Polyhedron Vol. 11, No. 21, pp. 2783–2786, 1992
Printed in Great Britain

0277–5387/92 \$5.00+.00

LASER INDUCED DECOMPOSITION OF URANIUM TETRAHYDROBORATE

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(*Received* 13 *May* 1992; *accepted* 1 *July* 1992)

Abstract—Electronic excitation of uranium tetrahydroborate, $U(BH_4)_4$, results in the decomposition of the molecule. Longer wavelength excitation seems to induce a molecular collapse and a larger quantum yield of hydrogen.

The salt-like metal tetrahydroborates containing isolated tetrahedral BH_4^- ions in the crystal lattice have been the subject of intensive investigation for the last forty years.[1] Considerably less attention has been paid to the tetrahydroborates of metals, the "cations" of which show high reduced moments, z/r (Be, Al, Zr, Hf, Th and U), where z is the charge and r the radius of the ion, probably due to difficulties associated with the preparations and investigations of these extremely reactive and volatile compounds. Interest in tetrahydroborates is linked with their application as starting materials in the preparation of new inorganic compounds containing M—H—B bonds, as components of rocket fuels and as highly volatile compounds for the possible separation of elements with very similar properties, i.e. Zr and Hf or the isotopes ^{235}U and ^{238}U.[2]

In the "molecular approach" of laser separation of isotopes (LIS),[3] knowledge of the photochemical behaviour of volatile uranium compounds is essential. Uranium tetrahydroborate, $U(BH_4)_4$, one of the most volatile uranium compounds known, is a prospective candidate for LIS.[4] It was first synthesized by Schlesinger *et al.*[5] and the physical and chemical properties of the green crystalline compound have since been studied.[6] At temperatures below 343 K, samples kept for a long time showed only a minute decomposition. However, when heated above this temperature the compound decomposes as:

$$U(BH_4)_4 \longrightarrow 1/2H_2 + 1/2B_2H_6 + \underset{\text{red–brown solid}}{U(BH_4)_3} \quad (1)$$

$$U(BH_4)_4 \longrightarrow 8H_2 + \underset{\text{silvery mirror}}{UB_4\ (\text{or } U+4B)}. \quad (2)$$

Decomposition occurs chiefly in the vapour phase, but increases by an increase of contact surface and by finely divided metals. The optical and magnetic properties of the compound have been widely studied.[6,7] $U(BH_4)_4$ offers the possibility of using the $(5f)^2$ electrons of U^{4+} for optical transitions. In the tetrahedral site symmetry both magnetic and forced electric dipole transitions are allowed for pure electronic origins. Well over 200 transitions between 5000 and 30,000 cm^{-1} were reported.[6] The gas phase absorption spectra at room temperature showed a strong UV absorption band around 250 nm. In spite of the available spectroscopic data there have been very few photochemical studies reported to-date. In a flash photolysis study of $U(BH_4)_4$, Engleman[8] reported emission lines of UI, UII and a molecular species BH in the regions 411–478 and 478–598 nm. More recently, enrichment of boron isotopes in the product B_2D_6 has been observed by TEA CO_2 laser irradiation of $U(BD_4)_4$.[9] The compound did not seem to decompose under CW irradiation with either CO_2 or Ar^+ lasers but decomposed on UV irradiation at 253.7 nm.[10] The wavelength dependence of UV-promoted photochemistry has not yet been determined.

An interesting phenomenon like gas–solid structural transitions also exists in this compound and

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such structural dynamics, presumably involving facile U—H—B bridge bond rearrangements,[11] is expected to generate an unusually interesting photochemical process. In the present investigations we report the photochemical behaviour of $U(BH_4)_4$ in different electronic origins using UV and visible radiation. The determination of the products at various photolysing wavelengths provides an opportunity to look into the complex nature of the photodecomposition process.

EXPERIMENTAL

$U(BH_4)_4$ was prepared by the method as described in the literature.[5] It was purified by vacuum sublimation and kept in a sealed evacuated ampoule. The compound was characterized by its X-ray powder pattern[12] and mass spectrometry.[13] The vapour phase absorption spectrum in the UV region was taken using a 10 cm long cell, which showed a broad absorption feature with maxima near 250 nm. The peak absorption cross section was estimated to be 8.9×10^{-18} cm^2. The solution phase spectra (4–5 mM) in solvents like n-heptane and diethyl ether were recorded to obtain the weak absorption characteristics in the visible region.

The Pyrex photolysis cell was 100 cm long and 2.5 cm in diameter, fitted with quartz end-windows, and was provided with a cold finger into which the sample can be vacuum distilled using a liquid nitrogen trap. Typical photolyses were carried out at room temperature (0.08 Torr) and 321 K (1.2 Torr) for 2 h with a UV–vis radiation provided by a 450 W high pressure xenon lamp. The light beam was collimated with proper quartz optics and the photon flux was determined by uranyl oxalate actinometry. A UV cut-off Pyrex filter before the cell provided broad band visible radiation (>300 nm).

A home-made pulsed ruby laser was used for photolysis at 694.3 nm. The laser consisted of a 3 in. long and 1/4 in. diameter ruby rod, which was optically pumped by two xenon flash lamps. The laser pulse energy was 0.7 J, with a pulse duration of 700 μs. For irradiation at 632.8 nm, a 2 mW He–Ne laser was used for which no detectable decomposition was observed, even after a long exposure time. This could be due to very poor absorption of the sample at this wavelength and also low power of the laser used.

The total gaseous products were measured in the vaccum-line using a Toeppler pump and Saunders–Taylors apparatus, and the hydrogen content was estimated by combustion techniques using hot (573 K) cupric oxide. The other product, namely diborane, B_2H_6, was characterized and estimated by IR spectrometry. Mass spectrometric analyses were also carried out on the total gas mixture for counter-checking the estimated products.

After photolysis, the non-volatile red–brown solid deposit on the cell walls was dissolved in a concentrated HCl–H_2O_2 mixture. The solution was then analysed for U-content by a fluorimetric technique by exciting at 360 nm and monitoring the resulting fluorescence at 550 nm.[14] The boron content was determined by a colorimetric method by complexing with curcumin, which formed a red coloured rosacyanin complex.[15] The deposit dissolved in THF was also checked for its UV–vis absorption, as described in ref. 9. The entrance window was found to be coated with a thin shining deposit which was analysed mass-spectrometrically after dissolving in an HCl–H_2O_2 mixture.

RESULTS AND DISCUSSION

A considerable decomposition of $U(BH_4)_4$ was noticed in all the experiments using UV–vis radiation with the formation of a red–brown solid on the cell walls. The mass spectra of the gases produced showed clearly the presence of diborane, B_2H_6 and H_2. Diborane was detected by its characteristic IR spectra and was estimated from the 1601 cm^{-1} band $[(B—H_t)_{asym}]$. Figure 1 shows the strong feature at 1601 cm^{-1} of B_2H_6, produced after photolysing for 2 h with a xenon lamp. Analysis of the U/B ratio of the solid deposit and its UV–vis absorption indicated it to be uranium trihydroborate, $U(BH_4)_3$.

From the actual stoichiometry the relative contributions of reactions (1) and (2) were computed, which agreed with those evaluated from the gaseous products. In the rest of the irradiation experiments using UV-filtered visible and laser radiation, only H_2/B_2H_6 product gas ratios were determined, since the solid deposit was much less. The results presented in Table 1 show that the relative yield as well as the quantum yield for H_2 increases as the excitation wavelength becomes longer. The decomposition process was shown to be monophotonic in nature by carrying out the photolysis with various laser intensities using calibrated filters. Although we assign a value for the relative contribution of reaction (2), it may be pointed out that the actual photolytic reaction must be more complex than indicated in (1) and (2) depending on the actual conditions of the experiment. The mass spectrometric analysis of the shining deposit on the window revealed the film was due to some uranium boride which was not successfully identified.

Although the stoichiometry and relative yields were generally reproducible, the absolute yields seemed to be dependent on the cell surface con-

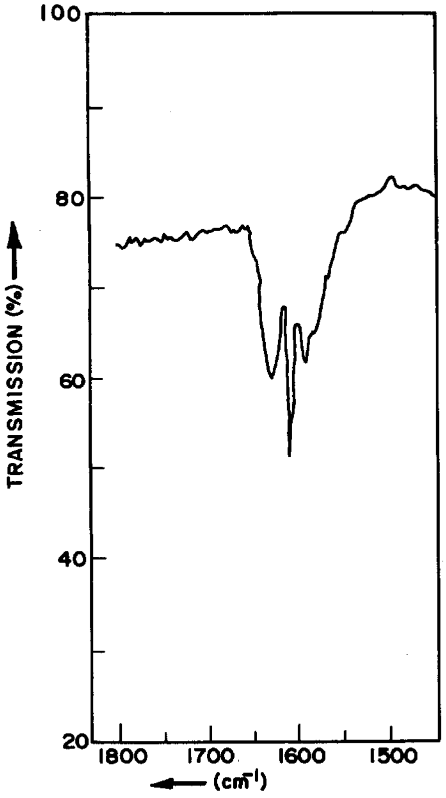

Fig. 1. IR absorption features of B_2H_6 at 1601 cm^{-1} after photolysing $U(BH_4)_4$ for 2 h with a 450 W xenon lamp. $U(BH_4)_4$ pressure at 48°C was 1.2 Torr in a cell volume of 500 cm^3. The IR cell was of 120 cm^3 volume with an 8 cm path length.

dition and solid deposit present, if any. For such a reason the quantum yields of H_2 values were obtained with some limits. However, the large net yield and typical quantum yield of as high as *ca* 8 at 694.3 nm photolysis could not be explained on the basis of a fractional contribution of reaction (2). In other words, such quantum yields suggest other mechanistic routes probably involving a "molecular collapse" of $U(BH_4)_4$, consequently generating hydrogen atoms and BH radicals which tend to give larger net yields of hydrogen.

Pyrolysis of the sample by a laser-induced temperature jump was ruled out in view of the following. Firstly, thermalization of the electronic excitation energy is not a usual process unless the electronic state rapidly relaxes to the upper vibrational manifold of the ground state. Secondly, it was calculated that even if all the absorbed laser energy is thermalized, it can induce a temperature rise of about 15 K in the excitation volume of 30 cm^3 at a pressure of ~0.1 Torr. A blank experiment on thermal decomposition at 323 K yielded no detectable decomposition.

In the gas phase, solution and mixed crystals with $Hf(BH_4)_4$, the structure of $U(BH_4)_4$ was determined by X-ray and neutron diffraction studied.[16] In the gas phase, the molecular symmetry is tetrahedral and each boron atom is attached to a uranium atom by three hydrogen bridges. Therefore, the molecule has 12 hydrogen bridges around the central U atom. Since the hydrogen bonds are rather weak (few kcal mol^{-1}), the primary step at a long wavelength excitation may involve a "molecular collapse" by knocking off the hydrogen bridges, leading to subsequent radical reactions to yield more hydrogen. This may account for the increase in the quantum yield by excitation at a longer wavelength.

$U(BH_4)_4$ has an extended electronic spectrum up to *ca* 1.6 μm. Thirty possible origins ranging from 5932 to 24,795 cm^{-1} have been reported by Keiderling *et al.*[17] The probable origins involving the excitation in our studies are tabulated in Table 2. Some of the differences observed in the product ratio for different photolysis wavelengths are probably due

Table 1. Relative yield and quantum yield as a function of excitation wavelengths

Wavelength (nm)	Relative yield $[H_2/B_2H_6]$	Reaction (2) contribution (%)	Typical quantum yield $(\phi)H_2$
Xe-lamp:			
Broad band UV (~253.7)	1.05	0.33	0.25
UV cut-off visible (>300)	2.3	7.4	0.59
He–Ne laser (632.8)	—	—	—
Ruby laser (694.3)	4.3	17.0	~8

Table 2. Probable assignment of electronic origins for various excitation wavelengths

Origin (relative intensity)	Transition[a]	Exciting wavelength (nm)	Vibrational assignment
Origin "n" at 13,831 cm^{-1} (100)	$E(^3H_4) \rightarrow T_2(b\text{-}^3H_6)$	694.3	n + 572 cm^{-1} i.e. $n+\nu_\eta+\nu_\beta$
Origin "p" at 15,400 cm^{-1} (11)	$E(^3H_4) \rightarrow E(^1D_2)$	632.8	p + 363 cm^{-1} i.e. $p+2\nu_\delta$
Origin "ee" at 24,795 cm^{-1} (27)	$E(^3H_4) \rightarrow T_2(^3P_2)$	Typical visible excitation 375.2	ee + 1850 cm^{-1} i.e. $ee+4\nu_\theta$

[a] On the basis of Zeeman effect data, the lack of EPR data and the density of transitions observed, it is known that the ground state of $U(BH_4)_4$ is $E(^3H_4)$.

to the fact that different electronic transitions are involved.

Acknowledgement—The authors thank Dr P. R. K. Rao for his keen interest in this work.

REFERENCES

1. B. D. James and M. G. Wallbridge, *Prog. Inorg. Chem.* 1970, **11**, 99.
2. (a) T. J. Marks and J. R. Kolb, *Chem. Rev.* 1977, **77**, 263; (b) R. M. Adams and A. R. Sindle, *Boron, Met–Boron Compounds and Boranes*. Interscience, New York (1964); (c) J. J. Katz and E. Rabinowitch, *The Chemistry of Uranium*. McGraw-Hill Book Co, New York (1951).
3. R. W. F. Gross, *Opt. Engng* 1974, **13**, 506.
4. Battelle-Institute eV, French Patent, 1972, **2119**, 214.
5. H. I. Schlesinger and H. C. Brown, *J. Am. Chem. Soc.* 1953, **75**, 219.
6. T. A. Keiderling, PhD Dissertation, Princeton University (1973).
7. (a) V. B. Kartha and V. N. P. Kaimal, *Ind. J. Phys.* 1976, **50**, 147; (b) K. Rajnak, E. Gamp, R. Banks, R. Shinomoto and N. Edelstein, *Inorg. Chim. Acta* 1984, **95**, 29.
8. R. Engleman, *Spectrosc. Lett.* 1974, **7**, 547.
9. R. T. Paine, P. R. Schonberg, R. W. Light, W. C. Danen and S. M. Freund, *J. Inorg. Nucl. Chem.* 1979, **41**, 1577.
10. N. Ghiassee, P. G. Clay and G. N. Walton, *Inorg. Nucl. Chem. Lett.* 1980, **16**, 149.
11. R. T. Paine, R. W. Light and M. Nelson, *Spectrochim. Acta* 1979, **35A**, 217.
12. B. D. James, B. E. Smith and M. G. H. Wallbridge, *J. Molec. Struct.* 1972, **14**, 327.
13. P. B. Armentrout and J. L. Beauchamp, *Inorg. Chem.* 1979, **18**, 1349.
14. J. C. Veselsky and A. Wolff, *Analyt. Chim. Acta* 1976, **85**, 135.
15. M. R. Hayes and J. Metcalfe, *Analyst* 1962, **87**, 956.
16. E. R. Bernstein, W. C. Hamilton, T. A. Kaiderling, S. J. LaPlaca, S. J. Lippard and J. J. Mayerle, *Inorg. Chem.* 1972, **11**, 3009.
17. E. R. Bernstein and T. A. Kaiderling, *J. Chem. Phys.* 1973, **59**, 2105.