

Unusual Uranium Isotope Effect Induced by Photolysis of Uranyl Salts in Micelles

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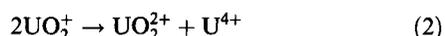
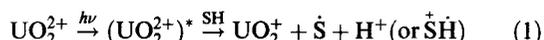
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An unusual uranium isotope distribution between the products of uranyl photolysis, in contrast to that predicted by the classical isotope effect, has been observed and is attributed to the magnetic isotope effect.

Modern methods of uranium isotope separation and modern uranium technologies are based on the mass isotope difference. Molecules and other chemical species containing the light isotope ²³⁵U nuclei are known to be more energy rich and therefore, chemically more reactive than those with the ²³⁸U isotope nuclei. The ²³⁵U compounds are more volatile than those with ²³⁸U nuclei and the diffusion rates and the velocities of the ²³⁵U molecules are higher than those for the ²³⁸U molecules, *etc.* Such differences in the physical and chemical properties of isotopic molecular forms are known as classical, mass-dependent, isotope effects.

We have observed an unusual, anti-classical uranium isotope effect which implies an unexpected result: the heavy, ²³⁸U-containing molecules appear to be chemically more reactive than those with ²³⁵U nuclei.

Photolysis of dioxouranium (or uranyl) salts in aqueous solution is known to occur *via* a sequence of two chemical reactions. Electron (or hydrogen atom) transfer from the substrate SH to excited uranyl ion (UO₂²⁺), reaction (1), is followed by generation of the intermediate uranyl ion UO₂⁺ and the substrate radical \dot{S} (or radical cation $\dot{S}H$) and the disproportionation of uranyl ions, reaction (2), which yields the U⁴⁺ salt, as a final photolysis product, and regenerates the starting uranyl ion.¹



We have irradiated a solution of isotopically-enriched [isotope ratio ²³⁵U/²³⁸U (11.198 ± 0.006) × 10⁻²] uranyl nitrate UO₂(NO₃)₂·6H₂O (8 × 10⁻² M) in D₂O at room temperature with a high pressure mercury lamp in the presence of 4-methoxyphenol (5 × 10⁻² M), ammonium fluoride NH₄F (1M) and sulfuric acid (0.5M). After 10% chemical conversion of the uranyl nitrate the insoluble reaction product uranium tetrafluoride UF₄ was isolated and re-oxidized into UO₂(NO₃)₂. The isotope ratio ²³⁵U/²³⁸U for this uranyl nitrate (and, therefore, for the reaction product UF₄) was found to be (11.148 ± 0.006) × 10⁻², being 0.5% lower than that for the starting uranyl nitrate. This implies unambiguously that the reaction product is diminished in light isotope nuclei, demonstrating the chemical reactivity predominance of uranyl ions with heavy isotope nuclei, in contrast to the predictions of the classical isotope effect. This result is in accordance with previously announced similar observations.^{2,3}

However, an even more pronounced anti-classical uranium isotope effect has been detected in the photolysis of an uranyl perchlorate salt UO₂(ClO₄)₂·6H₂O (5 × 10⁻³ M) in a D₂O micellar solution of sodium dodecyl sulfate (SDS) in the presence of NH₄F (5 × 10⁻² M) and 2,6-diphenyl-4-stearoyl phenol (5 × 10⁻² M), the latter being located in the micelle interior. In this case the isotope composition has been measured both for the reaction product UF₄ and for the remainder of the starting uranyl perchlorate. Table 1 lists the isotope ratios and their error limits measured mass spectrometrically after 15% chemical conversion.

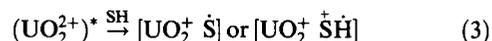
Again the reaction product is diminished in light isotope nuclei, while the UO₂(ClO₄)₂ remainder is enriched with heavy uranium nuclei. The balance of isotope composition is quite satisfactory: the isotope enrichment Δ = +0.3% of the 85%

Table 1 Isotope ratios and error limits measured mass spectrometrically after 15% chemical conversion

| Species | ²³⁵ U/ ²³⁸ U | Δ(%) |
|---|-------------------------------------|------|
| UO ₂ (ClO ₄) ₂ , before irradiation | (11.198 ± 0.008) × 10 ⁻² | — |
| UO ₂ (ClO ₄) ₂ , remainder after photolysis | (11.235 ± 0.009) × 10 ⁻² | +0.3 |
| UF ₄ , reaction product | (11.019 ± 0.006) × 10 ⁻² | -1.5 |

UO₂(ClO₄)₂ remainder is equivalent to the 1.5% reduction of the reaction product, which is formed in 15% chemical yield. This means that there is no indication of any significant isotope leakage into any other minor reaction by-products.

The enrichment of the starting uranyl salt with ²³⁵U isotope nuclei demonstrates an isotope effect which is opposite in sign to the classical one. We are therefore dealing with a new, anti-classical uranium isotope effect, which we suppose to be induced by magnetic electron-nuclear, or Fermi, interaction in the reaction intermediates [radical or ion-radical pairs, resulting from photoinduced electron or hydrogen atom transfer between an excited uranyl ion and a phenol molecule, reaction (3)].



These radical pairs are known to be in a triplet electron spin state⁴ because their chemical precursor, the excited uranyl ion, reacts in a triplet spin state. Back electron (or hydrogen atom) transfer returning to the starting uranyl ion in the ground singlet state is, therefore, spin forbidden. However, the Fermi interaction between the unpaired electron spin and magnetic moment of the ²³⁵U nucleus in the uranyl ion-radical UO₂⁺ induces triplet-singlet spin conversion of the radical pairs [UO₂⁺ \dot{S}] (or [UO₂⁺ $\dot{S}H$]) and removes the spin forbiddance for the back electron transfer in the pairs with ²³⁵U magnetic isotope nuclei (nuclear spin 7/2, magnetic moment -0.31 μ_N). Hence, being electron spin selective the intra-pair chemical reaction becomes nuclear spin selective and sorts the isotope nuclei. As a result, ²³⁵U magnetic nuclei are accumulated in the recovered uranyl ions while the reaction product is enriched with non-magnetic ²³⁸U nuclei. The reason is that in the pairs [UO₂⁺ \dot{S}] with ²³⁸U nuclei there is no Fermi interaction so that their triplet-singlet conversion is delayed and they predominantly dissociate into the individual radicals \dot{S} (or $\dot{S}H$) and UO₂⁺. The latter carry an excess of ²³⁸U nuclei and bring it into the reaction product, according to reaction (2).

The one-step enrichment coefficient α, estimated in terms of the well known Bernstein equation⁵ log S = (1 - α) log (1 - F) (which describes the isotope enrichment S as a function of chemical conversion F), has been found to be 1.02. This value is opposite in sign to the square root isotope mass ratio ²³⁵U/²³⁸U (0.996) which is predicted by the classical isotope effect and is at least one order of magnitude higher. We therefore conclude that the magnetic isotope effect^{6,7} may be significant even for uranium nuclei, especially in chemical reactions of micellized uranium compounds.

We are gratefully indebted to the referees for useful comments and the Russian Fund for Fundamental Research for financial support (Grant no. 93-03-5227).

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Received: Moscow, 26th January 1993

Cambridge, 23rd February 1993; Com. 3/00633F