oxides.[13] This approach can also explain the conversion[14] of *Z* allylic derivatives into olefins with predominant *E* configuration by α displacement with $LiCuMe_2$. The nature of the leaving group should be decisive in determining which mechanism will be operative; ion pairs should be easily formed from common allylic esters compared with the corresponding lithium carbamates in the presence of copper reagents acting as Lewis acids.[15]

This hypothesis is now under investigation, while evaluation of the scope and limits of the carbamate method is continuing in the case of substituted, noncyclic allylic substrates.

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Infrared Photochemistry of a Volatile Uranium Compound with 10-μ Absorption

Sir:

It has recently been demonstrated that efficient separation of isotopic species can be achieved by selective, laser-induced multiphoton vibrational excitation of polyatomic molecules.[1,2] Examples of separations reported to date include isotopes of hydrogen,[3] boron,[4] carbon,[4b] silicon,[4b] sulfur,[5] chlorine,[6] selenium,[7] molybdenum,[8] and osmium.[9] The key molecular requirements for such a process are volatility and the existence of an infrared-active normal vibrational mode (fundamental, overtone,[6b,8] or combination[6b,8]) which exhibits a nonzero isotopic shift. The molecular infrared absorption is brought into coincidence or near coincidence in the gas phase with an intense (~10^7-10^9 W/cm^2) infrared laser source, resulting in isotopically selective decomposition or reaction. To date, most laser-induced isotope separation (LIS) experiments have been performed with pulsed, discretely tunable CO_2 infrared gas lasers. These devices have a usable output in the 10-μ region (9.2-10.8 μ) and are by far the most powerful, reliable, monochromatic, and economical sources of mid-infrared laser radiation presently available.

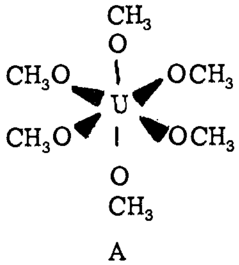
Table I. Irradiation Experiments with $U(OCH_3)_6$

expt	laser line	laser frequency, cm^{-1}	passes	enrichment factor (in ^{235}U)[a]
1	P(24)	940.56	1	0.9975 (22)
2	P(32)	933.01	1	1.0000 (20)
3	P(36)	929.02	1	1.0053 (17)
4	P(38)	927.04	1	1.0315 (46)
5	P(38)	927.04	1	1.0171 (26)
6	P(38)	927.04	1	1.0237 (27)
7	P(38)	927.04	1	1.0183 (26)[b]
8	P(38)	927.04	1	1.0258 (30)[b]
9	P(40)	924.98	1	1.0108 (27)

[a] Enrichment factor = $(^{235}U/^{238}U)_{final}/(^{235}U/^{238}U)_{initial}$; quantities in parenthesis are standard deviations. [b] Experiments with sample enriched (1.5%) in ^{235}U.

In principle, multiphoton infrared photochemistry would appear to be an ideal technique for the technologically important separation of uranium isotopes ^{235}U (0.72% natural abundance) and ^{238}U (99.27% natural abundance);[10] however, exhaustive spectral studies on the seemingly most attractive molecular candidate, UF_6, show it to lack significant absorption in the CO_2 laser region.[11] While the eventual development of powerful 16-μ lasers[10b,12] or other techniques using UF_6 may be possible, an attractive alternative approach would be the "tailoring" of uranium compounds for the CO_2 laser.[13] In this communication we report initial spectral and photochemical observations on a prototype molecule, $U(OCH_3)_6$. Among our results we note that it has proven possible, for the first time, to achieve uranium isotope separation by 10-μ infrared irradiation of a uranium-containing metal-organic molecule.

Uranium hexamethoxide, $U(OCH_3)_6$, was prepared by a modification of the original Gilman procedure[14] in which $U(OCH_3)_6^{-2}$ is oxidized in a single step,[13c,15a] or directly from UF_6 utilizing a procedure which will be discussed elsewhere.[15b] The compound readily sublimes (with minor decomposition) at 30 °C (10^{-5} mm) to form dark red, extremely moisture-sensitive crystals. Although $U(OCH_3)_6$ is less volatile than UF_6 (room temperature vapor pressure $\approx 10^{-3}$[16] vs. 120 Torr[17]), LIS, unlike gaseous diffusion, does not require high volatility, and operation at high pressures can actually decrease isotopic selectivity through intermolecular energy transfer.[1] Unlike UF_6, $U(OCH_3)_6$ does not attack glass.[18] The hexamethoxide is monomeric in benzene by cryoscopy and displays a singlet in the ^1H NMR (C_6D_6) at δ 7.66. Preliminary single-crystal X-ray diffraction results indicate discrete monomers with an octahedral UO_6 framework, A.[19] The vibrational spectra of $U(OCH_3)_6$ are in accord with this configuration; they can be assigned by analogy to UF_6[11] and by $^{18}OCH_3$ substitution.



A

Thus, the infrared spectrum (Nujol solution) of $U(OCH_3)_6$ exhibits a strong band at 464.8 cm^{-1} which, upon substitution of ~30% $^{18}OCH_3$,[20,21] appears as a multiplet centered at ~15-18 cm^{-1} to lower frequency. The 464.8-cm^{-1} transition is assigned to a ν_{U-O}, T_{1u} (ν_3) stretching mode.[22,23] The Raman spectrum of $U(OCH_3)_6$ (ν_0 = 6471 Å Kr^+, spinning polycrystalline sample at −33 °C) exhibits low frequency transitions at 495.5 (s) and 400.6 (m) cm^{-1}, which are assigned to the Raman-active A_{1g} (ν_1) and E_g (ν_2) U-O stretching modes,

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respectively.[11] No significant OCH_3 vibrations are expected in this region.[16a,22,23] The infrared spectra of UF_6[11d] and other metal hexafluorides[24] exhibit relatively intense $\nu_1 + \nu_3$ and $\nu_2 + \nu_3$ combination bands. By analogy, we tentatively assign weak $U(OCH_3)_6$ infrared transitions at 931 and ~860 cm^{-1} to $\nu_1 + \nu_3$ and $\nu_2 + \nu_3$, respectively. The infrared spectrum of $U(OCH_3)_6$ also exhibits a strong band at 1051 cm^{-1} which is assigned to a normal mode with predominant C–O stretching[22,23] character. This band shifts 18 cm^{-1} upon ^{18}O substitution. From product rule and first-order perturbation theory considerations[25] or by analogy to UF_6,[11d] the ^{235}U–^{238}U shift of the T_{1u} U–O stretch is anticipated to be on the order of 0.5–1.0 cm^{-1}.

The apparatus for irradiating $U(OCH_3)_6$ consisted of a Rogowski profile CO_2 TEA laser operating on a number of the P branch lines of the 00° 1–10° 0 laser transition. The output varied from 1.7 to 0.90 J/pulse[26] depending on the particular line. A pulse repetition rate of 1 Hz was employed, and typical pulse widths were 80-ns fwhm with a low intensity (~30% of total) 500-ns tail. The sample was irradiated with an unfocused beam in a 42-cm glass cell fitted with a KCl or KBr front window, and an aluminum-coated flat at the rear for double passing the laser beam. Two sample compartments were attached to the cell, and during irradiation the sample was allowed to pass between them (and through the laser beam) by cooling one compartment with liquid nitrogen. The irradiated product was analyzed mass spectrometrically using a Hewlett-Packard 5930A instrument interfaced to a data system for signal averaging and isotopic analysis.[27] Spectra for isotopic analysis were typically the result of 10 000–25 000 summed scans (50 000–125 000 data points) and were calibrated with nonirradiated standards, run immediately prior to and after the irradiated sample. Isotopic analyses were rejected if the two standards did not agree within 0.002%. The data (Table I) show that irradiation with the P(38) laser line, which is slightly to the red of the 931-cm^{-1} transition, results in enrichment of the sample in ^{235}U.[28] Use of enriched (1.5% ^{235}U) uranium (expt 7 and 8) shows similar enrichment factors but an increased absolute enrichment, as expected for isotopically specific chemistry. The average enrichment factor for expt 4–8 is 1.023 (3).[29] For comparison with these results, a single pass through a typical gaseous diffusion cell results in an enrichment factor of ~1.002.[10b] Thus, this rather simple LIS experiment has resulted in an average enrichment factor which is approximately ten times greater than for gaseous diffusion.

The results of the experiments described in this communication are the first reported indication of uranium isotope separation by infrared laser irradiation of a uranium-containing molecule. Clearly the simple apparatus employed is not suited for maximum enrichment, nor optimization of this procedure. Experiments with multiple-reflection cells, supersonic expansion nozzles, multiple lasers, and chemical scavengers are obvious extensions of this work. Such efforts are now in progress as are those to elucidate the mechanistic aspects of the photochemistry.

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