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Reactivity of Rare Earth Metal Thin Films with Naphthalene in Ether Solution

TSUYOSHI ARAKAWA*, SHINJI SHIMADA, GIN-YA ADACHI and JIRO SHIOKAWA

Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2-1 Yamadaoka, Suita-shi, Osaka-fu, Japan

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Abstract

Among rare earth metals cerium and europium metal, which have the lowest melting points, readily reacted with naphthalene or anthracene in diethyl ether solution, but praseodymium, neodymium, dysprosium, holmium and erbium metal thin films did not. With samarium metal, only the surface of the metal thin film reacted with naphthalene– or anthracene–ether solution. The formation of a complex is briefly discussed with reference to the UV spectra of Ln–naphthalene–ether solutions (Ln = Ce, Eu), together with the results of atomic weight determinations.

Introduction

During the past few years much attention has been paid to the organic chemistry of divalent lanthanide compound because divalent lanthanide salts behave as strong reducing agents. Kagan *et al.* established that samarium diiodide can induce several types of reactions of organic molecules [1, 2]. Also it has been reported that the zero-valent metals react with neutral unsaturated hydrocarbons [3–5]. However, less attention has been paid to the reactivity of rare earth metals with aromatic hydrocarbons. We have reported the reactivity of the rare earth thin films with oxygen at higher temperatures [6, 7]. In the present study, we have extended our general investigations of the reactivity of the rare earth thin films with various reactants to some aromatic hydrocarbons. A preliminary account of the reactivity of some rare earth metal thin films with naphthalene in diethyl ether solution is given in this paper.

Experimental

The rare earth thin films were obtained as follows. The rare earth metal vapors originating from a tungsten-wire basket source containing the desired metal chip (purity ≥99.9%; Mitsuwa Chemical Co. Ltd.) were deposited on the bottom of a 200-ml round-bottomed flask. The flask was connected via brass heads to a vacuum system ($\simeq 10^{-5}$ torr) via a vacuum stopcock, as shown in Fig. 1. The part A of Fig. 1 was transferred to a glove box. The reaction of the rare earth thin film ($\simeq 1.4 \times 10^{-4}$ mol) with a solution of the aromatic hydrocarbon ($\simeq 2.8 \times 10^{-4}$ mol) in a solvent (20 cm^3) was conducted under dry nitrogen with a glove box technique because the solutions in which the rare earth metal was dissolved were air- and moisture-sensitive. Benzene, naphthalene and anthracene were chosen as simple aromatic hydrocarbons. The solvents used were diethyl ether, dipropyl ether, diglyme, tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), trichloroethylene, chloroform and acetonitrile. The solvents and benzene were degassed by the conventional freeze–pump–thaw technique. Naphthalene and anthracene were purified by sublimation. The characterization of solutions was carried out with a Shimazu UV-180. Molecular weights were measured by a Hitachi Perkin-Elmer 115 vapor pressure osmometer.

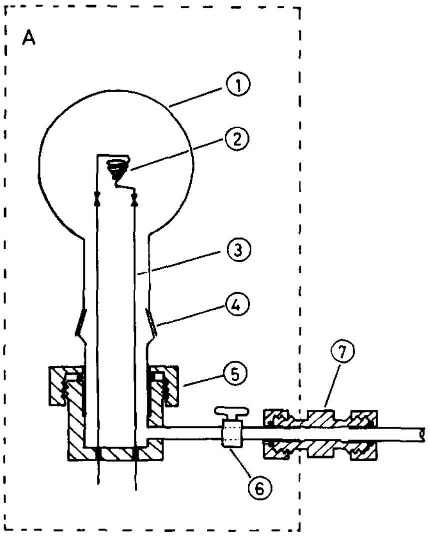

Fig. 1. Schematic diagram of the apparatus. 1, glass flask; 2, W-wire basket source; 3, Cu-wire; 4, ground glass joint; 5, brass head; 6, vacuum stopcock; 7, tube fitting.

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*Author to whom correspondence should be addressed.

Results and Discussion

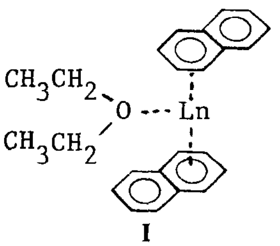
Reactivity of some Rare Earth Metal Thin Films

Not all of the rare earth thin films reacted with benzene–ether solution. But when the rare earth thin films reacted with naphthalene in ether at room temperature, they differed from one another in reactivity. The results are listed in Table I, together with the results in anthracene–ether solution. A europium (Eu) metal thin film was easily attacked by naphthalene–ether solution. Eu metal was completely dissolved in naphthalene–ether solution. The reaction between a cerium (Ce) thin film and naphthalene–ether solution at room temperature was slow and went to completion after about 6 h. With a samarium thin film, only the surface of the metal was dissolved. However, praseodymium, neodymium, dysprosium, holmium and erbium thin films did not react with naphthalene–ether solution. Thus, Ce and Eu in naphthalene–ether solution are usually attacked more rapidly than their immediate neighbors in the same manner as the corrosion of rare earth metals in sodium hydroxide [7]. Ce and Eu metal are considered to have higher chemical reactivity, judging from the fact that the melting points of these metals are lower than those of their neighbors. In the case of Sm metal thin films, it is suggested that the surface differs from the bulk. Recently, the surface of Sm metal was confirmed to be completely divalent [8]. Thus, the surface of a Sm metal thin film may be more active than that of the bulk. The reacted solutions are colorless. Reaction between Ce, Sm or Eu and anthracene–ether solution occurred, but the reactivity to anthracene–ether solution was lower than that to naphthalene–ether solution.

A unique phenomenon of the reaction of rare earth metal thin films with naphthalene is that the reactivity is strongly affected by the solvents used. When THF, DMSO and acetonitryl were used, the dissolution of Ce, and Sm and Eu metal was not observed. As described above, the reaction was seen to occur in the ethers alone (*i.e.*, diethyl ether, dipropyl ether or diglyme), which have lower polarity. Although the dielectric constants of $CHCl_3$ and C_2HCl_3 are close to that of ethers, Ce, Sm and Eu metal thin films were unreactive to naphthalene–$CHCl_3$ or –C_2HCl_3 solutions. The reasons for this phenomenon are not clear at present. However, it is considered that an ether molecule is closely related to the formation of Ce– or Eu–naphthalene complex as described later. Thus, the characteristics of Ln–aromatic hydrocarbon in a solvent were studied by use of Ln–naphthalene diethyl ether solutions (Ln = Ce, Eu).

Characteristics of Ln–Naphthalene–Ether Solutions (Ln = Ce, Eu)

When diethyl ether was partially evaporated *in vacuo* at room temperature from the reacted solution, the color of the solution changed from colorless to pale brown. After removal of the ether *in vacuo*, the excess of naphthalene was sublimated onto a liquid N_2 cooled cold trap (30 min, 40 °C). The molecular weight of the pale brown residue without purification was about 460 ± 10 for the sample containing Ce. However, we could not determine the fragment to be $(C_{10}H_8)_2Ce^+$ by mass spectroscopy as the residue was not easily volatile, as with bis(naphthalene)chromium as described elsewhere [8]. The pale brown residue easily decomposed on heating *in vacuo*. The ^1H NMR spectrum showed the existence of ether in the residue and the relative intensity of naphthalene to ether was clearly decided. Thus, it may be estimated that the molecular formula of the residue containing Ce is as follows. This complex is similar to $(\eta^6\text{-}C_{10}H_8)_2Ti$ in ether solution [9]. If the complex (structure **I**) is formed, the molecular weight of the complex is 470 for Ce. The molecular weight as described above is close to this value.



I

The formation of a complex was assumed from analysis of the UV spectra of Ln–naphthalene–ether solutions because the isolation of a Ln–naphthalene complex from ether solution was very difficult, as described above. We selected $(\eta^6\text{-}C_{10}H_8)_2Cr$

TABLE I. Reactivity of Rare Earth Thin Films to some Aromatic Hydrocarbons[a]

Rare earth metal	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er
Naphthalene–ether	++	–	–	+	++	–	–	–	–	–
Anthracene–ether	+	–	–	+	+	–	–	–	–	–
Melting point[b] (°C)	798	931	1021	1072	822	1313	1365	1414	1474	1529

[a] ++, completely dissolved; +, partially dissolved; –, not dissolved. [b] Ref. 14.

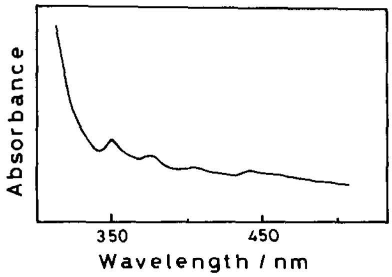


Fig. 2. Ultraviolet–visible spectrum of Ce–naphthalene–ether solution at 25 °C.

Table II. Values of λ_{max} and Tentative Assignments for the Electronic Spectra of the Bis(naphthalene)metal Complexes in Ether Solution

Metal	λ_{max}	Assignment
Cr	350	$1a_u \rightarrow 1b_u(1)$
	$(350)^a$	
	410	$1b_g \rightarrow 1b_u/1a_u(3/4)$
	$(412)^a$	
	480	$2a_g \rightarrow 1b_u/1a_u(5/6)$
	$(480)^a$	
Ce	350	$1A'' \rightarrow 2A''(1)$
Eu	350	
Ce	375	$1A' \rightarrow 1A''(2)$
Eu	375	
Ce	407	$3A' \rightarrow 2A''(3)$
Eu	405	
Ce	435	$3A' \rightarrow 1A''(4)$
Eu	450	

^{a}The values in parentheses were derived from the literature [9].

as the reference sample since the formation and the electronic spectral data of $(\eta^6\text{-}C_{10}H_8)_2M$ have been reported in detail. The authentic sample of $(\eta^6\text{-}C_{10}H_8)_2Cr$ was prepared by the method of Kundig and Timms [10]. A typical UV spectrum is shown in Fig. 2. Also, λ_{max} and the tentative assignments for the UV spectrum are summarized in Table II, together with the results of $(\eta^6\text{-}C_{10}H_8)_2Cr$ in ether solution. The data for $(\eta^6\text{-}C_{10}H_8)_2Cr$ are close to those reported by Francis and Morand [9]. Although $(\eta^6\text{-}C_{10}H_8)_2Cr$ has been shown to crystallize with C_{2v} symmetry, it is assumed that the C_{2h}(*trans*) form coexists within a fluid matrix [9]. Therefore, the UV spectrum of $(\eta^6\text{-}C_{10}H_8)_2Cr$ in ether solution was interpreted by terms of C_{2h} symmetry in a similar manner, as described elsewhere [9].

It is well known that the 18- or 16-electron rule also provides a useful guide in understanding the stoichiometries of stable organotransition metal complexes [11]. The $(\eta^6\text{-}C_{10}H_8)_2Cr$ complex in its zero oxidation state has the 18-electron species (d^6 system). Thus the highest energy band at 350 nm in Cr is assigned to transition 1 in Fig. 3 ($1a_g \rightarrow 1b_u$). The second band in Cr is assigned to the transition 3/4 ($1b_g \rightarrow 1b_u/1a_u$). The lowest energy band of Cr corresponds to the transition 5/6 ($2a_g \rightarrow 1b_u/1a_u$). The absorbance in the UV spectrum of the Ln–naphthalene ether solution was observed in the same region as that for $(\eta^6\text{-}C_{10}H_8)_2Cr$ in ether solution, but they differed from one another in λ_{max} values. The electronic configurations are $4f^15d6s^2$ for Ce and $4f^76s^2$ for Eu, respectively. Also, Mattias *et al.* [12] and Gschneidner [13] have suggested that the low melting points of Ce and Eu are due to hybridization of the 4f electrons with the sd valence electrons. Therefore it may be assumed that the number of d electrons in the Ln–naphthalene complex in its zero oxidation state is formally 3. That is, the electron count will be less than 18 or 16 if the complex between Ln and naphthalene is $(\eta^6\text{-}C_{10}H_8)_2Ln$. Thus the participation of the ether molecule in the coordination sphere around Ce or Eu increases in a similar way to that for the $(\eta^6\text{-}C_{10}H_8)_2Ti$ complex (d^4 system) [9]. It may be understood that the reaction between Ln (Ln = Ce, Eu) metal thin films and naphthalene requires ether molecules as solvent. However, the symmetry changes from C_{2h} to C_s, as shown in Fig. 3. The energy band at 350 nm may be assigned to the transition $1A'' \rightarrow 2A''$. Although the transition 2 is obscured for Cr, the second bands ($1A' \rightarrow 1A''$) in Ce and Eu are clear. Since the transition $3A' \rightarrow 2A''$ and $3A' \rightarrow 1A''$ will not exist for a d^3 system, the third and fourth band may be assigned to transitions $2A' \rightarrow 2A''$ and $2A' \rightarrow 1A''$, respectively. Thus we have focused our discussion on the spectra of the bis(naphthalene)Ln complexes in the presence of an ether

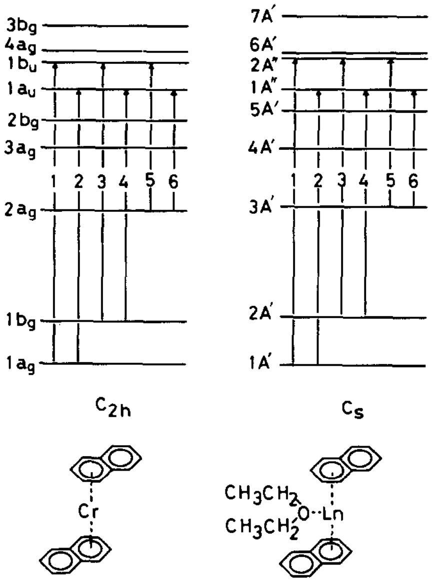


Fig. 3. Qualitative molecular orbital ordering for $(C_{10}H_8)_2Cr$ and $(C_{10}H_8)_2Ln$ in ether solution.

molecule as ligand. Since these complexes are a 17-electron species, however, the existence of an interaction of the type $(C_{10}H_8)_2Ln\cdots Ln(C_{10}H_8)_2$ in ether solution may be expected.

The major observation in this study is that Ce and Eu thin films are highly reactive to naphthalene in ether solution at room temperature. On the basis of UV spectroscopic data, we believe that this is best explained in terms of a bis(naphthalene)Ln (Ln = Ce, Eu) complex.

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