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The Reaction of Diiodoethane with Neptunium and Plutonium Metals*

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Samarium and ytterbium metals react with tetrahydrofuran (THF) solutions of diiodoethane to yield solutions of the respective diiodides [1, 2]. The blue SmI_2 solutions are quite stable in the absence of water and oxygen, and the use of SmI_2 as a reagent in organic reactions has been extensively studied by Kagan [3].

The chemical similarity between lanthanide and actinide metals suggests that alkyl diiodides might also react with actinide metals. Neptunium and plutonium have been found to react with THF solutions of $C_2H_4I_2$; thorium and uranium metal did not react. A preliminary study [4] of the reaction between $C_2H_4I_2$ and alpha-phase Pu metal has been reported; further work is reported here.

Experimental

Materials

Neptunium and plutonium metals (obtained from the Rocky Flats Plant, Golden, Colorado) were polished with an emery cloth and washed in petroleum ether before use. Lanthanide metals (La, Pr, Nd, Sm) were purchased as powder or chips from Alfa Products.

Diiodoethane (Aldrich) was purified by washing a diethyl ether solution with aqueous sodium thiosulfate. The ether phase was dried with anhydrous sodium sulfate and evaporated by vacuum to recover pure $C_2H_4I_2$. 1,3-Diiodopropane, 1,4-diiodobutane and 1,2-diiodobenzene (Aldrich) were used without purification.

Preparations

Preparations, purifications and sample handling were performed in a dry argon atmosphere. Metal samples and a THF solution of the organic diiodide were stirred at room temperature in the dark to minimize $C_2H_4I_2$ decomposition. All reactions had the lanthanide or actinide metal in excess; reaction times ranged from 16 h to one week. In a typical preparation, 0.52 g (1.82 mmol) in 20 ml THF was stirred at room temperature with a 4.19 g piece of Np metal. After 16 h the yellow precipitate was separated from the remaining Np metal (3.91 g) mechanically and the precipitate was filtered from the solution. The reaction consumed 0.284 g (1.20 mmol) of Np metal. *Anal.* Calc. for $NpI_3 \cdot 4THF$: Np, 26.2; I, 42.1; C, 21.1. Found: Np, 27.4; I, 41.3; C, 20.9%. The ratio of reactants consumed is $I_2C_2H_4/Np = 1.52$, indicating that the net reaction is

$$Np + \frac{3}{2}C_2H_4I_2 \xrightarrow{THF} NpI_3 \cdot x THF + \frac{3}{2}C_2H_4$$

Attempts to measure the gas evolution from the system were unsuccessful because of the solubility of ethylene in THF. In the reaction described above, 1.43 mmol of gas was evolved, or 1.20 mol per mol Np. Later tests found an appreciable solubility for C_2H_4 in THF, even at pressures in the range of 10–20 mm Hg. In one test, 50 ml THF dissolved 3.1 mmol of C_2H_4 at a C_2H_4 partial pressure of 330 mm Hg.

Except for reactions between Sm metal and diiodides, products precipitated from THF solution. The reactions of Sm with diiodobutane and *o*-diiodobenzene were exothermic and yielded purple solutions of SmI_2. Solid $SmI_2 \cdot 2THF$ was precipitated by adding petroleum ether and filtering.

Results and Discussion

Reaction Stoichiometry

The reaction between bulk Np and Pu metals and 0.07–0.14 M $C_2H_4I_2$ was normally slow, but when the reaction was allowed to run for several days the diiodide was completely consumed. Reactions with chips of lanthanide metals were more rapid and, in the case of Sm, usually exothermic. The ratio of the reactants consumed (Table I) demonstrates that the reaction for Np and Pu metals is

TABLE I. Reactant Ratio

Product	Amount consumed (mmol)		
	Metal	$C_2H_4I_2$	$C_2H_4I_2$/M ratio
$PuI_3 \cdot 5THF$ (I)	2.34	3.55	1.52
$PuI_3 \cdot 5THF$ (II)	2.30	3.37	1.47
$NpI_3 \cdot 4THF$	1.20	1.82	1.52
$NpI_3 \cdot 4THF$	2.27	3.38[a]	1.49
$SmI_2 \cdot 2THF$ (I)	3.31	3.30	1.00
$SmI_2 \cdot 2THF$ (II)	4.01	3.83[a]	0.96

[a] $C_3H_6I_2$.

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TABLE II. Analytical Data

Product	Diiodide	Composition (wt.%)						Color
		Calculated			Found			
		Metal	I	C	Metal	I	C	
$NpI_3 \cdot 4THF$	$C_2H_4I_2$	26.2	42.1	21.2	27.4	41.3	20.9	yellow
$NpI_3 \cdot 4THF$	$C_3H_6I_2$	26.2	42.1	21.2	27.5	40.8		yellow
$PuI_3 \cdot 5THF$	$C_2H_4I_2$	24.4	38.9	24.5	24.9	37.5	22.7	light gray
$LaI_3 \cdot 4THF$	$C_2H_4I_2$	17.4	47.2	17.8	17.7	46.5	22.9	gray
$PrI_3 \cdot 3THF$	$C_2H_4I_2$	19.1	51.6	19.5	17.5	50.3	18.9	red–brown
$NdI_3 \cdot 3THF$	$C_2H_4I_2$	19.5	51.4	19.4	18.4	49.6	19.0	gray
$SmI_2 \cdot 2THF$	$C_2H_4I_2$	27.4	46.3	17.5		48.3		purple
$SmI_2 \cdot 2THF$	$C_3H_6I_2$	27.4	46.3	17.5		45.9		purple
$SmI_2 \cdot 2THF$	$C_4H_8I_2$	27.4	46.3	17.5		45.0	16.2	purple
$SmI_2 \cdot 2THF$	$C_6H_4I_2$	27.4	46.3	17.5	27.6			purple
$NpI_2(MeCp) \cdot 3THF$		30.4	32.5	27.7	30.5	30.8	34.3	orange
$NpI(MeCp)_2 \cdot 3THF$		32.1	17.2	39.0	32.0	18.4	38.9	red–purple

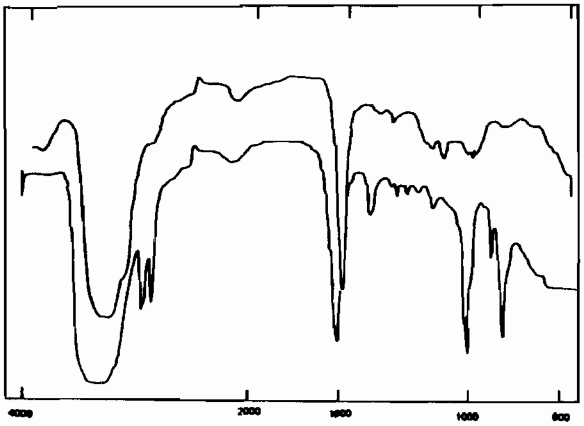

Fig. 1. Infrared spectra of $NpI_3 \cdot 4THF$ (above) and $SmI_2 \cdot 2THF$ (KBr pellet) (below).

$$Np + \tfrac{3}{2}C_2H_4I_2 \xrightarrow{THF} NpI_3 \cdot 4THF + \tfrac{3}{2}C_2H_4$$

and for Sm, the reaction is

$$Sm + C_2H_4I_2 \xrightarrow{THF} SmI_2 \cdot 2THF + C_2H_4$$

Np metal reacted with 1,3-$C_3H_6I_2$, but neither alpha-Pu nor the more active delta-Pu metal reacted with any diiodide except $C_2H_4I_2$. Every diiodide tested reacted with Sm powder. Analytical data for the compounds prepared are shown in Table II.

Infrared Spectra

Infrared spectra of the $PuI_3 \cdot 5THF$, $NpI_3 \cdot 4THF$, $NdI_3 \cdot 3THF$ and $SmI_2 \cdot 2THF$ are due to the coordinated THF; the spectra of $SmI_2 \cdot 2THF$ and $NpI_3 \cdot 4THF$ are shown in Fig. 1. Major features in the $SmI_2 \cdot 2THF$ spectra are the C–H stretching band in the 3000–3400 cm^{-1} region, a strong band at 1670 cm^{-1}, and the C–O–C stretching bands in the 1000–840 cm^{-1} region. These bands are shifted to lower frequencies from their positions in THF (1070–900 cm^{-1}) [2, 5], indicating that THF is coordinated through the oxygen atom [6]. The spectrum of the THF solvates of AnI_3 or LnI_3 shows only a weak absorption in this region, possibly because the coordination sphere around the trivalent metal ion is so crowded that the vibration is, in effect, damped out. In support of this proposal, the Sm^{2+} ion has an ionic radius of about 1.17 Å and coordinates four ligands; the trivalent ions have radii in the range 1.04–0.96 Å and coordinate six or more ligands in the triiodide solvates [7].

The strong band at 1670 cm^{-1} is probably due to a C–H motion. It lies in the region of the C=C stretching mode and, combined with incorrect data, led to the tentative proposal that $PuI_3 \cdot xTHF$ had coordinated C_2H_4 [4]. This proposal was demonstrated to be wrong in chemical tests where little gas was evolved on dissolution of the compounds in 2 M H_2SO_4, and where no C_2H_4 was found by gas chromatographic analysis of the recovered gas.

Reaction with $TlC_5H_4CH_3$

The solubility of the $MI_3 \cdot xTHF$ solvates is low in THF; the solubility of the Pu compound was measured as 10^{-3} M in THF. However, the solubilities of the anhydrous triiodides prepared by solid–gas reactions are very low, and reactions between triiodides and metalloorganic compounds can require days to complete.

The reaction of $NpI_3 \cdot 4THF$ with thallous methylcyclopentadienide (TlCpMe) with THF as a solvent was complete in 5–10 min. Both reactants are essentially insoluble in THF; the orange $NpI_2MeCp \cdot 3THF$ or the red–purple $NpI(MeCp)_2 \cdot 3THF$ product can be recovered essentially pure by evaporating the solution or by precipitating with petroleum ether. In spite of the difficulty of preparing $NpI_3 \cdot x$THF and $PuI_3 \cdot x$THF by reacting the metals with $C_2H_4I_2$, these solvates could be useful as reactants where the anhydrous compounds react very slowly or not at all.

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