

$= 5.2 \times 10^{-4} \text{ min.}^{-1}$  for dissociation (reverse Diels-Alder reaction) at  $180^\circ$ ; 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 presumption<sup>2</sup> 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)<sup>13</sup> is not rigorously excluded; but at least with methacrolein dimer, both reactions occur simultaneously.

Our thanks are due to Dr. S. L. Manatt and Mr. D. M. Kuwada of the Jet Propulsion Laboratory for their good offices and technical help in obtaining the mass spectra.

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

CONTRIBUTION No. 2685

GATES AND CRELLIN LABORATORIES OF CHEMISTRY  
CALIFORNIA INSTITUTE OF TECHNOLOGY RAYMOND P. LUTZ  
PASADENA, CALIFORNIA JOHN D. ROBERTS

RECEIVED MARCH 11, 1961

#### FIRST OBSERVATION OF AQUEOUS TETRAVALENT AMERICIUM<sup>1</sup>

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

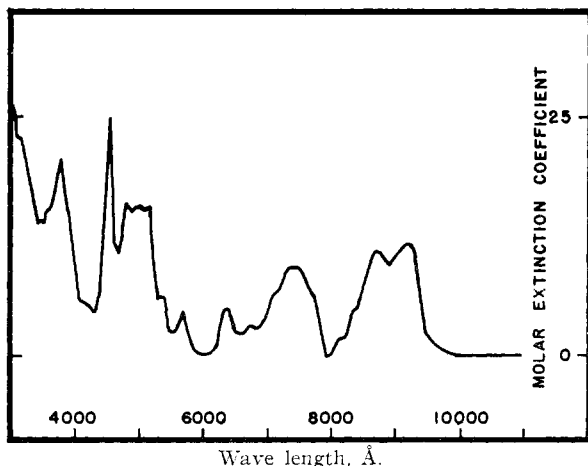


Fig. 1.—Absorption spectrum of Am(IV) in  $15M$   $NH_4F$ ; 5 cm. quartz cells,  $15M$   $NH_4F$  reference solution.

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)

(1) This work was sponsored by the U. S. Atomic Energy Commission.

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

Black Am(OH)<sub>3</sub> was freshly prepared by heating Am(OH)<sub>3</sub> with 0.2 *M* NaOCl-0.2 *M* NaOH.<sup>3</sup> 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 Am(OH)<sub>3</sub> completely dissolved in the 15 *M* NH<sub>4</sub>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<sub>4</sub>.<sup>4</sup>

PRINCIPAL Am(IV) PEAKS			
AmF <sub>4</sub> (solid)	Am(IV) in 15 <i>M</i> NH <sub>4</sub> F	AmF <sub>4</sub> (solid)	Am(IV) in 15 <i>M</i> NH <sub>4</sub> 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* NH<sub>4</sub>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* NH<sub>4</sub>F to  $90^\circ$  does not cause disproportionation of Am(IV) or its chemical reduction by water.

Treatment of Am(IV) in 15 *M* NH<sub>4</sub>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<sup>241</sup> alpha radiation. Iodide also reduces Am(IV) to Am(III).

Treatment of Am(OH)<sub>3</sub> 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.

LOS ALAMOS SCIENTIFIC LABORATORY  
UNIVERSITY OF CALIFORNIA  
LOS ALAMOS, NEW MEXICO

L. B. ASPREY  
R. A. PENNEMAN

RECEIVED MARCH 16, 1961

(2) L. B. Asprey and S. E. Stephanou, AECU-924 (1950); S. E. Stephanou, L. B. Asprey and R. A. Penneman, AECU-925 (1950); L. Fyring, H. R. Lohr and B. B. Cunningham, *J. Am. Chem. Soc.*, **74**, 1186 (1952); L. B. Asprey, *ibid.*, **76**, 2019 (1954); S. R. Gunn and B. B. Cunningham, *ibid.*, **79**, 1563 (1957); G. R. Hall and P. D. Herdman, *J. Chem. Soc.*, 2214 (1954); G. N. Yakovlev and V. N. Kosyakov, *Proc. Int'l. Conf. Peaceful Uses of Atomic Energy*, **7**, 363 (1956), and **28**, 373 (1958); R. A. Penneman and L. B. Asprey, *ibid.*, **7**, 355 (1956); G. R. Hall and T. L. Markin, *J. Inorg. & Nuclear Chem.*, **4**, 296 (1957); and R. A. Penneman and T. K. Keenan, National Academy of Sciences NS-3006 (1960).

(3) R. A. Penneman, J. S. Coleman and T. K. Keenan, "Preparation and Reactions of Am(IV) Hydroxide," *J. Inorg. Nuclear Chem.*, **17**, 138 (1961).

(4) L. B. Asprey and T. K. Keenan, *ibid.*, **7**, 27 (1958).