

$= 5.2 \times 10^{-4} \text{ min.}^{-1}$ for dissociation (reverse Diels-Alder reaction) at 180° ; these values represent a difference in free energy of activation of 1.1 kcal. per mole. More accurate determinations of the kinetic parameters are planned.

While our experiments offer no new insight into the mechanism of the Diels-Alder reaction, they exclude participation of a diradical intermediate with a long enough lifetime to permit racemization. Strong moral support is provided for the presumption² that the rearrangements and the reverse Diels-Alder reaction proceed along the same energy path. The possibility that different energy paths are involved (the rearrangements are formally Cope rearrangements)¹² is not rigorously excluded; but at least with methacrolein dimer, both reactions occur simultaneously.

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(12) A. C. Cope and E. M. Hardy, *J. Am. Chem. Soc.*, **62**, 441 (1940), and later papers.

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FIRST OBSERVATION OF AQUEOUS TETRAVALENT AMERICIUM¹

Sir:

Americium chemistry has been studied by workers at laboratories in the U.S., U.K., and U.S.S.R. for over ten years. However, only americium valence states of (III), (V), and (VI) have been

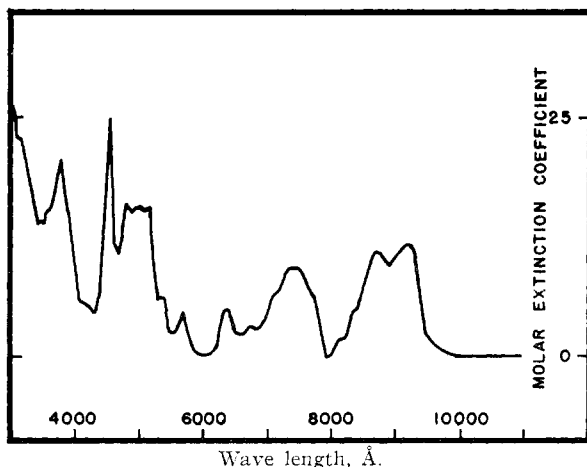


Fig. 1.—Absorption spectrum of Am(IV) in $15M \text{ NH}_4\text{F}$; 5 cm. quartz cells, $15M \text{ NH}_4\text{F}$ reference solution.

characterized in aqueous solution. Compounds of tetravalent americium prepared by anhydrous means are known, and tetravalent americium has been looked for in aqueous solution, e.g., during the reduction of Am(V) and (VI); during the disproportionation of Am(V); and on dissolution of americium dioxide. Although evidence was found for reactions involving Am(IV) as a kinetic intermediate, all previous work agrees that Am(IV)

has not heretofore been detected in solution.² We find that a solution of pure tetravalent americium can be prepared in saturated ammonium fluoride.

Black $\text{Am}(\text{OH})_3$ was freshly prepared by heating $\text{Am}(\text{OH})_3$ with $0.2 M \text{ NaOCl}$ – $0.2 M \text{ NaOH}$.³ It was treated with saturated aqueous ammonium fluoride in an attempt to produce a solid ammonium-Am(IV) fluoride compound. To our surprise, the slurry of $\text{Am}(\text{OH})_3$ completely dissolved in the $15 M \text{ NH}_4\text{F}$ solution to give an americium concentration of $0.01 M$. The resulting clear (pink-red) solution showed absorption peaks which could not be attributed to any soluble americium species previously known. Moreover, this spectrum bore a striking resemblance to the absorption spectrum of solid AmF_4 .⁴

| PRINCIPAL Am(IV) PEAKS | | | |
|-----------------------------|---------------------------------------|-----------------------------|--|
| AmF ₄ (solid) | Am(IV) in $15 M \text{ NH}_4\text{F}$ | AmF ₄ (solid) | Am(IV) in $15 M \text{ NH}_4\text{F}$ |
| 9180 | 9230 Broad, asym | 5680 | 5687 |
| 8620 | 8730 | 5360 | 5393 |
| 7440 | 7400 Broad | 4860 | 4818 |
| 7030 | .. | 4530 | 4560 |
| 6390 | 6387 | 3760 | 3777 |

The absorption spectrum of Am(IV) in $15 M \text{ NH}_4\text{F}$ was obtained from 3,000 to 12,000 Å. (Fig. 1). The peak at 4560 Å. ($\epsilon = 25$) is sharp and well separated from principal peaks of other americium valence states. It is useful for identification and determination of Am(IV).

Heating the solution of Am(IV) in $15 M \text{ NH}_4\text{F}$ to 90° does not cause disproportionation of Am(IV) or its chemical reduction by water.

Treatment of Am(IV) in $15 M \text{ NH}_4\text{F}$ with ozone at room temperature yields Am(VI) which, on reduction, again forms the soluble Am(IV) complex. Reduction of Am(IV) to Am(III) is observed due to Am^{241} alpha radiation. Iodide also reduces Am(IV) to Am(III).

Treatment of $\text{Am}(\text{OH})_3$ with saturated RbF or KF also gives solutions containing primarily Am(IV). Both Th(IV) and U(IV) are soluble in high concentrations of potassium, rubidium and ammonium fluorides. It would be expected that Pu(IV) and Np(IV) would behave similarly. Structures of the crystalline alkali-Am(IV) fluorides obtained from solution are currently being investigated by F. H. Kruse and L. B. Asprey of this laboratory.

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