DETERMINATION OF THE NO(II)-NO(III) POTENTIAL FROM TRACER EXPERIMENTS*

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Abstract – The value of the standard oxidation potential of the No(II)–No(III) couple in aqueous solution was estimated from the average behavior observed during repetitive series of experiments with 50–100 atoms per experiment. The distinction between No(II) and No(III) was made on a few atoms at a time basis by multiple solvent extractions with di(2-ethylhexyl)orthophosphoric acid (HDEHP) using the column elution technique of extraction chromatography. By comparing the extraction of nobelium from dilute acid solutions containing different oxidants with the extraction behavior of tracer quantities of radioactive elements of known standard oxidation potentials, the standard potential of the half-reaction No(II)–No(III) + e^- was estimated to be -1.4 to -1.5 V.

INTRODUCTION

ONLY VERY recently has an isotope of element 102, ²⁵⁵No[1-3], of sufficiently long half-life (3 min) become available in sufficient quantity (50–100 atoms per experiment) so that information about its tracer chemical behavior could be obtained from average behavior observed during repetitive series of experiments[4]. Ion exchange and coprecipitation studies showed nobelium to behave in aqueous solution like a divalent, alkaline earth element rather than a trivalent, rare earth element as expected. However, after oxidation with ceric ions, nobelium appeared to behave like a trivalent actinide. The experiments described in this work were conducted in order to estimate the value of the oxidation potential of the No(II)– No(III) couple in aqueous solution.

EXPERIMENTAL

The ²⁵⁵No was produced by irradiation of a 0.8 mg/cm^2 thick ²⁴⁴Pu target with 97-Mev ¹⁶0 ions from the Berkeley Heavy Ion Linear Accelerator. The details of the experimental procedures and system have been described in [4]. The ²⁵⁵No was identified from the emission of 8.1-MeV alpha particles and its 3 min half-life. 50–100 atoms were produced per experiment; however, only about 1/10 this number of events were recorded after chemistry because of decay, counting geometry and chemical losses.

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Therefore, it was necessary to repeat each kind of oxidation experiment 10 or more times in order to observe statistically significant numbers of events. Working with a total of approximately 4000 atoms, nearly 100 individual experiments were performed.

The distinction between No(II) and No(III) was made on a few atoms at a time basis by multiple solvent extractions with di(2-ethylhexyl) orthophosphoric acid (HDEHP) using the column elution technique of extraction chromatography [5]. In this method, the aqueous phase is passed through an inert Kel-F powder bed on which the extractant HDEHP has been adsorbed; the HDEHP behaves much like a liquid cation exchanger in that its ionizable hydrogen atoms can be replaced by other positive ions. In ~ 0.1 M acid, mono- and divalent metal ions are poorly adsorbed by the extractant [6] and pass through the column in a few column volumes, whereas tri- and tetravalent ions are strongly adsorbed in the extractant and are not eluted from the column. The trivalent ions can be subsequently displaced from the extractant by higher hydrogen ion concentrations (~ 1 M or greater). This method has been described in more detail in a recent report identifying the divalent state of mendelevium [7].

The method has an advantage in that oxidizing agents in the aqueous phase have no effect on the extractant or the column operation. Thus, we hoped to estimate the oxidation potential of the No(II)–No(III) couple by comparing the extraction of nobelium from dilute acid solutions containing different oxidants with the extraction behavior of tracer quantities of radioactive elements of known oxidation potentials; i.e. ²⁰⁴T1 and ¹⁴⁴Ce.

In our experiments, the nobelium recoil atoms were dissolved from a platinum catcher foil with ~1 column volume (3 drops) of a dilute acid solution containing an oxidizing agent and tracer quantities of 252 Cf(III) and 244 Cm(III). Tracer 213 Ra(II), produced by the (0^{16} , α xn) reactions from lead impurity in the target, was useful for comparison with the behavior of divalent nobelium. The tracers were used also as a check on proper column operation and chemical yield. After dissolution and oxidation by heating at 80–100°C for ~ 1 min, the solution was passed through a column bed 2 mm in diameter by 2 cm long. In the case of the oxidants HIO₃ and CrO₃, the solution was evaporated to near dryness to obtain a high acid concentration found necessary for oxidation of the T1. The solution was then diluted to ~ 0.1 M in the hydrogen ion with water before transfer to the column. The 3⁺ ions were recovered by elution with 2–3 column volumes of 3 M HNO₃. The ~ 0.1 M and 3 M HNO₃ fractions' were collected on platinum discs, evaporated to dryness and the number of alpha particles with energies between 5.4 and 9 MeV were measured with a gridded ionization chamber. The average time necessary for the chemical procedures was ~ 5 min.

RESULTS AND DISCUSSION

Table 1 shows the analysis of the tracers in the extracted phase for each set of oxidizing conditions together with the standard potentials of the oxidants. Also shown for comparison are the results of identical experiments performed with $^{204}T1$ and ^{144}Ce which were carried out during or immediately following the nobelium experiments. The percent extracted given for Ce is the amount left on the column after stripping the 3⁺ ions with 3 M HNO₃, i.e. the amount oxidized from the trivalent to the tetravalent state. The errors listed for nobelium are the standard deviations computed from the total number of events observed in both fractions. The probable error in the number of events for the other tracers is < 10 per cent of the number.

In general, the separation of Cf(III) and Cm(III) from Ra(II) indicated adequate column operation. However, low-energy tailing in the alpha particle energy spectrum in the region of 6.12 MeV by small amounts of the Ra decay products allowed only a lower limit to be set on the amount of 252 Cf in the dilute acid fraction.

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The hydrogen ion concentration and perhaps the volume of dilute acid used was sufficient to elute a small percentage of the Cm tracer in several of the oxidation experiments shown in Table 1. This effect should not affect the nobelium results since the extraction coefficients of transcurium elements are greater than that of Cm[8].

Conditions for oxidation	Standard potential of oxidant (V)	Extracted by HDEHP column (%)						Total No.
		Cf	Cm	Ra	T 1	Ce	No	observed
$\sim 0.1 \text{ M HNO}_3$	- 0.94	> 91	92	1	4	< 1	7±3	72
$\sim 0.1 \text{ M HIO}_3^*$	-1.20	> 87	93	2	58		6 ± 3	59
$\sim 0.1 \mathrm{M CrO_3^*}$	-1.33	> 94	89	1	63		22 ± 8	50
$\sim 0.1 \text{ M HBrO}_3$	-1.52	> 96	71	4	99	5	56 ± 10	68
~ $0.25 \text{ M H}_{5}\text{IO}_{6}$ ~ $0.1 \text{ M (NH_{2})} \text{s}_{2}\text{O}_{2}$	-1.6	> 90	88	2	97	28	86 ± 12	73
$+0.1 \text{ M HNO}_3^{\dagger}$	-2.01	> 89	77	2	92	79	69 ± 10	72

Table 1. Analysis of the tracers in the extracted phase for each set of oxidizing conditions

*Evaporated to near dryness.

†+ trace Ag.

In so far as extraction indicates oxidation from the 2+ to 3+ valence state, the results show nobelium to be oxidized appreciably by solutions of periodate, bromate and peroxysulfate-silver but only slightly, if at all, by dichromate, iodate and nitrate. The comparison made in Table 1 of the percent oxidation of Ce(III) and T1(I) under identical conditions suggests that the standard oxidation potential of the No(II)–No(III) couple in aqueous solution lies between that of the T1(I)– T1(III) and Ce(III)-Ce(IV) couples, i.e. assuming no complex ion effects, between about -1.25 and 1.6 V [9]. From the Nernst equation, one might expect the ratio of the per cent (i.e. the concentrations) of No, T1 and Ce extracted into HDEHP to the per cent remaining in the ~ 0.1 M acid phase to vary logarithmically with the standard potential of the oxidant present in the acid phase. The data given in Table 1 are presented in a semilog plot of Fig. 1. The values for the oxidant peroxysulfate-silver are consistently low for all three tracers indicating failure to approach equilibrium and are given as lower limits. If it is assumed equilibrium is reached with the other oxidants, the experiments indicate nobelous ions are oxidized approx. 50 per cent in the range 1.4-1.5 V. Therefore, our best estimate for the potential of the half-reaction, No(II) = No(III) + e^- , is $E^0 \simeq -1.4$ to -1.5 V.

The possible existence of a relatively stable 2+ oxidation state for element 102 was predicted nearly 20 yr ago by Seaborg[10] on the basis of the actinide theory. This stability was postulated to arise from the $5f^{14}$ electronic configuration, i.e. completely filled 5f electron shell, just as the appearance of a 2+ oxidation state of

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^{10.} G. T. Seaborg, J. J. Katz and W. M. Manning, *The Transuranium Elements*, Vol. 14B, Paper 21.1. McGraw-Hill, New York (1949).



Fig. 1. The per cent of nobelium, thallium and cerium extracted into HDEHP/per cent remaining in the ~ 0.1 M acid phase versus the standard potential of oxidant present in the ~ 0.1 M acid phase.

ytterbium is due to special stability of the $4f^{14}$ configuration in the lanthanide series.

Direct correlation between oxidation potentials and electronic configurations are difficult to make as conversion from one oxidation state to another in aqueous solution is controlled by the magnitude of the ionization and hydration energies of the gaseous ions. Spectroscopic data for the lanthanides [11, 12] indicate that after formation of the divalent state by ionization of the two 6s electrons, except for the half and fully filled f shell (i.e. Gd and Lu), removal of an f electron is necessary for the formation of the tripositive state. Thus the tripositive state owes its general stability to the somewhat fortuitous balance between the larger amounts of energy released in the hydration of the 3+ over the 2+ gaseous ions as compared to the smaller quantities of energy needed to form the 3+ gaseous ions from the 2+ by ionization of an f electron[13].

Early in the actinide series, the 5f, 6d and 7s electrons have comparable binding energies as evidenced by the multiple oxidation states [14, 15]. As the atomic

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number increases, the binding energy of the 5f electrons increases rapidly leading to the increased stability of the 3+ oxidation state and an increasing resemblence to the lanthanides. However, recent results [4, 7, 16] indicate that the 2+ oxidation state is more stable in the actinides than in the lanthanides as the end of the series is approached. Thus, by the time nobelium is reached, the larger hydration energy is not sufficient to overcome the increased 5f electron binding resulting from the filled shell and the 2+ oxidation state is the most stable species in aqueous solution by 30-40 kcal/mole.

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