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

Igor V. Khudyakov*[a] and Anatoly L. Buchachenko*[b]

[a] *Department of Chemistry, Columbia University, New York NY 10027, USA.*
[b] *N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 117977 Moscow, Russian Federation.*
Fax: +7 095 938 2156

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 ^{235}U nuclei are known to be more energy rich and therefore, chemically more reactive than those with the ^{238}U isotope nuclei. The ^{235}U compounds are more volatile than those with ^{238}U nuclei and the diffusion rates and the velocities of the ^{235}U molecules are higher than those for the ^{238}U 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, ^{238}U-containing molecules appear to be chemically more reactive than those with ^{235}U 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 (UO_2^{2+}), reaction (1), is followed by generation of the intermediate uranoyl ion UO_2^+ and the substrate radical $\dot{S}$ (or radical cation $\overset{+}{S}\dot{H}$) and the disproportionation of uranoyl ions, reaction (2), which yields the U^{4+} salt, as a final photolysis product, and regenerates the starting uranyl ion.[1]

$$UO_2^{2+} \xrightarrow{h\nu} (UO_2^{2+})^* \xrightarrow{SH} UO_2^+ + \dot{S} + H^+(\text{or } \overset{+}{S}\dot{H}) \quad (1)$$

$$2UO_2^+ \rightarrow UO_2^{2+} + U^{4+} \quad (2)$$

We have irradiated a solution of isotopically-enriched [isotope ratio $^{235}U/^{238}U$ $(11.198 \pm 0.006) \times 10^{-2}$] uranyl nitrate $UO_2(NO_3)_2 \cdot 6H_2O$ (8×10^{-2} M) in D_2O at room temperature with a high pressure mercury lamp in the presence of 4-methoxyphenol (5×10^{-2}M), ammonium fluoride NH_4F(1M) and sulfuric acid (0.5M). After 10% chemical conversion of the uranyl nitrate the insoluble reaction product uranium tetrafluoride UF_4 was isolated and re-oxidized into $UO_2(NO_3)_2$. The isotope ratio $^{235}U/^{238}U$ for this uranyl nitrate (and, therefore, for the reaction product UF_4) was found to be $(11.148 \pm 0.006) \times 10^{-2}$, 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 $UO_2(ClO_4)_2 \cdot 6H_2O$ (5×10^{-3}M) in a D_2O micellar solution of sodium dodecyl sulfate (SDS) in the presence of NH_4F (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 UF_4 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 $UO_2(ClO_4)_2$ remainder is enriched with heavy uranium nuclei. The balance of isotope composition is quite satisfactory: the isotope enrichment $\Delta = +0.3\%$ of the 85% $UO_2(ClO_4)_2$ 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.

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	$(11.198 \pm 0.008) \times 10^{-2}$	—
$UO_2(ClO_4)_2$, remainder after photolysis	$(11.235 \pm 0.009) \times 10^{-2}$	+0.3
UF_4, reaction product	$(11.019 \pm 0.006) \times 10^{-2}$	−1.5

The enrichment of the starting uranyl salt with ^{235}U 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)].

$$(UO_2^{2+})^* \xrightarrow{SH} [UO_2^+ \dot{S}] \text{ or } [UO_2^+ \overset{+}{S}\dot{H}] \quad (3)$$

These radical pairs are known to be in a triplet electron spin state[4] 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 ^{235}U nucleus in the uranoyl ion-radical UO_2^+ induces triplet–singlet spin conversion of the radical pairs $[UO_2^+ \dot{S}]$ (or $[UO_2^+ \overset{+}{S}\dot{H}]$) and removes the spin forbiddance for the back electron transfer in the pairs with ^{235}U magnetic isotope nuclei (nuclear spin 7/2, magnetic moment $-0.31\mu_N$). Hence, being electron spin selective the intra-pair chemical reaction becomes nuclear spin selective and sorts the isotope nuclei. As a result, ^{235}U magnetic nuclei are accumulated in the recovered uranyl ions while the reaction product is enriched with non-magnetic ^{238}U nuclei. The reason is that in the pairs $[UO_2^+ \dot{S}]$ with ^{238}U 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 $\overset{+}{S}\dot{H}$) and UO_2^+. The latter carry an excess of ^{238}U 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 equation[5] $\log S = (1-\alpha) \log (1-F)$ (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 $^{235}U/^{238}U$ (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).

References

1 For review see: E. Rabinowich and R. L. Belford, *Spectroscopy and Photochemistry of Uranyl Compounds*, Pergamon, London, 1964; H. D. Burrows and T. Kemp, *Chem. Soc. Rev.*, 1974, **3**, 139.
2 A. L. Buchachenko, I. V. Khudyakov, E. S. Klimchuk and N. A. Golubkova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 1902 (*Bull Acad. Sci. USSR, Div. Chem. Sci.*, 1990, 1729).
3 S. I. Nikitenko, A. P. Gai, M. P. Glazunov and N. N. Krot, *Dokl. Akad. Nauk SSSR*, 1990, **312**, 402 [*Dokl. Phys. Chem. (Engl. Transl.)*, 1990, **312**, 432].
4 A. L. Buchachenko and I. V. Khudyakov, *Acc. Chem. Res.*, 1991, **24**, 177.
5 R. Bernstein, *J. Phys. Chem.*, 1952, **56**, 893.
6 A. L. Buchachenko, *Prog. React. Kinet.*, 1984, **13**, 163.
7 I. R. Gould, N. J. Turro and M. B. Zimmt, *Phys. Org. Chem.*, 1984, **20**, 1.

Received: Moscow, 26th January 1993
Cambridge, 23rd February 1993; Com. 3/00633F