# THE ABSORPTION SPECTRA OF Bk<sup>3+</sup> AND Bk<sup>4+</sup> IN SOLUTION\*

## R. G. GUTMACHER, E. K. HULET, R. LOUGHEED, J. G. CONWAY,<sup>†</sup> W. T. CARNALL,<sup>‡</sup> D. COHEN,<sup>‡</sup> T. K. KEENAN§ and R. D. BAYBARZ Lawrence Radiation Laboratory, University of California, Livermore, California

(First received 5 December 1966; in revised form 6 February 1967)

Abstract—Sixteen absorption bands of  $Bk^{3+}$  in the region from 3200 to 15,000 Å are reported. The spectrum was studied in a variety of aqueous acid solutions, at Bk concentrations of  $3 \cdot 6 \times 10^{-3}$  M or less. The weaker bands were enhanced by the use of time-averaging techniques, followed by computer processing of the data. Berkelium was oxidized to the quadrivalent state with sodium bismuthate and a partial observation of its absorption spectrum was made. The radiolytic reduction of  $Bk^{4+}$  proceeds at a linear rate. The quadrivalent state has a half-life of 2.8 hr in 5 M HClO<sub>4</sub> solution.

#### INTRODUCTION

WE REPORT here the first observations of the absorption spectra of berkelium in solution. Earlier attempts to study the absorption spectrum of Bk<sup>3+</sup> by using a few micrograms absorbed on a bead of ion-exchange resin and in an aqueous acid solution were unsuccessful.<sup>(1)</sup> Some absorption lines were seen from 8  $\mu$ g of Bk contained in a crystal of LaCl<sub>3</sub>.<sup>(2)</sup> These experiments placed an upper limit of 10 on the molar absorptivities of bands in the visible region of the spectrum. Recently, by combining the Bk produced in two capsules of <sup>244</sup>Cm-<sup>248</sup>Cm after irradiation for 9.5 months at a neutron flux of 5 × 10<sup>5</sup> n/cm<sup>2</sup> per sec, we were able to isolate 45  $\mu$ g of <sup>249</sup>Bk (a beta emitter with a half-life of 310 days). Co-operative experiments were done at Livermore to study the solution absorption spectrum of Bk<sup>3+</sup> in various acidic media. We found sixteen absorption bands in the region from 3200 to 15,000 Å. In addition, the Bk was oxidized to the quadrivalent state and a partial observation of its absorption spectrum made. The rate of radiolytic reduction of Bk<sup>3+</sup> to Bk<sup>3+</sup> was studied and a half-life for the quadrivalent state in solution was obtained.

## EXPERIMENTAL

The initial step in the isolation and purification of the Bk was its separation in the quadrivalent state from all radioactive species except <sup>141–144</sup>Ce by extraction chromatography with bis-(2-ethyl-hexyl)orthophosphoric acid.<sup>(8)</sup> Cerium was later separated from Bk by elution from cation-exchange resin with 20% ethanol saturated with hydrogen chloride.<sup>(4)</sup> Final removal of common, non-radio-active impurities from the Bk was accomplished by elution of the impurities prior to the Bk from a

- \* Work performed under the auspices of the U.S. Atomic Energy Commission.
- † Lawrence Radiation Laboratory, University of California, Berkeley, California.
- ‡ Argonne National Laboratory, Argonne, Illinois.
- § Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico.
- || Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- <sup>(1)</sup> B. B. CUNNINGHAM, Lawrence Radiation Laboratory, Berkeley, California. Private Communication; B. B. CUNNINGHAM, J. chem. Educ. 36, 32 (1959).
- <sup>(2)</sup> R. G. GUTMACHER, E. K. HULET and J. G. CONWAY. (Unpublished data.)
- <sup>(8)</sup> E. K. HULET, J. inorg. nucl. Chem. 26, 1721 (1964).
- <sup>(4)</sup> S. G. THOMPSON, B. G. HARVEY, G. R. CHOPPIN and G. T. SEABORG, J. Am. chem. Soc. 76, 6229 (1954).

very small Dowex-50 colloidal resin bed using successively 1, 2, 6 and 13 M HCl.<sup>(5)</sup> The chemical purity of the Bk was checked by a spectrographic method.<sup>(6)</sup>

For the spectral studies, the entire 45  $\mu$ g of Bk or a smaller part thereof was contained in 50  $\mu$ l of the appropriate solution, yielding a maximum concentration of  $3 \cdot 6 \times 10^{-8}$  M. Investigations on Bk<sup>3+</sup> were done in the visible and near i.r. regions with 1 M and 12 M DCl, and in the visible region with 1  $\cdot$ 7 M, 5 M and 8 M HClO<sub>4</sub>, 10 M HNO<sub>3</sub>, and concentrated H<sub>2</sub>SO<sub>4</sub>. The variety of acids and their strengths listed here arises in part from the fact that a number of attempts were necessary before the Bk could be oxidized to the quadrivalent state. Even though many of these attempts failed, the Bk<sup>3+</sup> spectrum was still obtained in that medium.

The oxidation of Bk to the quadrivalent state was successful in 5 M HClO<sub>4</sub> with NaBiO<sub>3</sub> as oxidant. The usual technique of using sodium bromate in 8 M HNO<sub>3</sub> followed by extraction into 0.2 M bis-(2-ethylhexyl)orthophosphoric acid in hexane, would not have yielded a sample suitable for spectrophotometric studies, since a large part of the visible region of the spectrum would have been obscured. Oxidation attempts with oxone in several different solvent media proved unsuccessful.

The specially designed spectrophotometer cells were fabricated from silica capillary tubing with high-purity silica windows. The internal diameter of the tubing was 1 mm and the path length 5 cm. Special cell holders and cell compartments were used in conjunction with the Cary-14 Spectrophotometer for handling and aligning the cells, to prevent possible contamination of the spectrophotometer or loss of the valuable material. The weakness of the beta radiation of the <sup>240</sup>Bk made it unnecessary to observe any special precautions, as far as radiation exposure of the experimenters was concerned.

Since the absorption peaks were expected to be quite weak, it was thought that a means of signal enhancement would be quite desirable. Accordingly, provision was made for accumulating data by a time-averaging device<sup>(7)</sup> connected with the spectrophotometer through the Cary automatic-programming attachment. In a typical experiment, the region from 5000 to 3000 Å was scanned repeatedly at a rate of 25 Å/sec and the data read into the memory of the multichannel pulse-height analyser of the time-averaging device (data are recorded only when scanning from long to short wavelength). Enough channels were used so that each channel represented 2 Å of spectrum. In this technique, the signal is in theory enhanced by a factor equal to the square root of the number of scans, while the random background noise is averaged out. At least sixteen scans were found to be necessary for good results. An equal number of scans was taken on a blank solution. This method of signal enhancement was used during the studies of the Bk<sup>3+</sup> spectrum in 1 M and 12 M DCl and in 1.7 M HClO<sub>4</sub>.

A simple computer program was written to process the data from the time-averaging device. The sample and blank curves were smoothed with data convolution.<sup>\*(6)</sup> The blank curve was sub-tracted from the sample curve and the latter normalized to one scan. The original data and the smoothed net sample curve were plotted by the computer.

## **RESULTS AND DISCUSSION**

#### Trivalent berkelium

The most complete spectra were obtained in 1 M DCl solution. No difficulty was encountered from bubbling of the solution. Repeated scans could be made of spectral regions several thousand angstroms wide, and the spectra quite well reproduced. The time averaging helped significantly in bringing out weak bands in the u.v. region, in particular. From the computer results the peaks could be readily located within one or two channels (2-4 Å). There was good agreement between the stripchart recordings and the time-averaged data. A list of the bands seen in 1 M DCl solution and their molar absorptivities is given in Table 1. No bands due to lanthanides

\* The best convolution functions to use for smoothing the data were selected by means of a computer program (SADDLE) written by D. L. FRAZER at Livermore. We express our appreciation to him herewith.

<sup>(7)</sup> M. P. KLEIN and G. W. BARTON, JR., Rev. sci. Instrum. 34, 754 (1963).

<sup>&</sup>lt;sup>(5)</sup> A. CHETHAM-STRODE, JR., U.S. Atomic Energy Commission Report UCRL-3322 (1956).

<sup>&</sup>lt;sup>(0)</sup> R. G. GUTMACHER, E. K. HULET and R. LOUGHEED, J. opt. Soc. Am. 55, 1029 (1965).

<sup>&</sup>lt;sup>(8)</sup> A. SAVITZKY and M. J. E. GOLAY, Analyt. Chem. 36, 1627 (1964).

or other actinides appeared. As predicted, the molar absorptivities of the bands in the visible region are all less than 10. Still, the  $Bk^{3+}$  absorption spectrum is about ten times stronger than the spectrum<sup>(9)</sup> of its lanthanide analog,  $Tb^{3+}$ .

Wavelength (Å)	Molar absorptivity	Vac. wavenumbers (cm <sup>-1</sup> )
3275	1	30,530
3350	1	29,820
3450	1	28,990
3670	0.5	27,300
3744	0.5	26,700
3910	1	25,540
3958	0.5	25,260
4180	4	23,900
4300	2	23,320
4410	1	22,680
4600	3	21,730
4740	7	21,090
5040	1	19,840
6360	3	15,730
10,470	6	9550
12,240	13	8160

TABLE 1.—ABSORPTION PEAKS OF Bk<sup>8+</sup> in 1 M DCl solution



FIG. 1.—The absorption spectrum of Bk<sup>3+</sup> in 1 M DCl solution.

Figure 1 presents a reproduction of the  $Bk^{3+}$  spectrum, and shows that high absorption was encountered in the u.v. below 3300 Å, probably due to chlorine formation. The absorption bands of  $Bk^{3+}$  are relatively wide compared to those of the lanthanides. The grouping of bands in the 4100–4800 Å region, much like "leaning sentinels", is very characteristic of Bk.

<sup>(9)</sup> W. T. CARNALL, J. phys. Chem. 67, 1206 (1963).

No new bands were seen in 12 M DCl, nor were there any spectral shifts. The definition of the spectrum was poorer, however; the bands were wider and close neighbours could not be well resolved. There was no noticeable reduction of peak heights within the accuracy of measurement. The same statements are true for 10 M HNO<sub>3</sub> solutions. In concentrated  $H_2SO_4$  solutions, very good resolution of bands in the visible region was obtained. Both nitric acid and sulphuric acid solutions showed high absorption below 4100 Å, probably due to radiolytic decomposition products. The spectrum of  $Bk^{3+}$  in 1.7 M HClO<sub>4</sub> solution was essentially the same as that of the 1 M DCl solution in the region studied.

## Tetravalent berkelium

Experiments in which sodium bismuthate was used as the oxidant in 5 M HClO<sub>4</sub> were made at two concentrations, with 8 and 26  $\mu$ g of Bk in 50  $\mu$ l of solution (6·4 × 10<sup>-4</sup> M and 2·1 × 10<sup>-3</sup> M, respectively). Unfortunately, cerium impurity was introduced from the various reagents used in attempting to oxidize the Bk, and repeated attempts to remove it at this point were not completely successful. The Bk<sup>4+</sup> absorption bands were thus seen as shoulders on the strong Ce<sup>4+</sup> absorption band. For this reason, we do not include a figure of the spectrum as observed or with the strong Ce<sup>4+</sup> band subtracted by guessing the Ce concentration; to do so could only give a distorted picture and would be misleading. However, the Bk<sup>4+</sup> features were reproducibly seen in three separate experiments, with intervening purification procedures. Table 2 lists the Bk<sup>4+</sup> peaks together with an estimate of their strengths.

(**)	absorptivity	(cm <sup>-1</sup> )
3610	*	27,690
3690	*	27,090
3950	8	25,310
4240	5	23,580
4380	3	22,820
5950	2	16,800
	3610 3690 3950 4240 4380 5950	3610 *    3690 *    3950  8    4240  5    4380  3    5950  2

TABLE 2.—ABSORPTION PEAKS OF Bk4+ IN 5 M HClO4 SOLUTION

\* Not measurable.

The bands of tetravalent Bk were observed to disappear with time, and the spectrum of trivalent Bk appeared. This reduction is due to species generated by the radiolysis of the solution. For example, if an excess of hydrogen peroxide is added to the solution, the reduction is observed to take place instantaneously. The rate of growth of Bk<sup>3+</sup> was observed for a period of 6 hr. The height of the 4740-Å peak of Bk<sup>3+</sup> was used as a measure of the concentration at any given time. We found the Bk<sup>3+</sup> to grow in at a linear rate, with a rate constant k = 0.25 hr<sup>-1</sup>. This yields a half-life of 2.8 hr for the Bk<sup>4+</sup> ion in solution.

The failure to oxidize Bk to the tetravalent state with ozone (1.7 M and 8 M  $HClO_4$ ), with AgO in concentrated  $H_2SO_4$ , or with sodium bismuthate in 10 M  $HNO_3$  is puzzling. Cerium was readily oxidized under these conditions, although with ozone about 30 min bubbling was required. It may be that the potential of the Bk<sup>3+</sup>-Bk<sup>4+</sup>

couple is higher than that of the Ce<sup>3+</sup>-Ce<sup>4+</sup> couple, or else that radiolytic decomposition products in the Bk solution successfully compete for the oxidizing agent.

It is of interest to note that when ozone was bubbled into a solution of  $Bk^{3+}$  in 18 N H<sub>2</sub>SO<sub>4</sub>, an insoluble species was produced. The precipitate redissolved completely in concentrated (36 N) H<sub>2</sub>SO<sub>4</sub>. This aspect of Bk chemistry will be further investigated.

The positions of the few observed  $Bk^{4+}(5f^7)$  peaks show a strong resemblance to those of  $Cm^{3+}(5f^7)$ , as would be predicted.<sup>(10.11)</sup> It is unfortunate that the presence of Ce made it impossible to observe the u.v. cutoff of  $Bk^{4+}$  and to obtain some indication of the position of the  $5f^{6}6d$  configuration.

## CONCLUSION

The present investigation thus establishes the energy and intensity of a number of  $Bk^{3+}$  and  $Bk^{4+}$  transitions, and will provide a good framework upon which to proceed with the theoretical interpretation of the results. This work is already in progress and will be reported later.

We assume that not all of the  $Bk^{3+}$  or  $Bk^{4+}$  transitions that occur in the spectral region studied have actually been observed. Thus, as larger amounts of material become available it will be useful to re-examine the spectrum, particularly to establish the energies and intensities of the  $Bk^{3+}$  bands predicted to occur in the near i.r. region.<sup>(12)</sup>

Acknowledgements—We should like to thank ERVIN BEHRIN for his excellent assistance with the electronics, and ROMAN I. BYSTROFF and BERT E. HOLDER for the loan of equipment.

- <sup>(10)</sup> W. T. CARNALL and P. R. FIELDS, J. Am. chem. Soc. 81, 4445 (1959).
- <sup>(11)</sup> B. G. WYBOURNE, J. chem. Phys. 40, 1456 (1964).
- <sup>(12)</sup> P. R. FIELDS, B. G. WYBOURNE and W. T. CARNALL, U.S. Atomic Energy Commission Report ANL-6911 (1964).