Chemical Properties of Transactinide Elements

P.K. Mohapatra
Radiochemistry Division
Bhabha Atomic Research Centre

A b s t r a c t

The chemical properties of transactinide elements viz. rutherfordium (Rf), dubnium (Db) and Seaborgium (Sg) are found to be similar to their homologs in the periodic table in group IV, V and VI respectively. Deviations are also predicted in many cases due to the relativistic effects which lead to unusual chemical properties. The chemical investigations in gas phase involve thermo chromatography and in aqueous phase using ARCA (Automated Rapid Chemistry Apparatus), MCT (Multi Column Technique), and SISAK (Short-lived Isotope Separation by AKUFVE). The radiochemical methods involved are fast separations followed by detection of correlated alphas of the daughter and grand daughter with those of the parent.

Introduction

THERE HAVE BEEN CONSIDERABLE efforts in recent years for expanding the periodic table beyond the actinides. The chemical studies involving the shortlived transactinides have, however, always been challenging, as it involves careful planning of the experiment at the 'one-atom-at-a-time' scale. This is due to the very short half-lives and extremely low production cross section of these elements. They often require fast radiochemical separations with very high transportation yield and efficient counting set-up.

As per the actinide concept brought out by Seaborg [1], the actinide series should end with lawrencium and a new 6d series should start with element 104 (Rf). Accordingly, the electronic configuration of Rf should be similar to the group IV elements. The early work on the chemical properties of Rf had indicated that it is tetravalent in nature and resembled, more often than not, the main group elements Zr and Hf. The chemical properties of element 105 also followed suit and resembled those of Nb and Ta. Early work on Sg too have indicated its resemblance to Mo and W. Based on these observations, the new set of transactinide elements occupy the periodic table as shown in Fig. 1.

Fig. 1 Periodic table of elements including the transactinides

In spite of the parallels observed with the transactinides and their main group homologs, the chemical behaviour of the former is not as simple as one may expect and is full of surprises. The chemistry of Rf and Db, till recently the only transactinides whose chemical properties have been studied, have shown deviations from the chemical properties of their lighter homologs and often shown resemblances to their pseudo-homologs Th and Pa respectively. These have been attributed to the relativistic effect arising due to the stabilization of the 7 s and 7 $p_{1/2}$ orbitals [2]. This can destabilise and expand the d and f orbitals leading to unusual oxidations states and hence chemical properties.

One of the several challenges associated with the transactinide elements, is the rapidity with which the separations need to be carried out and the informations can be gathered thereafter. The chemical techniques often used in these fast radiochemical separations are ion-exchange chromatography, exraction chromatography, ermochromatography and solvent extraction using the AKUFVE. During the time period in which the entire process of transport, separation and detection is done in all probability most of the transactinide decay. Therefore, correlation of the gammas of the daughter and grand daughter is done to conclude that an event has taken place.

Synthesis of Transactinides

Transactinides are synthesized by nuclear fusion reactions with heavy ion projectiles [3]. These reactions have very low cross section and the production rates as well as half-lives decrease with increasing atomic number. Consequently, one deals with atom-at-a-time chemistry in these cases. Cold fusion reactions in which Ti-50, Cr-54, Fe-58, Ni-62,64 and Zn-70 are fused with Pb-208 and Bi-209 targets tend to give the highest

possible cross sections. However, the n-deficient product nuclei have half lives less than one second and hence are not useful for any chemical studies. More n-rich and hence longer lived products are obtained in hot fusion reactions of O-18, Ne-22, Mg-26, S-34 targets with actinide targets. Recent chemical studies of rutherfordium deal with the 78-s ^{261}Rf produced in the ^{248}Cm (^{18}O, 5n) reaction which has a cross section of 5 nb. Due to reasonable half-life of ^{261}Rf (78 s), most chemical studies involve this route for the production of element 104. Recent studies on element 105 used 34-s ^{262}Db and 27-s ^{263}Db produced in 5n- and 4n- reactions of ^{18}O with ^{249}Bk targets with cross sections of 6 nb and 2 nb, respectively. Early works on the chemical studies on element 106 involved the 0.9 s ^{263}Sg produced at a 0.6 nb cross section by the ^{249}Cf(^{18}O, 4n) reaction. The recent discovery of the neutron rich ^{265}Sg and ^{266}Sg isotopes have longer half-lives (in the range of 3-30 s) but much reduced cross section of 260 pb and 60 pb for the ^{248}Cm(^{22}Ne, 5n) and ^{248}Cm(^{22}Ne, 4n) reactions respectively.
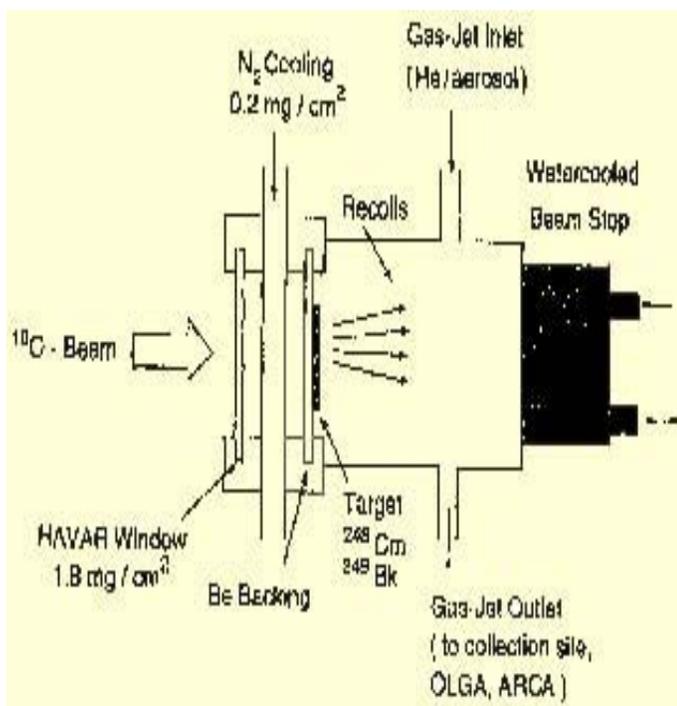

Fig. 2 Schematic diagram of the target and recoil chamber used for the production of transactinides

Experimental Techniques

As shown in Fig.2, the schematic of the target and recoil chamber clearly bring out the product in the recoil beam which is later thermalised and transported by a fine aerosol particles in He as the transport gas. The typical transport yield is about 50% over a distance of few tens of meters with the transport time being in the order of 2-5 s. The gas phase chemistry involves an isothermal on-line gas chemistry apparatus (OLGA) which enables the detection by the PIPS (Passivated Ion-implanted Planar Silicon) detectors. For the aqueous chemistry work involving ion-exchange as well as extraction chromatography, the automated rapid chemistry apparatus (ARCA) have been employed. It is a computer controlled apparatus for the fast HPLC based separations containing micro columns etched out in stainless steel magazines. The ARCA technique has been used for the study of elements up to 105. The ARCA studies with element 106 were not very encouraging and it needed another on-line chromatographic technique called the multi column technique.

The multi column technique (MCT) involves three columns in series. The first column (F) filters all the decay products coming from the accelerator along the KCl aerosol containing He jet. The second column (C) is the true chromatographic column where the element of interest experiences the retention time, t_R, which is of the order of its nuclear half-life which acts as an internal clock. The daughter nuclides that are formed during the passage of the mother through C are strongly retained on the third column (D). From the activity of the daughter in column D (A_D) and in the effluent (A_E) the retention time can be obtained as

$$t_R = (t_{1/2} / \ln 2) . \ln[(A_D + A_E)/A_E] \qquad (1)$$

and the K_d value can be given as

$$K_d = (t_R - t_0).V/m \qquad (2)$$

where t_0 is the column hold up time due to the void volume, V, the flow rate of the mobile phase and m is the mass of the resin.

Gas Phase Chemistry

The gas phase chemistry has been studied by thermochromatography. The transported transactinide is allowed to react with HCl or Cl_2 / $SOCl_2$ mixture to give volatile chloride and oxychlorides respectively. Vapour pressure curves indicate the relative volatility of the chlorides and oxychlorides which can be calculated from the sublimation entropy as well as sublimation enthalpy data. However, as the gas phase chemistry of Rf, Db and Sg involves one-atom-at-a-time chemistry, it is reasonable to use the adsoption enthalpy data in place of the sublimation enthalpy based on which the relative yield vs temperature plots are generated. By a comparison with the relative yield vs temperature curves of the element of interest, homolog and pseudo-homolog, one gathers information on their chemical behaviour.

The first volatility experiments of Rf-chloride by Zvara et al. [4], have indicated that it has similar volatility to that of its analog Hf, which in turn is much higher as compared to the actinides. On the other hand, a recent experiment by OLGA (On-Line Gas chemistry Apparatus) has indicated much higher volatility for $RfCl_4$ as compared to $HfCl_4$ while comparable results were obtained with $ZrCl_4$. The gas phase chemistry studies of Db and its analogs Nb and Ta have been carried out with their respective bromides made from HBr and BBr_3 as the brominating agent. The volatility trend is Ta ~ Nb > Db which disagree with results from relativistic molecular calculations [5]. The respective chlorides were found to have higher volatility. The experimental data on the volatility of the oxychlorides of Sg and its analogs have shown the trend MoO_2Cl_2 > WO_2Cl_2 > SgO_2Cl_2 which agreed very well with the theoretical predictions based on DS DVM calculations [6]. On the other hand, the first experiments on Sg by the russian scientists at JINR, Dubna involved the 0.9-s [263]Sg and have shown an opposite trend in the volatility viz. SgO_2Cl_2 > WO_2Cl_2. The first gas phase chemistry of Hassium (element 108) was studied by the research group at Mainz, Germany recently [7]. Successful experiment with volatile HsO_4 was

deposited in a thin film of wet NaOH forming the salt $Na_2HsO_4(OH)_2$. This demonstrated that HsO_4 is an acid anhydride.

Solution Chemistry

The first separation of Rf in solution phase was performed on the cation exchange column using α-hydroxy isobutyric acid as the eluent, which showed that it eluted along with Zr and Hf while the trivalent actinides were strongly retained in the column [8]. Similarity in the chemical nature of Zr, Hf and Rf was also observed while investigating their anion exchange behaviour using Aliquat 336 as the extractant [9]. The extraction studies involving TTA have indicated that Rf is less readily hydrolysed as compared to Zr, Hf and Pu [10]. This is not in agreement with the results obtained by Bilewicz et al., who have reported the trend in the ease of hydrolysis as Rf > Zr > Hf. TBP extraction of Rf was studied by several groups who have reported solvated type of species being extracted into the organic phase the extraction sequence being Zr > Rf > Hf. Chloride complexation studies of Rf have indicated formation of species of the type $RfCl_6^{2-}$ and it formed stronger complexes than those with Zr, Hf and Th [11]. Strub et al., [12] have conclusively shown that Rf forms anionic complexes with fluoride ion. The continuous on-line studies involving the MCT were carried out by Mohapatra et al. [13], at 0.01M HF as well as at 0.1M HNO_3 + 0.5M HF which yielded K_d values of 234 and 2.1 respectively.

Gregorich et al., have performed the first studies on the chemistry of Db where its extraction into MIBK (methyl isobutyl ketone) was investigated from a mixture of 3.8 M HNO_3 + 1.1 M HF [14]. Under these conditions Db and Nb do not extract into MIBK while Ta gets quantitatively extracted suggesting the formation of anionic complexes with the former. The non Ta-like behaviour is further confirmed in the extraction of halide complexes with TiOA from an aqueous medium comprising of 12 M HCl + 0.03 M HF. The penta valency of Db was confirmed in an ARCA experiment using cation exchangers and alpha-hydroxy isobutyric acid as the eluent. Db, together with Nb and Ta were eluted promptly from the column while tri- and tetravalent ions were strongly sorbed on to the column [15].
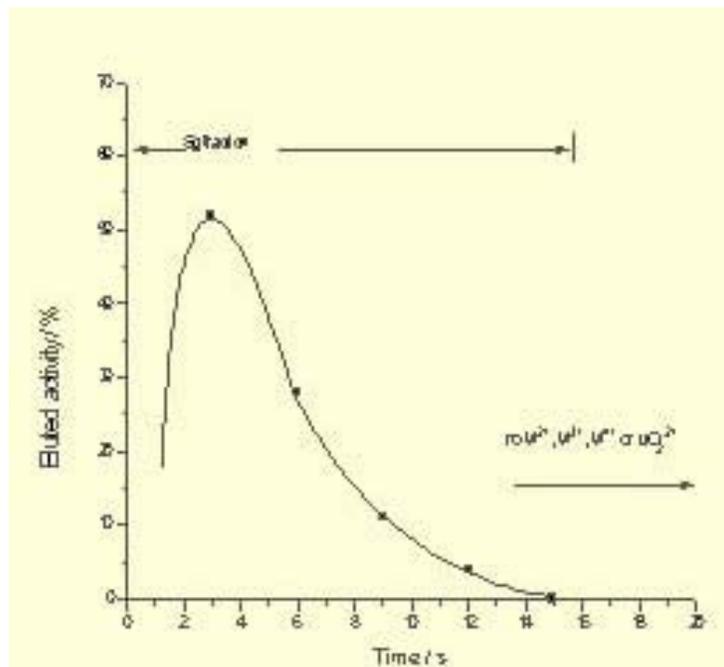

Fig. 3 Elution curve for W used as a model for Sg separation in ARCA using 0.1 M HNO_3 / $5x10^{-4}$M HF [ref.16]

There is almost no solution chemistry data with Sg as the longest lived isotope till recently was the 0.9-s ^{263}Sg. The discovery of the 3-30 s ^{265}Sg and ^{266}Sg opened the possibility for the solution chemistry studies. Based on various models, theoretical predictions have been made on the chemical behaviour of Sg. For such calculations relativistic corrections are made which take into account the changes in the electronic configuration associated with the heavy elements. Based on the DS DVM calculations, the trend in the extractability of the group VI elements from HCl medium using tertiary /

quarternary amines follow the trend: U > Mo > W > Sg. However, no such experiments have actually been carried out with seaborgium.

Fig. 4 Dependence of log K_d values of Mo and W on HF concentration at 0.1M HCl / HNO$_3$

The first aqueous chemistry of seaborgium [16] involved about 5000 identical chemical separations using ARCA. It was observed that in 0.1M HNO$_3$ / 5·10^{-4} M HF, Sg forms neutral or anionic oxofluoro species, similar to W and Mo. This behaviour was in sharp contrast to the behaviour of uranyl ion which forms cationic species under similar conditions and could not be eluted from the column. As a trial run for the actual separation experiment, the homolgs of Sg, Rf and trivalent actinides along with W isotopes produced by the ^{20}Ne + ^{152}Gd reaction were used in an ARCA experiment (Fig.3). The behaviour of Sg was similar to that of W and the analogy was seen from 3 parent daughter correlations [17]. The profiles of ion exchange behaviour of Mo and W in HNO$_3$ + HF medium is depicted in Fig. 4. The trend in the K_d values are in the same line as their ability to form anionic complexes. Based on the theoretical complex formation trend: Mo > W > Sg, it is

presumed that Sg may not form anionic complexes with low concentration of F$^-$.

Future Challenges

Though the studies on the chemical properties of Rf, Db and Sg have settled few questions such as their position in the periodic table, they have raised quite a few doubts too. More often than not, there is an uncertainity about their chemical speciation. In some cases Rf is found to mimic Zr and Hf, while in some other it behaved like Th or may be even like Pu. The chemical nature of these elements in atom-at-a-time scale is obviously expected to be very different from their bulk properties. Though the deviations from the chemic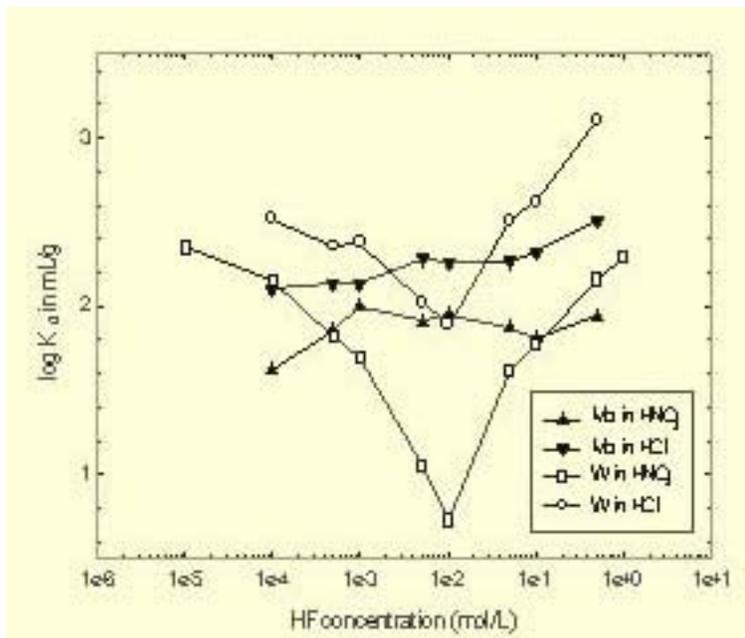al behaviour of their homologs are explained in terms of relativistic effects, much more studies are required to settle some of the unanswered questions.

Acknowledgement

The author thanks the Alexander von Humboldt Foundation, Germany, for financial assistance by granting a fellowship.

References

1. G.T. Seaborg; Chem. Engg. News **23**, 2190 (1945).
2. V. Pershina; Chem. Rev., **96**, 1977 (1996).
3. J.V. Kratz; in "Heavy Elements and Related New Phenomena", W. Greiner and R.K. Gupta (Eds.), World Scientific, Singapore, pp. 129-193 (1999).
4. I. Zvara et al., Sov. Radiochemist. **11**, 161 (1969).
5. H. W. Gaeggeler; J. Radioanal. Nucl. Chem.., Articles, **183**, 261 (1994).

6. V. Pershina and B. Frike: J. Chem. Phys., **100**, 8748 (1996).
7. J.V. Kratz; Private communication.
8. R. J. Silva, et al., Inorg. Nucl. Chem. Lett, **6**, 871 (1970).
9. E.K. Hulet, et al., J. Inorg. Nucl. Chem., **42**, 79 (1980).
10. K.R. Czerwinski, Ph. D. Thesis, Univ. of California (1992).
11. D.C. Hoffman, in "The Robert A. Welch Foundation Conference on Chemical Research XXXIV Fifty Years with Transuranium Elements", Houston, Texas, 22-23 October 1990, p. 255, and Lawrence Berkely Report LBL-29815 (1990).
12. E. Strub, et al., Radiochim. Acta, **88**, 265 (2000).
13. A. Kronenberg, P.K. Mohapatra, et al., Radiochim. Acta (Communicated).
14. K.E. Gregorich, et al., Radiochim. Acta, **43**, 223 (1988).
15. M. Schaedel, et al., Radiochim. Acta, **57**, 85 (1992).
16. M. Schaedel, et al., Nature, **388**, 55 (1997).
17. M. Schaedel, et al., Radiochim. Acta, **77**, 149 (1997).

The author was conferred the Prof. R.C. Tripathy Award of the Orissa Chemical Society at Khalikote College, Berhampur, Orissa, in December 2002.

About the author ...

Dr P.K. Mohapatra joined the Radiochemistry Division, BARC, in 1987 after completing his M.Sc. in Inorganic Chemistry from Utkal University and graduating from the 30th batch of the BARC Training School. He was awarded Ph.D. by Mumbai University in 1994. Dr Mohapatra did his Post-Doctoral research work at University of Liege, Belgium, under BOYSCAST Fellowship, DST (1998-1999) and at University of Mainz, Germany, under Humboldt Fellowship (1999-2000) on MRI contrast agents and chemistry of super heavy elements, respectively. His research interests include the chemistry of macrocyclic compounds and separation studies of actinides and fission products using novel extractants. Dr Mohapatra has to his credit over 50 publications in international journals and over 100 conference papers.