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Photochemical dehalogenation mediated by macrocyclic nickel(II) complexes

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Introduction

Tetraaza macrocyclic metal complexes are known to act as effective catalysts in the oxidation and reduction of organic substrates because of their high resistance to decomposition in relatively high or low valence states and the potential for coordination of substrates at the apical positions with respect to the macrocyclic plane. It has been reported that some macrocyclic metal complexes catalyze reductive dehalogenation [1] of alkyl [2,3] and aryl halides [4–6]. These reductive dehalogenation systems for aryl halides are comprised of a macrocyclic nickel(II) complex as a catalyst, NaBH₄ as a sacrificial reductant, and an organic halide substrate [4–6]. During the dehalogenation reaction, an intermediate nickel(I) complex, which can be produced from reduction by NaBH₄, is thought to play an important role as an active species [7–10]. In this study, we applied photochemically produced macrocyclic nickel(I) complexes to dehalogenation reactions and developed a new photochemical debromination system. Our photochemical system, comprising a macrocyclic nickel(II) complex catalyst, the ruthenium complex $[Ru(bpy)_3]^{2+}$ as a photosensitizer, and triethanolamine (TEOA) as a sacrificial reductant, was effective in the catalytic debromination of 1-bromo-4-t-butylbenzene in acetonitrile. Various reaction conditions were investigated, as well as the catalytic capabilities of various nickel(II) macrocyclic complexes.

Results and discussion

The photochemical system we designed was successful in the catalytic debromination of 1-bromo-4-*t*-butylbenzene; the results of

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ABSTRACT

A new photochemical dehalogenation system mediated by macrocyclic nickel(II) complexes was developed. Using this system, which consists of a macrocyclic nickel(II) complex catalyst, triethanolamine (TEOA) as a sacrificial reductant, and the ruthenium complex [Ru(bpy)₃](ClO₄)₂ as a photosensitizer, catalytic debromination of 1-bromo-4-*t*-butylbenzene in acetonitrile was effectively carried out. The catalytic capabilities of various macrocyclic nickel(II) complexes in debromination reactions were also elucidated. © 2011 Elsevier B.V. All rights reserved.

> the reactions under various conditions are shown in Table 1. The debromination reaction was guantitative (100% conversion) when an acetonitrile solution containing the nickel(II) complex **1a** (catalyst: 0.8 mM), the ruthenium(II) complex (photosensitizer: 4 mM), triethanolamine (TEOA) (sacrificial reductant: 0.4 M), and 1-bromo-4-t-butylbenzene (substrate: 40 mM) was irradiated with visible light for 3 h (entry 1) at room temperature (ca. 25 °C). In the absence of either the nickel(II) complex **1a** (entry 2), $[Ru(bpy)_3](ClO_4)_2$ (entry 3), or TEOA (entry 4), debromination did not proceed to any large extent, which showed that the presence of each of these components was required for the reaction. When the reaction mixture containing the three components was kept in the dark for 3 h (i.e., without photo-irradiation) at room temperature (entry 5) and at 60 °C (entry 6), almost no debromination occurred, which proved that photoirradiation, rather than heating, is required for the reaction to take place. Thus, it was found that three components-the nickel(II) complex, the ruthenium(II) complex, and TEOA-and light irradiation are all essential for this debromination reaction.

> The debromination of 1-bromo-4-*t*-butylbenzene in this reaction was confirmed by gas chromatography-mass spectroscopy (GC-MS) analysis. The GC-MS spectrum of the reaction solution after photoirradiation showed a peak at m/z 134, which was ascribable to the debromination product, [t-butylbenzene]⁺. The bromine liberated from 1-bromo-4-*t*-butylbenzene was converted to bromide anions; this was confirmed by the formation of AgBr precipitate upon addition of AgNO₃ to an aqueous solution made from the reaction solution. As the reaction proceeded, a white precipitate appeared in suspension; this was identified as $(CH_2CH_2OH)_3NHBr$ by comparison of its IR and ¹H NMR spectra with those of an authentic sample prepared from the reaction between TEOA and HBr.

> Fig. 1 shows the dependence of the debromination reaction upon photo-irradiation time. As the irradiation time was prolonged, the

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 Table 1

 Photochemical debromination of 1-bromo-4-t-butylbenzene under various conditions^a.

_					
_	Entry	Complex ^b	Photosensitizer	Sacrificial reductant	Conversion ^c /%
	1	1a	$[Ru(bpy)_3](ClO_4)_2$	TEOA	100
	2	None	$[Ru(bpy)_3](ClO_4)_2$	TEOA	2
	3	1a	None	TEOA	1
	4	1a	$[Ru(bpy)_3](ClO_4)_2$	None	2
	5 ^d	1a	$[Ru(bpy)_3](ClO_4)_2$	TEOA	3
	6 ^e	1a	$[Ru(bpy)_3](ClO_4)_2$	TEOA	1

^a Ni complex: 0.8 mM, photosensitizer: 4 mM, 1-bromo-4-*t*-butylbenzene: 40 mM, triethanolamine(TEOA): 0.4 M, acetonitrile, room temperature (ca. 25 °C), irradiated for 3 h by visible light.

^b ClO₄⁻ salt.

^c GC conversion.

^d The reaction was carried out in the dark.

^e The reaction was carried out at 60 °C in the dark.

conversion increased to ca. 100% in 3 h and then remained at a high value up to 6 h. The debromination reaction was completed within 3 h under the experimental conditions used. Fig. 2 shows the change in conversion rate against the concentration of the photosensitizer [Ru (bpy)₃](ClO₄)₂, with the other reaction conditions being kept constant. The conversion increased as the concentration of [Ru (bpy)₃](ClO₄)₂ increased, reaching a plateau (ca. 100%) at a photosensitizer concentration of 4 mM ([**1a**]:[[Ru(bpy)₃](ClO₄)₂]= 1:5). The dependence of the conversion on the concentration of **1a**–(**1a**]:[[Ru(bpy)₃](ClO₄)₂]=1:1, 1-bromo-4-*t*-butylbenzene = 40 mM, and TEOA = 0.4 M-is shown in Fig. S1. The yield increased as [**1a**] increased, reaching saturation point at [**1a**] ([[Ru(bpy)₃](ClO₄)₂])= 1.6 mM. The dependence of the conversion on the proportion of ethanol (protic solvent) in the acetonitrile–ethanol mixed solvent was also investigated (Fig. S2). The conversion yield was highest in neat



Fig. 1. Dependence of debromination reaction on photo-irradiation time for an acetonitrile solution containing **1a** (0.8 mM), $[\text{Ru}(\text{bpy})_3](\text{CIO}_4)_2$ (4 mM), 1-bromo-4-*t*-butylbenzene (40 mM), and TEOA (0.4 M).



Fig. 2. Conversion vs. concentration of $[Ru(bpy)_3](ClO_4)_2$. 1a: 0.8 mM, 1-bromo-4-tbutylbenzene: 40 mM, and TEOA: 0.4 M.



Scheme 1. Structural formulae of nickel(II) complexes.

acetonitrile solution and decreased as the ethanol content increased. At an ethanol content of 60%, the yield was down to ca. 50%. Based on these results, the optimum experimental conditions were concluded to be as follows: [Ni complex] = 0.8 mM, [[Ru(bpy)₃](ClO₄)₂] = 4 mM, [1-bromo-4-*t*-butylbenzene] = 40 mM, [triethanolamine (TEOA)] = 0.4 M, acetonitrile as solvent, and 3 h visible light irradiation. These conditions were used in subsequent experiments.

The catalytic capabilities of various macrocyclic nickel(II) complexes were investigated (see Scheme 1 and Table 2). For analogous Ni (II) complexes containing a pyridine moiety, the introduction of a benzyloxy group to the 4-position of the pyridine ring of **1b** did not affect their catalytic capabilities (entries 1 (**1a**) and 7 (**1b**)). The introduction of one methyl group to the nitrogen atom at the 7position of the macrocyclic skeleton of **1b** or **2a** decreased the conversion yield only slightly (entries 8 (**1c**) and 11 (**2b**)), whereas the introduction of methyl groups to the three nitrogen atoms at the 3-, 7-, and 11-positions of **1b** largely diminished its catalytic capability, with the conversion decreasing from 97% to 18% (entry 9 (**1d**)). The introduction of methyl groups to the carbon atoms at the 2and 12-positions of **1b** did not affect the conversion (entry 12 (**2c**)). The introduction of unsaturated C=N bonds to the macrocyclic

Table 2						
Photochemical	debromination	of	1-bromo-4-t-butylbenzene	using	various	Ni(II)
complexes ^a .						

Entry	Complex ^b	Conversion ^c /%	Entry	Complex ^b	Conversion ^c /%
1	1a	100	14	3a	100
7	1b	97	15	3b	97
8	1c	82	16	3c	93
9	1d	18	17	3d	98
10	2a	89	18	3e	99
11	2b	86	19	4a	10
12	2c	100	20	4b	7
13	2d	77	21	4c	12

 $^{\rm a}$ Ni complex: 0.8 mM, photosensitizer: 4 mM, 1-bromo-4-*t*-butylbenzene: 40 mM, triethanolamine(TEOA): 0.4 M, acetonitrile, room temperature (ca. 25 °C), irradiated for 3 h by visible light.

^b ClO₄⁻ salt.

^c GC conversion.



Scheme 2. Dehalogenation reactions.

skeleton of **2c** slightly decreased the conversion without systematic change (entries 10 (**2a**) and 13 (**2d**)).

It was found that nickel(II) complexes with 14-membered N4 macrocycles but without pyridine rings also showed catalytic capabilities. The nickel(II) complex with cyclam **3a**, which had no substituents in its macrocyclic skeleton, gave a high conversion (entry 14). Although the introduction of methyl groups to the macrocyclic skeleton affected the conversion only to a small extent (entries 15 (**3b**), 16 (**3c**), 17 (**3d**), and 18 (**3e**)), the introduction of unsaturated bonds to **3e** and **3b** largely resulted in decreased yields (entries 19 (**4a**), 20 (**4b**: isomer of **4a**), and 21 (**4c**)), in contrast to the abovementioned pyridine-containing macrocyclic nickel(II) complexes.

The photochemical reaction system under discussion was applied to the dehalogenation of various other substrates (Scheme 2 and Table 3). The yields for the debromination of 2-bromo-*m*-xylene (**A**) to m-xylene (E) were 95% and 99% for 1a and 3a, respectively (entries 22 and 26), indicating that the presence of methyl groups near the bromine atom does not affect the catalytic debromination reaction. The dechlorination of 2-chloro-m-xylene (**B**) did not proceed to any appreciable extent: the yields were very low, at 1% and 3% for 1a and 3a, respectively (entries 23 and 27). The debromination of 2,5dibromo-*p*-xylene (**C**) afforded a mixture of 2-bromo-*p*-xylene (**F**) and *p*-xylene (**H**); however, the yield ratios of these products were different for 1a (F: 39% and H: 61%, entry 24) and 3a (F: 62% and H: 38%, entry 28). Interestingly, in the dechlorination of 2,5-dichloro-pxylene (**D**), mono-dechlorination, resulting in the production of 2chloro-p-xylene (G), was observed (1a: 7%, entry 25, and 3a: 10%, entry 29), although products of complete dechlorination were not obtained using any of the Ni(II) complexes.

Fig. 3 shows cyclic voltammograms illustrating the effect of 1bromo-4-*t*-butylbenzene on the electrochemical reduction of **3a**. The nickel(II) complex **3a** showed one reversible wave, ascribable to the Ni^{II}/Ni^I process, around -1.5 V. The addition of 1-bromo-4-*t*-butylbenzene to a solution of **3a** resulted in the appearance of a new

Table 3			
Photochemical	dehalogenation	of various	substrates ^a .

	-					
Entry	Complex ^b	Substrate ^c	Conversion ^d /%			
			E	F	G	Н
22	1a	А	95	-	-	-
23	1a	В	1	-	-	-
24	1a	С	-	39	-	61
25	1a	D	-	-	7	0
26	3a	А	99	-	-	-
27	3a	В	3	-	-	-
28	3a	С	-	62	-	38
29	3a	D	-	-	10	0

^a Ni complex: 0.8 mM, photosensitizer: 4 mM, triethanolamine(TEOA): 0.4 M, acetonitrile, room temperature (ca. 25 °C), irradiated for 3 h by visible light.

^b ClO₄⁻ salt.

^c 40 mM.

^d GC conversion.

irreversible cathodic wave, different from the original, around -1.5 V. Because 1-bromo-4-*t*-butylbenzene was not reduced at -1.5 V in the absence of the nickel(II) complex, the appearance of this irreversible wave was probably due to the reaction of the reduced Ni(I) complex with 1-bromo-4-*t*-butylbenzene, which suggests that the Ni(I) complex is the active species in the debromination reaction. The addition of 1-bromo-4-*t*-butylbenzene to a solution of [Ru(bpy)₃]²⁺ did not affect its cyclic voltammogram.

Although various mechanisms for the reductive dehalogenation of aryl halides have been discussed [7-10], there has not yet been a clear conclusion. For this photochemical dehalogenation system we propose a tentative mechanism with two possible pathways based on previously reported dehalogenations [7-10]. As shown in Scheme 3, $[Ru^{II}(bpy)_3]^{2+}$ is initially exited to $[Ru^{II}(bpy)_3]^{2+*}$ by irradiation with visible light. [Ru^{II}(bpy)₃]^{2+*} then reacts with triethanolamine (the sacrificial reductant) to become $[Ru^{I}(bpy)_{3}]^{+}$, which reduces the macrocyclic Ni(II) complex to the active Ni(I) complex. The thus formed Ni(I) complex may react with the aryl halide to form an unstable intermediate Ni(III)-aryl complex, which has not yet been identified, or may cause direct formation of an aryl halide radical. In the former case, the unstable aryl complex immediately decomposes to a Ni(II) complex and an aryl radical Ar, whereas in the latter case, the aryl halide radical immediately decomposes to $Ar \cdot and a$ halide, X⁻. In either case, $Ar \cdot abstracts a$ proton from triethanolamine to form Ar, the liberated X⁻ forms the triethanolamine adduct, and the parent Ni(II) and Ru(II) complexes are recovered. In order to establish the mechanism with certainty, further studies will be necessary.

Thus, a new photochemical dehalogenation system mediated by macrocyclic nickel(II) complexes has been developed. It was found that various macrocyclic nickel(II) complexes show catalytic capabilities in the debromination of 1-bromo-4-*t*-butylbenzene and that these capabilities depend on the number and the positions of methyl groups on the macrocyclic skeletons.



Fig. 3. Cyclic voltammograms of **3a** (2 mM) (1) and **3a** (2 mM)+1-Bromo-*t*butylbenzene (20 mM) (2) in acetonitrile containing 0.1 M TEAP (electrolyte). Potential sweep rate: 0.1 V s^{-1} . Potentials vs. Ag/Ag⁺ reference electrode.



Scheme 3. Proposed mechanism for photochemical dehalogenation.

Experimental

Materials

The complexes **1a** [6], **1b** [11], **1c** [12], **1d** [13], **2a** [14], **2b** [15], **2c** [16], **2d** [17], **3a** [18], **3b** [19], **3c** [20], **3d** [21], **4a** [22], **4b** [23], **4c** [24], and **4d** [25] were prepared according to the previously reported methods. Biotech-grade acetonitrile stored under argon was used, applying syringe techniques. Argon gas (99.9999%) was used for purging. Other reagents were purchased from Wako, Sigma-Aldrich, and Tokyo Chemical Industry Co. and used as received unless otherwise specified.

Photochemical reactions

Photolysis samples were placed in a quartz cell (light path: 1 cm) with a stopcock, purged with argon gas, and irradiated with an ultrahigh-pressure mercury lamp (USIO, 475 W), with ultraviolet light and infrared light cut by L-39 and IRA-25S filters, respectively (the distance between the cell and the light source was 42 cm). The sample solution was stirred with a small stirring bar at a room temperature (ca. 25 °C). Although a water-filled round-bottomed flask was further inserted between the cell and the light source in order to eliminate thermal reactions completely, no difference was observed in the results of the photolysis experiments with and without the round-bottomed flask. After photolysis, the products were immediately analyzed by gas chromatography (GC) using a previously reported method [6]. Sample analysis was performed at least three times and sufficient reproducibility was obtained.

Physical measurements

Cyclic voltammograms were measured using an ALS voltammetric analyzer, model 610 (reference electrode: BAS RE5 Ag/Ag⁺; working electrode: platinum or glassy carbon; counter electrode: platinum wire; supporting electrolyte: tetraethylammonium perchlorate). GC-MS spectra were measured at the instrumental analysis division of Hokkaido University.

Appendix A. Supplementary material

Supplementary data to this article can be found online at doi:10.1016/j.inoche.2011.03.024.

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