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Complete List of Authors:	Tereshatov, Evgeny; Texas A&M University College Station, Cyclotron Institute Semelová, Miroslava; Czech Technical University in Prague Faculty of Nuclear Sciences and Physical Engineering, Department of Nuclear Chemistry Cubova, Katerina; Czech Technical University in Prague Faculty of Nuclear Sciences and Physical Engineering Bartl, Pavel; Czech Technical University in Prague Faculty of Nuclear Sciences and Physical Engineering, Nuclear Chemistry Němec, Mojmír; Czech Technical University in Prague Faculty of Nuclear Sciences and Physical Engineering Stursa, Jan; Nuclear Physics Institute Czech Academy of Sciences Zach, Václav; Nuclear Physics Institute Czech Academy of Sciences Folden III, Charles; Texas A&M University College Station, Cyclotron Institute; Texas A&M University College Station, Department of Chemistry Omtvedt, Jon; University of Oslo, Department of Chemistry John, Jan; Czech Technical University in Prague Faculty of Nuclear Sciences and Physical Engineering, Nuclear Chemistry

COMMUNICATION

Valence states of cyclotron-produced thallium

Evgeny E. Tereshatov,*[a] Miroslava Semelová,[b] Kateřina Čubová,[b] Pavel Bartl,[b] Mojmír Němec,[b] Jan Štursa,[c] Václav Zach,[c] Charles M. Folden III,[ad] Jon Petter Omtvedt,[e] and Jan John[b]

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Unexpected behavior of thallium atoms, produced in a reaction of gold target with accelerated ^{3}He ions, in liquid-liquid extraction with [C$_n$mim][NTf$_2$] ionic liquids (n = 2, 4, 6–8, 10) was investigated. Contrary to the general expectations, a significant proportion of thallium produced in the nuclear reaction was found in a non-monovalent state upon dissolution of the KCl aerosol collector. This finding is critical for the design and evaluation of the forthcoming chemistry experiments with the superheavy element nihonium.

The equilibrium charge-state of recoil atoms is a crucial parameter for charged particle physics[1] and chemical investigations[2] with such species. Thermalization of cyclotron-produced excited ions (interaction with gaseous or solid matter) leads to capture of electrons and formation of thermodynamically stable ions with reduced charges.[3] Upon leaving the target in a highly charged state the ions will, when electrons are available, quickly pick up electrons resulting in lower charge states. The speed at which this occurs depends on the ion's ionization potential.[3] Under a given set of conditions equilibrium is quickly established. Thus, any physical or chemical manipulations can be done only with the survived recoil, which is expected to be the most stable form of such an element/molecule. This approach is very important especially in the light of chemical studies of superheavy elements due to their extremely low production rate, rapid decay and absence of stable nuclei.[4]

For example, a few experiments on Nh chemical properties[5] did not provide conclusive results due to similarities in behavior of atomic and molecular (NhOH) forms of the metal.[6]

The chemical properties of Nh were predicted already in 1970s and the most stable oxidation state is expected to be +1.[7] Despite that the +3 oxidation state is less stable, it is still possible[7b,8] and thus the experiments with this element are very challenging. It must be noted that the study of transactinide elements is usually performed in comparison with their lighter homologues.[9] Thus, a good understanding of Tl's chemical state under identical conditions that Nh is produced is very important for experiments aimed at studies of elements synthetized this way. According to a computational study on the thallium and nihonium energy levels,[8a] the theoretically calculated thallium ionization potentials (IP) are in good agreement with the experimentally measured values, namely IP1 = 6.108 eV, IP2 = 20.428 eV, and IP3 = 29.83 eV. The standard electrode potential for the reaction $Tl^{3+} + 2e^- = Tl^+$ is +1.25 V.[10] However, strong complexing agents result in the decrease of Tl(III) reduction potential and at 1 M HCl this value drops to +0.77 V.[11] It should be noted that the Tl(III) to Tl(I) reduction process in the solution is faster than the Tl(III) complexation[12] and the rate depends on the stability constants of Tl(III) complexes[12] while those of Tl(I) are very low.[13]

Researchers[14] investigated effects of thermal neutron irradiation (10^{12} cm^{-2} s^{-1}) and subsequent annealing (up to 300 °C) of mixed valence $Tl_3^{I}Tl^{III}Cl_6$ salt on formation of additional amount of trivalent thallium. And it was found that the former (also gamma-irradiation)[15] does not result in production of Tl(III). However, the latter already at 209 °C leads to an exchange reaction triggered by a vacancy diffusion mechanism,[16] resulting in a 10 percent increase in yield. If the salt is not irradiated, the thermal decomposition competes with the exchange reaction.[17] The ambient atmosphere (air or vacuum) does not affect the exchange reaction as well.[18] Thus, the thallium oxidation happens at the moment of recoil and "bare" trivalent thallium should not persist in the lattice.[19] Moreover, if TlCl and InCl$_3$ are mixed together and heated at 300 °C, then the trivalent thallium is found as well.[20]

Also, the trivalent thallium was found in solutions of radioactive ^{212}Bi in mineral acids.[21] Different salts (mostly chlorides) were used as targets for implantation of ^{208}Tl originated from the ^{212}Bi.[22] These targets then were partially dissolved in the mineral acids and up to 60 % of collected ^{208}Tl

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[a] *Cyclotron Institute, Texas A&M University, College Station, TX 77843, USA*
[b] *Department of Nuclear Chemistry, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University in Prague, 115 19 Prague, Czech Republic*
[c] *Nuclear Physics Institute, Czech Academy of Sciences, 25068 Řež, Czech Republic*
[d] *Department of Chemistry, Texas A&M University, College Station, TX 77843, USA*
[e] *Department of Chemistry, University of Oslo, Blindern, P.O. Box 1033, NO-0315 Oslo, Norway*
* Corresponding author: etereshatov@tamu.edu

was assigned to the trivalent thallium. Furthermore, the presence of water on the salt surfaces was found to have a strong impact on the increased production of multi-charged species.[22a] To the best of our knowledge there are no published data on oxidation states of Tl produced in heavy ion-induced reactions.

It is also known that thallium is a subject of photochemical reactions and UVC light can easily oxidize thallium to its trivalent state.[23] Moreover, it was shown that heavy ion induced ionization populates states with higher excitation energy than those of photoionization.[24] This means that partial thallium oxidation by the beam plasma is certainly possible.

In a previous study, it was demonstrated that liquid-liquid extraction into 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ionic liquids (marked as $[C_nmim][NTf_2]$ where n = 2, 4, 8) from hydrochloric acid media can be used as a tool to distinguish between mono- and tri-valent thallium in off-line experiments.[25] A recent attempt to confirm these observations in an on-line study with thallium atoms recoiling from a gold target after reaction with accelerated ^3He ions[26] provided unique results highlighting deviation of the recoiling atoms from expected monovalent thallium behavior.

Therefore, a new study was designed to investigate the reasons for this unexpected behavior. Comparison of off-line and on-line results is shown in Fig. 1. Similarly to Ref. 26, short-lived thallium isotopes were produced by irradiating Au self-supporting target foils with natural isotopic composition (10 µm thick, obtained from Goodfellow AU000160) using the U-120M cyclotron at the Nuclear Physics Institute of the Czech Academy of Science in Řež near Prague. The irradiation was performed with 47.3 MeV $^3He^{2+}$ ion-beam with an intensity of 250–400 nA (electrical) which resulted in the nuclear reaction $^{197}Au(^3He;xn)^{200-x}Tl$. Products recoiling out of the target foil were stopped in a chamber filled with He-gas, transported by a He gas-jet (1.5 L/min through a 25 m long, 1/8" ID tube) seeded with KCl aerosols to the laboratory and collected on glass-microfiber filters (Whatman GF/C Cat.No. 1822-050). The aerosols with the radionuclides were then dissolved in hydrochloric acid and used for the liquid–liquid extraction experiments. No carrier for Tl was added.

High-purity grade (99%) 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ionic liquids $[C_nmim][NTf_2]$ (where n = 2, 4, 6, 7, 10) and $[C_8mim][NTf_2]$ were purchased from Iolitec, Germany, and Solvionic, France, respectively. The extractions were carried out from the medium of hydrochloric acid in the concentration range from 0.2 to 8.0 mol/L. In some experiments 0.1 M Na_2SO_3 and 50-60% $N_2H_4{\cdot}xH_2O$ were tested as reduction agents. Any reducing agent was added (20 µL per 750 µL of the aqueous phase) prior to the contact with the organic phase. All chemical reagents used were of analytical grade.

In all the experiments, equal volumes of both phases were contacted and violently shaken by a vortex mixer for 4 min at 1800 rpm at ambient temperature. Aqueous and organic phases were then separated by centrifugation (30 s at 3000 rpm). Aliquots of both phases were sampled and measured with a 50% HPGe detector. To track thallium in the samples, the most intense γ-rays from the decay of ^{194m}Tl, ^{195}Tl, and ^{196m}Tl were chosen. The distribution ratio (D) and extraction yield (E) values were calculated as the ratio of the decay-corrected net areas of the peaks measured for both the organic and aqueous phases as:

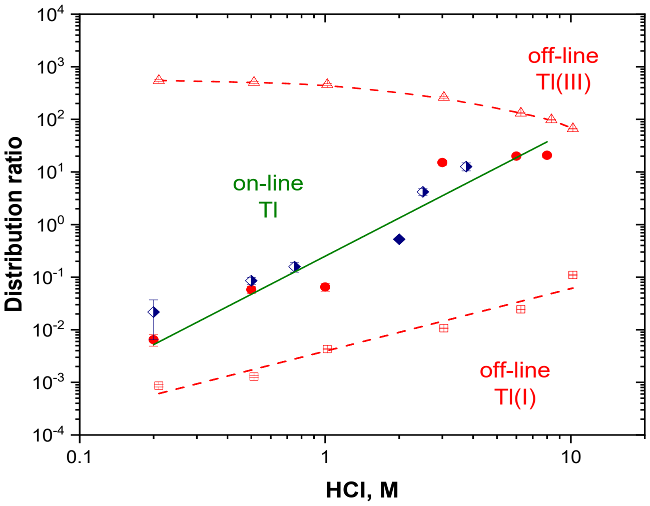

Fig. 1 Off-line (red dashed lines) behavior of Tl(III) oxidized with Cl_2 water (open red triangles) and Tl(I) (open red squares) extracted into $[C_8mim][NTf_2]$ ionic liquid (data taken from Ref. 25b) and on-line (solid green line) behavior of non-redox-treated thallium extracted into $[C_8mim][NTf_2]$ ionic liquid (closed red circles) and $[C_6mim][NTf_2]$ ionic liquid (navy diamonds) from hydrochloric acid. Semi-closed diamonds represent data taken from Ref. 26 and all closed symbols represent results of this work. Lines are given to guide the eye.

$$D = \frac{I_{org}}{I_{aq}} \cdot \frac{V_{aq} \cdot \rho_{org}}{m_{org}} \qquad \text{Eq. 1}$$

$$E = \frac{D}{1+D} \cdot 100\ \% \qquad \text{Eq. 2}$$

where I_{org}, I_{aq} are decay-corrected net count rates of the measured nuclide per V_{aq} volume of aqueous phases and m_{org} and ρ_{org} are masses and densities of organic phases, respectively. The manufacturer provided density values were used except for $[C_7mim][NTf_2]$ value taken from literature.[27]

The uncertainty of the distribution ratios was evaluated as a combined uncertainty of the statistics of the measurement and pipetting. Any additional random errors induced e.g. by problems in separation of the aqueous and viscous organic phases have not been accounted for here.

In the first phase of this study, the unexpected thallium behavior found earlier[26] for the system with $[C_6mim][NTf_2]$ was verified with the same ionic liquid again and then a new series of experiments with $[C_8mim][NTf_2]$ was performed. As can be seen from Fig. 1, the new results obtained are virtually identical with the earlier on-line study and significantly differ from the results observed in off-line experiments.[25b]

It was shown earlier that Tl(III) is extracted into imidazolium-,[25b] pyrrolydinium-,[28] and betainium-based[29] ionic liquids from HCl media in the form of $TlCl_4^-$ which is supported by the Tl(III) speciation study in the chloride media.[30] The mechanism of this transfer can be written as

$$TlCl_4^-{}_{aq} + C^+{}_{aq} \rightleftarrows [C]TlCl_{4\ org} \qquad \text{Eq. 3}$$

where $[C]^+$ is the equilibrium aqueous concentration of the ionic liquids' cation which is a function of HCl concentration.[31] However, authors[32] suggested that a non-extractable species

$TlCl_5^{2-}$ is also formed in HCl solutions at higher acidity with an average stepwise stability-constant $K_5 = 0.68$. This explains a decline of Tl(III) extraction in off-line experiments with increase of acidity.

Similar behavior is attributed to Tl(I). According to its speciation in chloride media,[33] if the HCl concentration increases in the aqueous phase, it promotes the presence of $TlCl_2^-$ species and the following reaction mechanism applies

$$TlCl_2^-{}_{aq} + C^+{}_{aq} \rightleftarrows [C]TlCl_{2\ org} \qquad \text{Eq. 4}$$

Thus, increase of Tl(I) extraction with increase of the aqueous phase acidity is expected and confirmed in off-line experiments (see Fig. 1).

The on-line observed D values of thallium are in between of those of Tl(III) and Tl(I) measured off-line. This implies that, most probably, the cyclotron-produced thallium samples dissolved in the HCl solutions contain the metal in both oxidation states simultaneously. The ratio of Tl(I) and Tl(III) concentrations in these solutions can be easily calculated from the measured on-line D values and those observed for Tl(I) and Tl(III) in off-line experiments.

Keeping in mind that there are Tl(I) and Tl(III) in the solution prior to extraction, they theoretically both can be extracted but their contribution to the overall on-line extraction efficiency will be different

$$E_{on-line} = E_{Tl(I)} \cdot P_{Tl(I)} + E_{Tl(III)} \cdot P_{Tl(III)} \qquad \text{Eq. 5}$$

where E is an extraction efficiency and P is weight (proportion) of the metal in either a mono- or trivalent state. The Tl(III) proportion is

$$P_{Tl(III)} = \frac{[Tl(III)]_{init}}{[Tl(III)]_{init} + [Tl(I)]_{init}} \qquad \text{Eq. 6}$$

where "init" denotes conditions before extraction and an analogous equation holds for $P_{Tl(I)}$.

For example, results of off-line experiments on Tl(I) and Tl(III) extraction into ionic liquids from 2 M HCl show[25b] that extraction efficiency of Tl(I) is less than 1 % ($E_{Tl(I)} \approx 0$). On the contrary, the Tl(III) extraction efficiency under the same conditions is greater than 99 % ($E_{Tl(III)} \approx 1$). Thus, we can say that

$$E_{on-line} \approx P_{Tl(III)} \qquad \text{Eq. 7}$$

As one may see in Fig. 1, $E_{on-line} = f([HCl])$. The dependence of the on-line extraction efficiency on the acid concentration can be easily seen mathematically if the initial metal concentrations in Eq. 6 are expressed via a combination of corresponding stepwise stability constants and Cl^--anion concentrations in the solution.

The increase of on-line measured D values with increase of acidity can be associated with formation of $TlCl_4^-$ species which drive the extraction process. Also, the higher acid concentration provides more complexing agent ions (Cl^--anions) and this almost completely prevents the Tl(III) from the reduction. Hence, the high extraction yield observed for the on-line produced thallium at 8 M HCl (more than 95 % extracted) is a clear indication that majority of thallium is present in the solution as Tl(III). Similarly, the small proportion of Tl(III) and the corresponding low on-line D values at low acidity correlate with a fact that the reduction of Tl(III) to Tl(I) under such conditions is faster than the Tl(III) complexation.[12] Thus, the low concentration of Cl^--anions in the solution cannot limit the reduction process and Tl(III) is converted to Tl(I).

Bearing in mind the fact that Tl(I) cannot be oxidized to Tl(III) in the absence of oxidizing agents, these findings allow us to conclude that almost no Tl(I) is present among the thallium species stabilized on the KCl aerosol collector. If we believe that no oxidation occurs upon aerosol transport, than thallium stabilizes on the collector in higher than Tl(I) state already after its production.

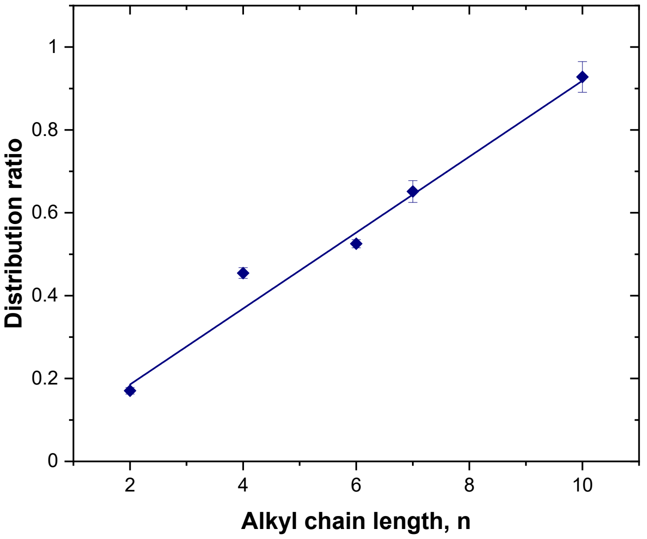

Fig. 2 Effect of alkyl chain length attached to the imidazolium ring of studied ionic liquids $[C_nmim][NTf_2]$ (where n = 2, 4, 6, 7, 10) on the thallium distribution ratios at 2 M HCl obtained for the non-redox-treated solutions. Line is given to guide the eye.

In order to check the presence of reducible thallium species, a series of reducing agents were considered to be added to the solution prior to the metal extraction into $[C_4mim][NTf_2]$ ionic liquid. It is known that Tl(III) can be successfully reduced to Tl(I) by means of diverse compounds, e.g. sodium sulphite[34] or hydrazine.[35] The results of our study summarized in Table 1 clearly demonstrate that upon the reducing agent addition only low D values were found and this behavior can be attributed to monovalent thallium.

To rule out the presence of some other extractable species, an extraction/back-extraction experiment was designed where initially thallium was extracted to $[C_{10}mim][NTf_2]$ from the non-redox-treated 2 M HCl solution and then back-extraction was carried out from the separated ionic liquid phase into the fresh aqueous phase of the same composition. This HCl concentration was used because of the expected quantitative Tl(III) and negligible Tl(I) extraction. This assumption is based on results in paper[25b] where it was shown that Tl(III) extraction increases and Tl(I) extraction decreases with increase of alkyl chain length attached to the imidazolium ring and for $[C_8mim][NTf_2]$ the D values at 2 M HCl were ~360 and ~0.0075 for Tl(III) and Tl(I), respectively. Figure 2 shows that extraction of cyclotron-produced Tl from non-redox-treated solution is proportional to the alkyl chain length and it also correlates with increasing hydrophobicity of ionic liquids.[36]

Table 1 Influence of various reducing agents on Tl extraction by $[C_4mim][NTf_2]$ ionic liquid from the solution of KCl aerosols in 2 M HCl

Reducing agent	Extraction yield, %
No reducing agent	31.2 ± 0.6
500 mM N_2H_4	1.26 ± 0.12
2.7 mM Na_2SO_3	1.04 ± 0.08

Table 2 Extraction efficiency of Tl by [C$_{10}$mim][NTf$_2$] ionic liquid from the non-redox-treated solution of KCl aerosols in 2 M HCl and back-extraction of Tl into a fresh HCl solution of the same composition

Percent of Tl in the organic phase	
Extraction	Back-extraction
44.9 ± 1.1	98.91 ± 0.12

As shown in Table 2, only about 45 % of the thallium was extracted from the original solution which is in agreement with data shown in Fig. 1. Almost no back-extraction was observed; only 1.09% ± 0.12% of activity was transferred to the aqueous phase. The most straightforward interpretation of this result is that only trivalent thallium was extracted that cannot be back-extracted under the same conditions. Thus, one can see from Eq. 7 that at 2 M HCl ~45 % of thallium in the initial solution prior to extraction can be attributed to Tl(III) and ~55 % belongs to Tl(I). Together with the other results described above, this may serve as a final proof that thallium is present as a mixture of Tl(I) and T(III) in the solution of thermalized nuclear reaction products.

It should be mentioned that some literature sources indicate the formation of Tl(II) intermediate both in solid (crystal γ-irradiation)[37] and liquid (pulse radiolysis)[38] phases. Despite that our experiment was not designed to detect this species, its potential existence in the system does not contradict to our results because of its instability and immediate disproportionation in the solution according to the following reaction

$$2\cdot\mathrm{Tl}^{2+}_{aq} \rightarrow \mathrm{Tl}^{+}_{aq} + \mathrm{Tl}^{3+}_{aq} \qquad \text{Eq. 8}$$

The ratio of forward and backward rates of this reaction is greater than 10^{33}, making the reaction depicted in Eq. 8 the only one that deserves attention.[10b]

Conclusions

Overall, the most important conclusion of this study is that, contrary to the general expectations, a significant proportion of thallium produced in the nuclear reaction of ^{197}Au with accelerated ^{3}He^{2+} ions stabilizes in a non-monovalent state on the KCl aerosol collector. This finding is critical for the design and evaluation of the forthcoming chemistry experiments with the superheavy element nihonium, for which thallium serves as a homologue.

Conflicts of interest

There are no conflicts to declare.

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