Inorganica Chimica Acta, *146* (1988) 255–259

Search for Lawrencium as a p-Element Using Gas Chromatography Techniques

D. T. JOST, H. W. GÄGGELER*, CH. VOGEL
Eidg. Institut für Reaktorforschung, Würenlingen, Switzerland
M. SCHÄDEL, E. JÄGER
Gesellschaft für Schwerionenforschung, Darmstadt, F.R.G.
B. EICHLER
Zentralinstitut für Kernforschung, Rossendorf, G.D.R.
K. E. GREGORICH and D. C. HOFFMAN
Lawrence Berkeley Laboratory, Berkeley, Calif. 94720, U.S.A.

(Received October 26, 1987)

Abstract

Multidimensional relativistic Dirac–Fock calculations predict that the last member of the actinides series, Lr, might behave like a p-element with a $[Rn]5f^{14}7s^{2}7p_{1/2}$ ground state electronic configuration, rather than the traditionally expected $[Rn]5f^{14}6d7s^{2}$ configuration. On-line gas chromatography was applied to search for Lr as a volatile p-element. These investigations were performed with ^{260}Lr ($T_{1/2}$ = 3 min), produced in the $^{249}Bk(^{18}O, \alpha 3n)$ reaction. Quartz and Pt chromatography columns were used. No evidence for Lr as a volatile element was found under reducing conditions and at a temperature of about 1000 °C. Our results give a lower limit for the adsorption enthalpy $-\Delta H_a$ for Lr on quartz and Pt surfaces of 290 kJ/mol. This value is significantly higher than the estimated values for Lr(p).

Introduction

Investigations of chemical properties of the heaviest elements have recently received considerable attention because of expected relativistic effects [1–3] which might cause changes in their electronic configurations [4]. The result of these relativistic effects in the heaviest elements is to stabilize the lower angular momentum electronic configurations. The p-orbitals are split into $p_{1/2}$ and $p_{3/2}$ groups with the $p_{1/2}$ being strongly stabilized. For Lr, the last member of the actinide series (atomic number Z = 103), the multidimensional relativistic Dirac–Fock calculations [5] predict a ground state configuration $[Rn]5f^{14}7s^{2}7p_{1/2}$ (Lr(p)) rather than the $[Rn]5f^{14}6d7s^{2}$ (Lr(d)) configuration traditionally expected with analogy to Lu. If this configuration with a $7p_{1/2}$ electron exists as the ground state, this would have implications on the chemical properties of this element such as a high volatility in the elemental state, similar to other p-elements such as Tl ($[Xe]4f^{14}5d^{10}6s^{2}6p$) [4]. An experimental determination of the Lr ground state could demonstrate the magnitude of the influence of the relativistic effects and lead to new insights into the chemical properties of the heaviest elements.

In the following we describe a gas-phase chromatography experiment designed to yield some information on the ground state electronic configuration of Lr. It has been estimated that Lr(d) with an electronic configuration analogous to that for Lu would have a high sublimation enthalpy of −350 to −410 kJ/mol [6, 7]. On the other hand, Lr(p) should have a much smaller sublimation enthalpy of only about −135 kJ/mol [8].

This predicted difference in sublimation enthalpies was used in an attempt to separate Lr(p) from other actinide elements using high-temperature gas-phase chromatography in quartz columns. In order to keep the gaseous Lr atoms in the elemental state, a reducing atmosphere of He/H_2 was used. Such conditions were found to be applicable to separations of the 6p-elements, which pass through the chromatography column at about 1000 °C, from the nonvolatile elements such as the actinides, which are strongly adsorbed on the column [9].

In a second experiment, a Pt tube was used as chromatography column. A semi-empirical model by Eichler *et al.* [8] predicts for Lr(p) an adsorption enthalpy of −187 kJ/mol on Pt, whereas for Lr(d) the calculated value is −750 kJ/mol. This large difference in adsorption enthalpies should allow the separation of Lr(p) from Lr(d) and the actinides in

---

*Author to whom correspondence should be addressed.

0020-1693/88/$3.50

high-temperature gas-phase chromatography experiments.

For these experiments the isotope ^{260}Lr with a half-life of 3 min is well suited. It decays by α-emission with $E_\alpha = 8.03$ MeV [10]. ^{260}Lr was produced in the reaction of 101 MeV ^{18}O + ^{249}Bk with a cross section of 8.3 ± 1.7 nb [11].

Experimental

An $^{18}O^{5+}$ beam with a typical intensity of 2.5 μA was provided by the 88-inch cyclotron at LBL. The target consisted of 880 μg/cm^2 ^{249}Bk as the oxide on a 3.06 mg/cm^2 thick Be backing, prepared by the molecular plating technique [12, 13]. Due to the decay of ^{249}Bk ($T_{1/2} = 330$ d), at the time of the experiments the target consisted of 792 μg/cm^2 ^{249}Bk and 88 μg/cm^2 ^{249}Cf. The beam passed through a vacuum window, a volume of rapidly flowing N_2 cooling gas and the Be target backing before passing through the Bk target material at an energy of 101 MeV. Reaction products recoiling out of the target were stopped in a collection chamber which was continuously flushed with 2 l/min of He/H_2 (96:4 vol%) gas which was loaded with KCl aerosols. The pressure in the collection chamber was kept at 1.1 bar. The reaction products attached themselves to the aerosols and were transported through an 8 m long capillary (1.5 mm i.d.) to the gas chromatography system [14].

Figure 1 shows schematically the apparatus used for this gas-phase chromatography experiment. The quartz chromatography column was 28 cm long with a diameter of 3 mm. Reaction products transported by the gas-jet system were stopped on a graphite wool plug which was inserted into the chromatography column which was kept at about 1000 °C. At this temperature, the KCl aerosol particles are destroyed in the graphite wool plug and the reaction products which were volatile under these conditions were transported with the carrier gas further along the column. The non-volatile products remained in the graphite wool plug or were adsorbed near the beginning of the column. The volatile products, after travelling the length of the column, were ejected through a capillary-shaped end-piece into the recluster unit. This recluster unit was flushed with an additional 2 l/min of Ar gas which was loaded with KCl aerosols. The products from the chromatography column became attached to the new KCl aerosol particles and were transported through a 2 mm i.d. teflon capillary to the LBL MG counting system [15, 16]. Here the activity-bearing KCl aerosol particles were deposited onto thin polypropylene foils at the perimeter of an 80-position rotating wheel. Every 2 min the wheel was stopped to position the newly collected activity between a pair of surface barrier detectors, while moving the previous source between a second pair of detectors, etc. For these experiments, opposing pairs of surface barrier detectors were located at counting positions 1 to 4, and top detectors only were located at positions 5 to 7 and 12. This allowed us to monitor the decay of short-lived alpha and spontaneous fission activities for 24 min after deposition on the rotating wheel. The counting geometry in this system was found to be 25% for the top detectors and 20% for the bottom detectors, resulting in an overall efficiency of 45% at positions 1 to 4 and 25% at positions 5 to 7 and 12. Due to the polypropylene foil between the source and the bottom detectors, these have a lower energy resolution than the top detectors. Bottom detectors were therefore used only in the gas chromatography experiments to increase the detection probability for ^{260}Lr.

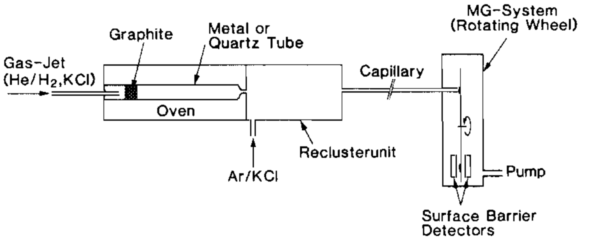

Fig. 1. Schematic diagram of the gas chromatography apparatus and the counting system. Reaction products attached to aerosols enter the gas chromatography column through a capillary and are stopped on a graphite plug. In the hot column (about 1000 °C), volatile products are evaporated and move through the column into the recluster unit. After cooling they attach to new aerosols and are transported to the counting device. There the aerosols with the volatile products are deposited on thin polypropylene foils mounted on an 80-position rotating wheel (MG-system at LBL).

Results and Discussion

In a first direct-catch experiment the integral spectrum of the reaction products was studied. For this measurement the chromatography system was kept at room temperature and the graphite wool plug was removed in order to let the activity-bearing aerosols from the reaction chamber pass directly through the chromatography apparatus to the detection system. The overall detection efficiency (ODE) of this experiment was determined by comparing the count rate of ^{252,255}Fm with the known production cross-sections with ^{249}Bk [17] and ^{249}Cf [18], including a correction for the incomplete escape of ^{252,255}Fm due to the relatively thick target [19]. It includes: (a) the collection of products recoiling out of the target on KCl aerosol particles; (b) the transportation of these aerosols through the capillary, the cold chromatography tube, the

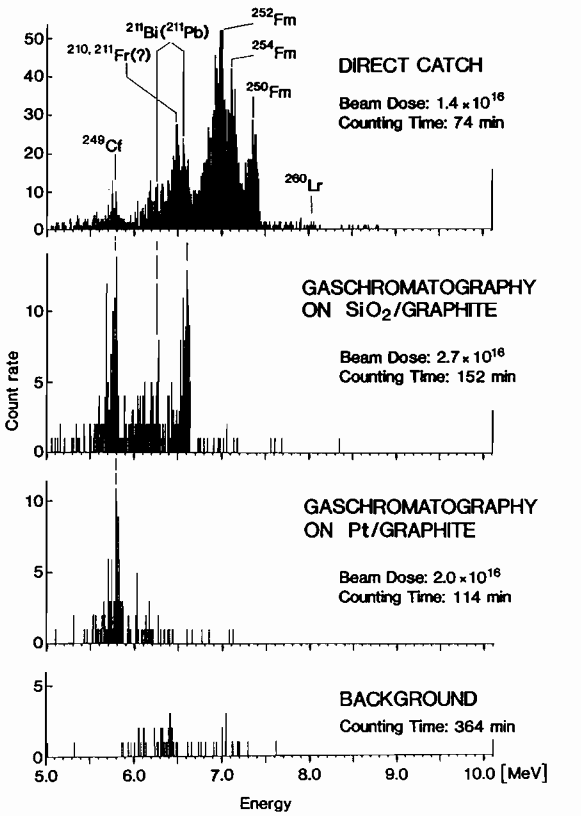

Fig. 2. Integral α-spectra from detector 2 top (covering the time from 2 to 4 min after the end of the deposition) for the three experiments: (i) 'DIRECT CATCH', no chemistry; (ii) 'SiO_2/GRAPHITE', separation in a quartz column with a graphite plug at about 1000 °C; (iii) 'Pt/GRAPHITE', same as above with a platinum column with a graphite plug; and (iv) a background measurement of detector 2 without the collecting wheel. Also shown are the beam integrals and the counting times.

reclustering chamber and the second capillary; (c) the deposition of the products on the polypropylene foils of the rotating wheel; and (d) the detection efficiency of the top and bottom detectors. This ODE was determined to be 33%. The uppermost part of Fig. 2 (labelled 'DIRECT CATCH') shows the integral α-spectrum from the top detector at position 2, *i.e.* covering a time interval from 2 to 4 min from the end of deposition of the products on the rotating wheel. Also given in Fig. 2 are the integrated beam and the counting time for this experiment. The main α-peaks are due to the decay of $^{250-254}$Fm, ^{249}Cf, ^{211}Bi and ^{210,211}Fr. The Fr and Bi activities are due to the interaction of the beam with a small Pb impurity in the target, and were useful for monitoring the yield of the volatile products in the chromatography experiment. We attribute the small α-activity between 7.97 and 8.06 MeV to ^{260}Lr. This activity corresponds to a production cross-section of 9.6 ± 1.6 nb,

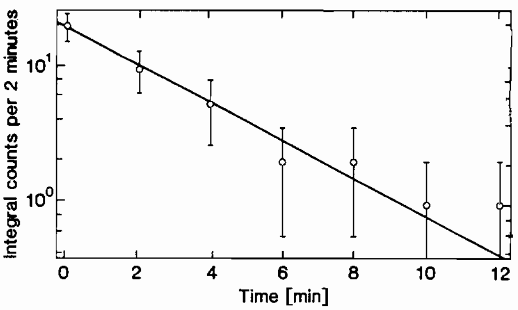

Fig. 3. Decay analysis of ^{260}Lr (E_α = 7.97–8.06 MeV). Data from the first seven top detectors are shown.

which is in good agreement with the value of 8.3 ± 1.7 nb from Hoffman *et al.* [11]. This assignment is further corroborated by a decay analysis of this event group. Figure 3 shows the corresponding counts collected with the first seven top detectors of the counting device, covering 14 min after deposition. The experimental value for the half-life of 2.3 ± 1.0 min is in reasonable agreement with the literature value of 3.0 min.

The second part of Fig. 2 shows the result of the gas-phase chromatography experiment in which the quartz chromatography column was used at about 1000 °C. These data were taken in the same detector as in the upper spectrum in Fig. 2. Obviously, despite the beam dose being higher by a factor of about two compared to the direct-catch experiment, the α-activity is much lower. As expected, the Fm isotopes are adsorbed on the quartz column at this temperature and do not appear in this spectrum. The α-peaks are due to ^{211}Bi, ^{211}Pb and to ^{249}Cf. It is assumed that the ^{249}Cf activity is from a contamination on the polypropylene foils in the counting system from previous experiments.

Pb passes through the quartz chromatography column. This can be explained by an adsorption model for mobile adsorption at zero coverage [20]. This model describes the relationship of the enthalpy and entropy of adsorption and the migration of a species in a chromatography tube under laminar flow conditions. For Pb on quartz surfaces with hydrogen as carrier gas [21], an adsorption enthalpy of −222 kJ/mol was measured. According to this model for mobile adsorption the retention time t_r for isothermal gas chromatography can be calculated [22] from:

$$t_r = (z_1 - z_2) \times \left\{ \frac{T_0\phi\left(1 + \frac{a}{v}\frac{V}{A}\exp\left(\frac{-\Delta H_a^\circ}{RT}\right)\exp\left(\frac{\Delta S_a^\circ}{R}\right)\right)}{v_0 T} \right\} \qquad (1)$$

where t_r = retention time, $(z_1 - z_2)$ = length of the column (28 cm), T_0 = 298 K, ϕ = cross-section of the column (7.07×10^{-2} cm^2), a = surface per unit length, ν = volume per unit length (a/ν = 13.3 cm^{-1}), A and V = standard molar surface and volume, respectively, (V/A = 1 cm, see ref. 20), T = temperature (1273 K), R = gas constant (8.37 J/mol K), ν_0 = carrier gas flow (33.3 cm^3/s STP), ΔH_a° = adsorption enthalpy and ΔS_a° = adsorption entropy. With the values given in ref. 21 ($\Delta H_a^\circ = -222$ kJ/mol and $\Delta S_a^\circ = -222$ J/mol K), eqn. (1) leads to a retention time of $t_r \ll 1$ s for Pb.

The overall detection efficiency for volatile activities was determined by a quantitative decay analysis of the amounts of ^{211}Bi and ^{211}Pb in the top detectors in this experiment compared with the direct-catch experiment. This together with the 33% ODE in the direct-catch experiment gives an ODE for the 6p-elements Pb and Bi (sum of top and bottom detectors) of 6%.

No activity due to Fr or Fm was found behind the chromatography column. This indicates, as expected, that their retention times are considerably longer than the corresponding half-lives or the 152 min duration of the on-line experiment (see Fig. 2). Again the ^{249}Cf is due to a contamination of the polypropylene foils in the counting system.

No activity attributable to ^{260}Lr was found. An analysis of all detectors gave zero events in the energy range E_α = 7.95 to 8.1 MeV. On the basis of the 6% ODE determined for Pb and Bi, and a cross-section of 8.3 nb [11], a total of 20 events should have been observed if Lr were volatile.

The third part of Fig. 2 shows the spectrum in the second detector obtained with a Pt chromatography column at about 1000 °C. As in the experiment with the quartz column, the KCl aerosols were stopped on a graphite wool plug which was inserted into the column. No activities other than the ^{249}Cf contamination were observed. No ^{211}Bi or ^{211}Pb were detected, which indicates that they are retained in the Pt column at 1000 °C. This is consistent with a measurement of the adsorption enthalpy of Pb on Pt of $\Delta H_a^\circ = -335$ kJ/mol [23] which was calculated from a desorption study [24]. Using eqn. (1) from the preceding section and a value of −164 J/mol K for the adsorption entropy of Pb on Pt [22], a retention time of nearly 8 h was calculated and similar values are expected for Bi.

No activity due to the decay of ^{260}Lr was found in the gas chromatography experiment with the Pt column. Because of the lack of ^{211}Pb or ^{211}Bi activity, the ODE for this experiment could not be determined. Assuming the same 6% ODE as in the experiment with the quartz chromatography column, we calculate that a total of 15 ^{260}Lr events should have been observed.

Conclusions

The existence of the [Rn]5f^{14}7s^{2}7p$_{1/2}$ electronic structure for the ground state of Lr could not be confirmed by our gas chromatography experiments.

It is known that volatile elements such as Tl, Pb, Bi or Po (all 6p-elements) can be separated from non-volatile elements using gas chromatography in quartz columns under reducing conditions at a temperature of about 1000 °C [9]. From the predicted sublimation enthalpy for Lr(p) of −135 kJ/mol [8] one can estimate a similar value for the adsorption enthalpy on quartz [21].

It could also be expected that Lr(p) would act as a volatile element in the Pt chromatography columns based on the rather low predicted adsorption enthalpy of −187 kJ/mol, whereas Lr(d) with a predicted adsorption enthalpy of −750 kJ/mol would not be volatile at 1000 °C.

The negative results for the detection of volatile Lr(p) in these experiments is statistically significant because in each experiment a sizable number of events should have been observed. 20 in the case of the quartz chromatography column and 15 in the case of the Pt column. The absence of any ^{260}Lr activity behind the chromatography columns can be transformed to lower limits of retention times of ^{260}Lr of about 2.5 half-lives = 7.5 min for both columns. Inserting this value into eqn. (1) and using an estimated adsorption entropy of −165 J/mol K [22] gives a lower limit for the adsorption enthalpy for Lr on both surfaces of $-\Delta H_a^\circ \geqslant 290$ kJ/mol. This value is significantly higher than the expected values for Lr(p) on quartz and Pt.

These experiments, however, do not allow us to exclude the existence of Lr(p). It is still possible that in the presence of the column surface because of the higher adsorption enthalpy of Lr(d) with respect to Lr(p), the [Rn]5f^{14}7s^{2}7p$_{1/2}$ configuration promotes to [Rn]5f^{14}6d7s^2 which is predicted to be only about 93 kJ/mol higher in energy [25].

Acknowledgements

We wish to thank the operating staff of the LBL 88-inch cyclotron for their permanent support of this experiment and for delivering stable beams of ^{18}O. The valuable discussions with the members of the LBL-GSI-Mainz nuclear chemistry groups and Dr. G. L. Seaborg are highly appreciated. The target material was provided by the Office of Basic Energy Science, U.S. Department of Energy, through the transplutonium production facilities at the Oak Ridge National Laboratory. This work was supported by the Swiss National Science Foundation.

References

1 R. A. Penman and J. B. Mann, in V. I. Spitsyn and J. J. Katz (eds.), 'Proc. Moscow Symp. Chem. Transuranium Elem.', *J. Inorg. Nucl. Chem., Suppl.* Pergamon, Oxford, 1976, pp. 257–263.
2 K. S. Pitzer, *Acc. Chem. Res., 12,* 271 (1979).
3 P. A. Christiansen, W. C. Ermler and K. S. Pitzer, *Ann. Rev. Phys. Chem., 36,* 407 (1985).
4 O. L. Keller, *Radiochim. Acta, 37,* 169 (1984).
5 J. P. Desclaux and B. Fricke, *J. Phys., 41,* 943 (1980).
6 F. David, K. Samhoun, R. Guillaumont and N. Edelstein, *J. Inorg. Nucl. Chem., 40,* 69 (1978).
7 P. D. Kleinschmidt, J. W. Ward and R. G. Haire, in Z. A. Munir and D. Cubicciotti (eds.), 'Proc. Symp. High Temp. Mater., Chem. II', Vol. 83-7, The Electrochem. Soc. Inc., Pennington, N.J., 1983, p. 23.
8 B. Eichler, S. Hübener, H. Gäggeler and D. T. Jost, *Inorg. Chim. Acta, 146,* 162 (1988).
9 B. Eichler, *J. Inorg. Nucl. Chem., 35,* 4001 (1973).
10 K. Eskola, P. Eskola, M. Nurmia and A. Ghiorso, *Phys. Rev., C4,* 632 (1971).
11 D. C. Hoffman, R. A. Henderson, K. E. Gregorich, D. A. Bennett, R. M. Chasteler, C. M. Gannett, H. L. Hall, D. Lee, M. J. Nurmia, S. Cai, R. Agarwal, A. W. Charlop and Y. Y. Chu, 'Proc. Conf. on Methods and Applications of Radioanalytical Chemistry, Koña, Hawaii, April, 1987', *J. Radioanal. Chem.,* in press.
12 J. E. Evans, R. W. Lougheed, M. S. Hoff and E. K. Hulet, *Nucl. Instrum. Methods, 102,* 389 (1972).
13 G. Müllen and D. C. Aumann, *Nucl. Instrum. Methods, 128,* 425 (1975).
14 E. Stender, N. Trautmann and G. Herrmann, *Radiochem. Radioanal. Lett., 42,* 291 (1980).
15 K. E. Gregorich, D. Lee, R. Leres, M. J. Nurmia, D. C. Hoffman, R. M. Chasteler and R. Henderson, *Nuclear Science Division Annual Report 1984–1985, LBL-21570,* Lawrence Berkeley Laboratory, Berkeley, Calif., 1986, p. 203.
16 D. C. Hoffman, D. Lee, A. Ghiorso, M. J. Nurmia and K. Aleklett, *Phys. Rev., C22,* 1581 (1980).
17 C. M. Gannett, D. A. Bennett, R. B. Chadwick, R. M. Chasteler, K. E. Gregorich, H. L. Hall, R. Henderson, D. M. Lee, J. Leyba, M. Nurmia and D. C. Hoffman, *194th ACS National Meeting, Symposium on the Nuclear Properties of the Transplutonium Elements,* New Orleans, La., U.S.A., 1987, NUCL 126, to be published.
18 D. Lee, K. J. Moody, M. J. Nurmia, G. T. Seaborg, H. R. von Gunten and D. C. Hoffman, *Phys. Rev., C27,* 2656 (1983).
19 R. M. McFarland, *Ph.D. Thesis,* Report of the Lawrence Berkeley Laboratory, LBL-15029, 1982.
20 B. Eichler and I. Zvara, *Radiochim. Acta, 30,* 233 (1982).
21 W. Fan and H. Gäggeler, *Radiochim. Acta, 31,* 95 (1982).
22 H. Gäggeler, H. Dornhöfer, W. D. Schmidt-Ott, N. Greulich and B. Eichler, *Radiochim. Acta, 38,* 103 (1985).
23 B. Eichler, *Report ZfK-396,* Zentralinstitut für Kernforschung, Rossendorf, 1979.
24 H. Schrader, *Philos. Mag., 24,* H. 6, 125 (1912).
25 L. Brewer, *High Temp. Sci., 17,* 1 (1984).