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Probing the participation of 5f electrons in gas-phase reactions of actinide cations with small alkanes and alkenes

Marta Santos¹, Joaquim Marçalo¹, António Pires de Matos¹,
John K. Gibson², Richard G. Haire²

¹*Departamento de Química, Instituto Tecnológico e Nuclear, 2686-953 Sacavém, Portugal*

²*Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA*

Introduction

We have recently made the first Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) studies of gas-phase ion chemistry of the transuranium actinides Np, Pu and Am [1-2]. As can be assessed in a recent review paper [3], prior to these studies, gas-phase ion chemistry experiments with the highly radioactive members of the actinide series Pa, Np, Pu, Am, Cm, Bk, Cf and Es had been based on the use of Laser Ablation with Prompt Reaction and Detection (LAPRD) technique, while FTICR-MS studies of An ions had been limited to Th and U.

One of the questions raised by this type of studies is the possible participation of 5f electrons in the observed chemistry. With this question in mind, we decided to study the gas-phase reactions of doubly-charged actinide cations, An^{2+} ($An = Th, U, Np, Pu$ and Am), with various alkanes (CH_4, C_2H_6, C_3H_8 and C_4H_{10}) and alkenes (C_2H_4, C_3H_6 and C_4H_8). For comparative purposes we also studied the reactivity of doubly-charged lanthanide (Ln) cations with the same hydrocarbons.

Experimental

FTICR-MS is a technique that is specially suited to study the chemistry of ion-molecule systems in gas-phase. As a result of applied magnetic and electrical fields, it is possible to trap ions for long periods of time and complex sequences of operations can be performed. To different event sequences correspond different types of experiments in which the structure of the ions can be probed, reagent/product sequences can be determined and kinetic and thermochemical studies can be made.

All the experiments were performed in a Finnigan FT/MS 2001-DT mass spectrometer equipped with a 3 Tesla superconducting magnet and with a Nd:YAG laser, which was used to produce the actinide ions from An-Pt alloys and the lanthanide ions from pure metal pieces.

Results and Discussion

In the reactions of An^{2+} with the alkanes and alkenes electron, hydride and CH_3^- transfer products were observed. In addition, dehydrogenation and alkane-loss products were also

formed. Product distributions and reaction rate constants are reported and related to the electronic configurations of the reacting ions.

The second ionization energies of the An studied lie between 11-12 eV, being higher than the first ionization energies of the alkanes and alkenes with the exception of CH₄. These differences explain the observed electron, hydride and CH₃⁻ transfer pathways. The elimination of H₂ and other small neutrals could indicate that bond insertion mechanisms might be operative. This type of mechanism involves two unpaired electrons, that in the case of Th²⁺ are available in the ground state electron configuration, 5f6d, and also in the configurations 6d² and 6d7s at 0.008 and 0.684 eV respectively. All the other An²⁺ studied have ground state configurations of the type 5fⁿ and 5fⁿ⁻¹6d configurations available at 0.026 eV for U²⁺, 0.7 eV for Np²⁺, 1.6 eV for Pu²⁺ and 3.0 eV for Am²⁺. Configurations with two non-f unpaired electrons are only available at higher energies: 2.407 eV for U²⁺, 4.2 eV for Np²⁺, 6.2 eV for Pu²⁺ and 8.7 eV for Am²⁺.

Freiser and co-workers have studied the reactions of Y²⁺[4] and La²⁺[5], which only have one valence electron d¹, with the alkanes and proposed an alternative mechanism. This mechanism consists in the formation of a three-centered intermediate in an electrostatic manner, not involving a direct insertion into a C-C or C-H bond, from which H₂ and saturated hydrocarbons can be lost.

Comparing the reactivity of An²⁺ with Ln²⁺ with similar second ionization energies (Tb²⁺, Dy²⁺, Ho²⁺ and Er²⁺), we observed that Th²⁺, U²⁺ and Np²⁺ were more reactive, forming significantly more doubly charged bond activation products, while Pu²⁺ and Am²⁺ were similar to the referred Ln²⁺. The ground state configurations of these Ln²⁺ are of the type 4fⁿ, with promotion energies to 4fⁿ⁻¹6d configurations of 1.112 eV for Tb²⁺, ca. 2.1 eV for Dy²⁺, 2.236 eV for Ho²⁺ and 2.104 eV for Er²⁺.

The greater reactivity of U²⁺ and Np²⁺ could indicate a possible participation of the 5f electrons if a bond insertion mechanism is occurring, or it could evidence the greater accessibility of the 6d configurations, in the case of an electrostatic mechanism being operative. The involvement of 5f electrons in the gas-phase reactivity of actinide cations remains unclear and further experiments are needed. Theoretical calculations on these systems would also be very helpful.

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