaction of $[\mathrm{Rh_2(dicp)_4}]^{2+}$ with *n*-BuI on irradiation with the 553 nm light under various conditions are listed in Table 1, which indicates that the Φ value for the reaction under nitrogen atmosphere increases with increasing the *n*-BuI concentration, and an exceptionally high quantum yield (Φ=25.2) is achieved with the concentration of 1.75×10^{-1} mol dm^{-3}. The reaction with 1.0×10^{-1} mol dm^{-3} *i*-PrI also gives a similar high quantum yield (footnote b) in Table 1. Such high quantum yields strongly suggest that the photoinduced oxidative addition of $[\mathrm{Rh_2(dicp)_4}]^{2+}$ with *n*-BuI as well as *i*-PrI is a chain process.

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

Additive (mol dm^{-3})	[*n*-BuI]/mol dm^{-3}	Φ
None	2.92×10^{-3}	1.9
None	1.75×10^{-2}	4.2
None	4.38×10^{-2}	6.8
None	8.76×10^{-2}	14.0
None	1.75×10^{-1}	25.2
None	1.00×10^{-1} b)	22.6b)
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 c)	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) The addendum is *i*-PrI. c) Under an oxygen atmospheric pressure.

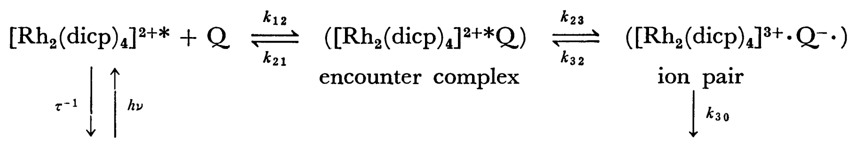
In order to elucidate the chain process, the effect of electron acceptors such as *p*-dinitrobenzene, *p*-benzoquinone, and chloranil on the quantum yields was examined. The quantum yields are drastically decreased (*e.g.*, from 25.2 to 0.87) by the addition of *p*-dinitrobenzene which is known as a powerful one electron acceptor.[13)] Similarly, the decrease in the quantum yield is observed in the presence of *p*-benzoquinone and chloranil (Table 1). Oxygen, which is a typical radical scavenger, also reduces the quantum yield (Table 1). The addition of isopentyl nitrite which also is a radical scavenger[14)] results in the reduction of the quantum yield although less effective than oxygen. Thus, the electron acceptors and radical scavengers act as inhibitors for the photoinduced oxidative addition of *n*-BuI to $[\mathrm{Rh_2(dicp)_4}]^{2+}$, providing unambiguous evidence for the chain character of this process where strong one electron donors and radical species must be involved. The photoinitiation step of the chain process is discussed in the following section.

Fluorescence Quenching by Electron Transfer. The excitation of the lowest energy band (553 nm) of $[\mathrm{Rh_2(dicp)_4}]^{2+}$ results in fluorescence ($\lambda_{\max}$=656 nm, $h\nu_f$= 1.89 eV, τ=1.3 ns).[7)] The fluorescence was efficiently quenched by the electron acceptors in Table 1 without change in the shape of the fluorescence spectrum.

Table 2. Quenching rate constants (k_q) of the $[\mathrm{Rh_2(dicp)_4}]^{2+*}$ fluorescence and reduction potentials (E^0_{red}) of electron acceptors

Quencher	E^0_{red} a) *vs.* SCE / V	k_q / mol^{-1} dm^3 s^{-1}
Chloranil	0.01	1.6×10^{10}
p-Benzoquinone	−0.51	4.0×10^{10}
p-Dinitrobenzene	−0.69	1.8×10^{10}
m-Dinitrobenzene	−0.90	1.5×10^{10}
Methyl *p*-nitrobenzoate	−0.95	1.4×10^{10}
m-Nitrobenzaldehyde	−1.02	1.3×10^{10}
p-Chloronitrobenzene	−1.06	1.2×10^{10}
Nitrobenzene	−1.15	1.3×10^{10}
Diethyl fumarate	−1.50	6.8×10^{9}
Benzophenone	−1.86	5.9×10^{8}
Butyl iodide	b)	2.6×10^{8}

a) Taken from Ref. 15. b) The reduction is irreversible.



$$k_q = \frac{k_{12}}{1+\dfrac{k_{21}}{k_{23}}\left(1+\dfrac{k_{32}}{k_{30}}\right)} \tag{4}$$

Scheme 1.

Quenching rate constants of the $[Rh_2(dicp)_4]^{2+*}$ emission by various electron acceptors determined by the Stern-Volmer plots (see Experimental Section) are given in Table 2 together with the reduction potentials of the electron acceptors.

By analogy with the reaction scheme for fluorescence quenching by electron transfer in polar solvents reported previously,[16] the reaction of $[Rh_2(dicp)_4]^{2+*}$ with Q (quencher) may be shown in Scheme 1, according to which the quenching rate constant k_q is given by Eq. 4.[16] The free energy change of the actual electron transfer process, ΔG_{23}, (encounter complex→ion pair in Scheme 1) may be evaluated by Eq.5,[16]

$$\Delta G_{23} = E^0_{ox} - E^0_{red} + w_p - E_{0,0}, \tag{5}$$

where E^0_{ox} and E^0_{red} are the oxidation potential of $[Rh_2(dicp)_4]^{2+}$ and the reduction potential of electron acceptors, respectively, w_p is the work required to bring the product ions $[Rh_2(dicp)_4]^{3+}\cdot$ and $Q^-\cdot$ together to form the ion pair (Scheme 1),[17,18] and $E_{0,0}$ is the zero-zero transition energy between the ground state $[Rh_2(dicp)_4]^{2+}$ and the excited state $[Rh_2(dicp)_4]^{2+*}$. The $E_{0,0}$ value is obtained as 2.07 eV from the absorption spectrum (λ_{max}=553 nm, $h\nu$=2.24 eV) and the fluorescence spectrum (λ_{max}=656 nm, $h\nu_f$=1.89 eV) by the equation $E_{0,0}=(h\nu+h\nu_f)/2$.[16] Thus, the oxidation potential of the excited state $[Rh_2(dicp)_4]^{2+*}$ is decreased by 2.07 V relative to that of the ground state. Unfortunately, the oxidation potential of $[Rh_2(dicp)_4]^{2+}$ is unknown because the electrochemical oxidation is irreversible.[5] However, the peak potential E^p_{ox} of the cyclic voltammogram of $[Rh_2(dicp)_4]^{2+}$ (E^p_{ox}=0.92 V *vs.* SCE at the sweep rate of 0.1 V s^{-1})[5,19] gives the upper limit of the E^0_{ox} value. By using the w_p and $E_{0,0}$ values (−0.06 V[18] and 2.07 V, respectively), the upper limit of ΔG_{23} is then given as $\Delta G_{23} < -1.21 - E^0_{red}$. Thus, the quenching process by the electron acceptors except for diethyl fumarate and benzophenone in Table 2 (k_{23}) is exothermic and the reverse process (k_{32}) is thereby endothermic. Then, the relation $k_{30} \gg k_{32}$ may be valid since the free energy change of the back electron transfer to the ground state (k_{30}) is exceedingly negative. Under such a condition, Eq. 4 is reduced to Eq. 6. The

$$k_q = \frac{k_{12}k_{23}}{k_{23}+k_{21}} \tag{6}$$

quenching rate constants by the electron acceptors in Table 2 are thus close to the limiting value in Eq. 6, which is the diffusion rate constant, $k_{12}=2\times10^{10}$ mol^{-1} dm^3 s^{-1}.[16] The fluorescence of $[Rh_2(dicp)_4]^{2+*}$ is quenched also by *n*-BuI although the quenching rate constant k_q (2.6×10^8 mol^{-1} dm^3 s^{-1}) is smaller than those with the other electron acceptors in Table 2. Thus, the excited state $[Rh_2(dicp)_4]^{2+*}$ acts as an excellent electron donor toward various electron acceptors.

One electron transfer to *n*-BuI is known to result in the facile dissociation of the *n*-Bu–I bond, yielding butyl radicals.[20,21] The electron transfer quenching process shown in Eq. 7 is thus followed by the subsequent fast reaction expressed by Eq. 8, producing

$$([Rh_2(dicp)_4]^{2+*}n\text{-BuI}) \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} ([Rh_2(dicp)_4]^{3+}\cdot n\text{-BuI}^-\cdot) \tag{7}$$

$$([Rh_2(dicp)_4]^{3+}\cdot n\text{-BuI}^-\cdot \xrightarrow{\text{fast}} [Rh_2(dicp)_4(I)]^{2+}\cdot + n\text{-Bu}\cdot \tag{8}$$

butyl radicals, in competition with the back electron transfer to the ground state (k_{30} in Scheme 1). The presence of $[Rh_2(dicp)_4(I)]^{2+}\cdot$ and *n*-Bu· is supported from the formation of the coupling products, $[Rh_4(dicp)_8(I)_2]^{4+}$ and octane (Eq. 3), respectively, as described above.

Formation of Butyl Radicals in the Initiation Step. The formation of butyl radicals in the photoinitiation step (Eq. 8) is confirmed also by the effect of oxygen, which is a typical radical scavenger, on the photochemical reaction. The GLC analysis of the products in 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}) by the irradiation (λ>550 nm) under oxygen atmosphere showed the formation of equimolar amounts of 1-butanol and butyraldehyde (26% based on the initial Rh concentration). A coupling product $[Rh_4(dicp)_8(I)_2]^{4+}$ also was obtained in a 33% yield, being close to those of 1-butanol and butyraldehyde. Thus, the stoichiometry of the photochemical reaction under oxygen may be given by Eq. 9. In the presence of oxygen, the butyl radicals should be trapped by oxygen molecules to yield butylperoxyl radicals (Eq. 10), which is known to undergo a bimolecular self-reaction, producing equimolar amounts of 1-butanol and butyraldehyde as well as oxygen (Eq. 11).[22] Thus, the formation of equimolar amounts of 1-butanol and butyraldehyde (Eq. 9) provides unambiguous evidence for

$$2[Rh_2(picp)_4]^{2+} + 2C_4H_9I + O_2 \xrightarrow[>550\,\text{nm}]{h\nu} [Rh_4(dicp)_8(I)_2]^{4+} + C_4H_9OH + C_3H_7CHO \tag{9}$$

$$C_4H_9\cdot + O_2 \longrightarrow C_4H_9O_2\cdot \tag{10}$$

$$2C_4H_9O_2\cdot \longrightarrow C_4H_9OH + C_3H_7CHO + O_2 \tag{11}$$

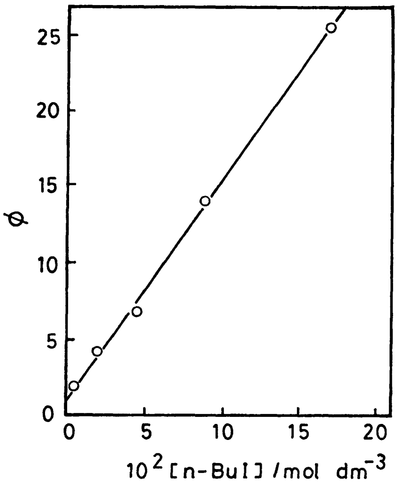


Fig. 2. Quantum yields for the photoinduced oxidative addition of *n*-BuI to $[Rh_2(dicp)_4]^{2+}$ (7.59×10^{-4} mol dm^{-3}) in MeCN at 298 K, as a function of the *n*-BuI concentration.

the formation of the butyl radicals in the photoinitiation step (Eq. 8). Oxygen molecules thus suppress the chain process to yield the oxidative adduct, where the butyl radical may act as a chain carrier, resulting in the reduction of the quantum yields (Table 1).

Kinetics and Mechanism of the Photoinduced Oxidative Addition. At a constant light intensity (7.08×10^{-9} einsteins min^{-1}) the quantum yield for the disappearance of $[\mathrm{Rh_2(dicp)_4}]^{2+}$ in the photochemical reaction with *n*-BuI shows a linear dependence on the *n*-BuI concentration with the intercept of unity as shown in Fig. 2, from which Eq. 12 is derived,

$$\Phi = 1 + a[n\text{-BuI}], \tag{12}$$

where a is equal to $1.37\times10^{2}\ \mathrm{mol^{-1}\ dm^{3}}$. A reaction scheme to account for the kinetic result (Eq. 12) is proposed as follows,

Initiation:

$$[\mathrm{Rh_2(dicp)_4}]^{2+} + n\text{-BuI} \xrightarrow[h\nu]{\alpha In} [\mathrm{Rh_2(dicp)_4(I)}]^{2+}\cdot + n\text{-Bu}\cdot \tag{13}$$

Propagation:

$$n\text{-Bu}\cdot + [\mathrm{Rh_2(dicp)_4}]^{2+} \xrightarrow{k_1} [\mathrm{Rh_2(dicp)_4}(n\text{-Bu})]^{2+}\cdot \tag{14}$$

$$[\mathrm{Rh_2(dicp)_4}(n\text{-Bu})]^{2+}\cdot + n\text{-BuI} \xrightarrow{k_2} [\mathrm{Rh_2(dicp)_4}(n\text{-Bu})(\mathrm{I})]^{2+} + n\text{-Bu}\cdot \tag{15}$$

Termination:

$$2[\mathrm{Rh_2(dicp)_4}(n\text{-Bu})]^{2+}\cdot \xrightarrow{k_3} \text{Bu–Bu} + 2[\mathrm{Rh_2(dicp)_4}]^{2+} \tag{16}$$

$$2[\mathrm{Rh_2(dicp)_4(I)}]^{2+}\cdot \xrightarrow{k_4} [\mathrm{Rh_4(dicp)_8(I)_2}]^{4+}, \tag{17}$$

Scheme 2.

where In is the light intensity absorbed by $[\mathrm{Rh_2(dicp)_4}]^{2+}$ and α is the quantum yield for the photoinitiation step. The initiation step (Eq. 13) consists of the electron transfer quenching of $[\mathrm{Rh_2(dicp)_4}]^{2+*}$ with *n*-BuI (Eq. 7) and the subsequent fast reaction to yield butyl radicals (Eq. 8). One of the propagation reactions (Eq. 15) also may consist of essentially the same reaction sequence as Eqs. 7 and 8, *i.e.*, an electron transfer from $[\mathrm{Rh_2(dicp)_4}(n\text{-Bu})]^{2+}\cdot$ to *n*-BuI, followed by the facile fission of *n*-Bu–I bond to reproduce butyl radicals since the donor ability of $[\mathrm{Rh_2(dicp)_4}(n\text{-Bu})]^{2+}\cdot$ is enhanced by the electron donating *n*-Bu group. The termination reactions (Eqs. 16 and 17) account for the coupling products in Eq. 3. The coupling of butyl radicals as a termination reaction is excluded since the rate-limiting step in the propagation process may be the reaction of $[\mathrm{Rh_2(dicp)_4}(n\text{-Bu})]^{2+}\cdot$ with *n*-BuI (Eq. 15).[23)]

Applying the steady-state approximation to the radical species involved in Scheme 2, the rate of the disappearance of $[\mathrm{Rh_2(dicp)_4}]^{2+}$, $-\mathrm{d}[\mathrm{Rh_2}^{2+}]/\mathrm{d}t$, is expressed as Eq. 18, from which the quantum

$$-\frac{\mathrm{d}[\mathrm{Rh_2}^{2+}]}{\mathrm{d}t} = \alpha In + k_2\left(\frac{\alpha In}{2k_3}\right)^{1/2}[n\text{-BuI}] \tag{18}$$

yield Φ is given by Eq. 19.

$$\Phi = \alpha + k_2\left(\frac{\alpha}{2k_3 In}\right)^{1/2}[n\text{-BuI}] \tag{19}$$

This equation is consistent with the kinetic result (Eq. 12) with respect to the dependence of the quantum yield on the *n*-BuI concentration. The comparison of Eq. 19 with Eq. 12 indicates that the quantum yield α for the photoinitiation step is *unity* and neither the back electron transfer to the ground state (k_{30} in Scheme 1) nor geminate recombination of the radical pair (Eq. 20) occurs in the photoinitiation step.

$$([\mathrm{Rh_2(dicp)_4(I)}]^{2+}\cdot n\text{-Bu}\cdot) \not\longrightarrow [\mathrm{Rh_2(dicp)_4}(n\text{-Bu})(\mathrm{I})]^{2+} \tag{20}$$

The fluorescence quantum yield of $[\mathrm{Rh_2(dicp)_4}]^{2+*}$ ($^1\mathrm{A_{2u}}$) is 0.056[7)] and therefore the remaining 94% of the excited species falls in the excited triplet state $^3\mathrm{A_{2u}}$ by intersystem crossing. Then, the fluorescence quenching by *n*-BuI which is only 0.1% for the smallest concentration of *n*-BuI in Table 1 (2.92×10^{-3} mol $\mathrm{dm^{-3}}$)[24)] cannot account for the high efficiency of the photoinitiation, $\alpha=1$. The much longer lifetime of the $^3\mathrm{A_{2u}}$ state (8.5 μs)[7)] than the $^1\mathrm{A_{2u}}$ sate (1.3 ns) may, however, make it possible that the $^3\mathrm{A_{2u}}$ sate is efficiently quenched by *n*-BuI with $\alpha=1$. The contribution of the lower excited states such as vibrationally excited state to the electron transfer reaction may be negligible since the donor ability of such states is much less than that of the $^3\mathrm{A_{2u}}$ state. Thus, the excited state $[\mathrm{Rh_2(dicp)_4}]^{2+*}$ involved in the photoinitiation step (Eq. 7) may be the triplet state ($^3\mathrm{A_{2u}}$) rather than the singlet state ($^1\mathrm{A_{2u}}$). The absence of the singlet geminate recombination of the radical pair (Eq. 20) also supports the electron transfer from the $^3\mathrm{A_{2u}}$ state to *n*-BuI since the resultant triplet radical pair may diffusively separate without the singlet geminate recombination, yielding the free radicals (Eq. 8) which initiate the chain process (Eqs. 14 and 15).

It should be noted that a similar electron transfer chain mechanism has been proposed for some organic systems, *e.g.*, a substitution reaction of *p*-nitrobenzyl chloride with the sodium salt of 2-nitropropane which proceeds *via* a multi-stage chain sequence involving radical anions and free radicals as intermediates.[13,25)] Recently, Chanon and Tobe in their excellent review[26)] have formulated such chain reactions in the organic systems as the "DAISET" (Double Activation Induced by Single Electron Transfer) mechanism. The first activation results from the transfer of an electron to a molecular species (*e.g.*, Eq. 7); the second activation results from the build-up of a reaction chain capable of reproducing the species formed in the first step (*e.g.*, Eqs. 14 and 15). They have attempted to expand the "DAISET" mechanism in organic systems to some inorganic reactions in which the "DAISET" behavior is much less common, and have discussed a possibility of the existence of the "DAISET" mechanism in some reactions of $\mathrm{d^8}$ square-planar complexes (*e.g.*, $\mathrm{Rh^I}$). The present study thus provides an unique and unambiguous example of the "DAISET" mechanism in the inorganic counterpart.

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11) The extinction coefficient of the absorption band due to $[Rh_4(dicp)_8(I)_2]^{4+}$ in MeCN was determined from the absorption spectrum of this cation prepared *in situ* as the mixture with $[Rh_2(dicp)_4(I)_2]^{2+}$ by the iodinolysis of $[Rh_2(dicp)_4]^{2+}$ in the dark. The concentration of $[Rh_4(dicp)_8(I)_2]^{4+}$ was determined by converting it to $[Rh_2(dicp)_4(I)_2]^{2+}$ ($\lambda_{max}=403$ and 467 nm, $\varepsilon=6.77\times10^5$ and 2.53×10^5 mol^{-1} dm^2, respectively) by irradiation of the visible light in the presence of excess iodine.

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