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SOME OBSERVATIONS AND COMMENTS ON THE OXIDATION POTENTIAL OF THE BERKELIUM III-IV COUPLE

M. E. Jones and B. B. Cunningham

August 1, 1950

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SOME OBSERVATIONS AND COMMENTS ON THE OXIDATION POTENTIAL OF THE BERKELIUM III-IV COUPLE

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Aug. 1, 1950

Some of the chemical properties of element 97 (berkelium), deduced from trace-concentration studies, are described by Thompson, Ghiorso, and Seaborg[1]

(1) Thompson, Ghiorso, and Seaborg, Phys. Rev., 77, 838 (1950).

in their paper announcing the discovery of the element. More detailed information, particularly with regard to the oxidation potential of the Bk(III)-Bk(IV) couple, and the elution behavior of the element from cation exchange columns has been published by Thompson, Cunningham and Seaborg.[2]

(2) Thompson, Cunningham, and Seaborg, J. Am. Chem. Soc., 72, 2798 (1950).

The latter authors conclude that the formal potential of the Bk(III)-Bk(IV) couple is very close to that of Ce(III)-Ce(IV).

In the present work we have investigated the oxidation of Bk(III) to Bk(IV) in greater detail and under somewhat more favorable experimental conditions.

It has been shown previously by Voigt, Sleight, Hein and Wright[3] that

(3) Voigt, Sleight, Hein, and Wright, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 15.9 (McGraw-Hill Book Co., Inc., New York, 1949).

zirconium phenylarsonate is a relatively specific carrier for the +4 actinides and is superior to zirconium phosphate or ceric iodate in this respect. We have therefore used carrying by zirconium phenylarsonate as a test for berkelium in

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the +4 oxidation state.

The experimental procedure used was as follows:

Trace concentrations of berkelium were prepared and purified as described by Thompson, Cunningham, and Seaborg.[2]

In the oxidation experiments summarized in Table I, appropriate quantities of berkelium and cerium (275-day cerium^{144}) tracers were added to 300 µl of 1.3M nitric acid solution containing the specified oxidizing agent at about 0.07M concentration. The solutions were then diluted to 400 µl and heated in a water bath at 100°C. for 30 minutes.

Fifty micrograms of Zr as $Zr(NO_3)_4$ solution was added to the warm solution, followed by 100 µl of warm 0.16M phenylarsonoic acid. The solution was stirred, and the precipitate was collected in the bottom of the 1 ml. centrifuge cone by centrifugation. The precipitate was washed with 100 µl of water and was then spread evenly and dried on a 1-in. diameter platinum disc for analysis for Ce and Bk by differential counting.

Table I

Oxidation of Berkelium and Cerium by Various Oxidizing Agents

Oxidizing Agent	% of Berkelium Oxidized	% of Cerium Oxidized
$Cr_2O_7^{=}$	24	24
ClO_3^-	0	0
HClO	0	0
BrO_3^-	14	13

In Table I the oxidizing agents have been listed in order of increasing negativity of their standard thermodynamic potentials,[4] and it is to be noted that

(4) Latimer, "Oxidation Potentials," Prentice Hall, Inc., New York, 1938.

the oxidation of cerium and berkelium does not follow this order. In general, it is not feasible in experiments of this kind to approximate closely the conditions required for the direct application of the thermodynamic potential values. For example, in the present case, a high concentration of hydrogen ion is necessary in order to prevent hydrolysis of the tetrapositive ions of cerium and berkelium, and consequently the oxidations must be carried out in solutions of high ionic strength. The activity coefficients of most ionic species are therefore highly uncertain in these solutions. This, together with the fact that extensive complex ion formation may also occur leads to departures of considerable magnitude from the assumed ideal behavior. The value of incorporating in the experiments an element of similar chemistry and known potential is well illustrated by the data.

All experiments are consistent in indicating a near-identity in the values of the oxidation potentials for the Bk(III)-Bk(IV) and Ce(III)-Ce(IV) potentials, in agreement with the earlier observations by Thompson, Cunningham and Seaborg[2] on the oxidation of Bk(III) by Ce(IV).

Because of the anticipated smaller ionic radius of Bk^{+4} it might be expected that it would hydrolyze more readily than Ce^{+4}.

Oxidation with bromate in lithium perchlorate-perchloric acid solutions at various hydrogen ion concentrations and a constant ionic strength of 1 did not show any marked differences between berkelium and cerium, however. The data are summarized in Table II. The data are not as consistent as might be desired, but in view of the rather large errors involved in the counting of the samples, indicate no real difference in the oxidation of berkelium and cerium within the range of 0.1-1.0M hydrogen ion concentration.

Table II

Oxidation of Berkelium and Cerium by Bromate as a Function of Hydrogen Ion Concentration

H^+ (moles/liter)	% Berkelium Oxidized	% Cerium Oxidized
0.1	12	15
0.3	10	6
0.6	18	10
1.0	7	6

The less negative potential for the bromate-bromine couple at lower hydrogen ion concentration appears to be largely balanced by an increased hydrolysis of both ions.

We conclude that the oxidation potential of the Bk(III)-Bk(IV) couple does not differ by more than 50 Mev from that of the Ce(III)-Ce(IV) couple.

Accepting -1.62v. for the formal potential of the latter,[4] we write

$$Bk(III) = Bk(IV) + e^-, \; E_f = -1.62 \pm 0.06v.$$

This work was performed under the auspices of the U. S. Atomic Energy Commission.

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