

It has previously been shown in our laboratory that photodecomposition in the solid state of  $\text{UO}_2(\text{HCCO})_2$ ,  $\text{H}_2\text{O}$  yields uranium IV and  $\text{CO}_2$  and  $\text{H}_2\text{O}$  as gaseous products [1]. The aim of the present communication is to report on the results gained with monochromatic light ( $\lambda = 366 \text{ nm}$ ) on the transformation from  $\text{U}^{\text{VI}}$  to  $\text{U}^{\text{IV}}$  in the solid state.

The used set-up allows the simultaneous measurement of the reflectance of the sample surface and of the photoluminescence intensity during reaction. The incident intensity is determined by actinometry, so that the intensity absorbed by the sample is known by dissolution of the sample into phosphoric acid and absorption spectrophotometry. The intermediate  $\text{U}^{\text{V}}$  can be detected and titrated by polarography in perchloric medium, according to an already described technique [2]. This intermediate, formed in the solid, is relatively stable at room temperature, but completely vanishes at 363 K, in yielding the same number of moles of  $\text{U}^{\text{IV}}$ . The curves giving the numbers of moles of  $\text{U}^{\text{V}}$  and  $\text{U}^{\text{IV}}$  formed during irradiation at 298 K as functions of the number of absorbed einsteins will be presented. The initial quantum yield of uranium V formation is at least equal to 0.83, that of uranium IV formation is nil, to the accuracy of its determination. Besides, the photoluminescence quantum yield is negligible ( $4 \times 10^{-4}$  at 298 K). Thus, the photoexcitation of  $\text{UO}_2^{2+}$  in the first electronically excited state [3] is followed by a chemical quenching step leading to  $\text{U}^{\text{V}}$ .

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#### X10

#### Photochemistry of Borazine and Other Boron Compounds\*

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For several years [1] our research group has been investigating the photochemistry

of boron compounds with special interest in cyclic borazines and borolanes. In this lecture we will present a brief survey of the photochemistry of borazine, sometimes referred to as "inorganic benzene", some recent work on the N-methylborazines and conclude with a discussion of matrix isolation studies of some photochemical intermediates.

Photolysis of borazine in the gas phase with 1849 Å radiation yields  $\text{H}_2$ , diborazinyl and borazanaphthalene. Quantum yield studies and chemical evidence indicate that borazyne ( $\text{B}_3\text{N}_3\text{H}_4$ ) is a probable intermediate in these reactions [2]. A number of B-monosubstituted amino, alkoxy, and haloborazines have been synthesised by photochemical reactions of borazine with primary amines, alcohols and alkylhalides, respectively (several references given in ref. 3). In an attempt to probe substituent effects on the borazine ring we have investigated the photochemical behavior of the N-methylborazines in the presence of ammonia, methanol or dimethylamine [3]. The relative quantities of ortho/para isomers in the B-substituted products were determined by N.M.R. In the presence of photochemically generated H atoms, N-trimethylborazine reacts by a radical mechanism to form 1,2-di(3', 5'-dimethylborazinyl) ethane.

Matrix-isolated intermediates [4] in the vacuum U.V. photolysis of cyclic  $\text{H}_2\text{B}_2\text{O}_3$  include molecular  $\text{B}_2\text{O}_3$ , HBO and a H-bonded species believed to be a dimer of HBO<sub>2</sub>. Photolysis of borane-amine ( $\text{BH}_3\text{NH}_3$ ) in the vapor phase yields molecular HBNH and HBN. An unidentified intermediate isolated in the photolysis of borazine with 1215 Å radiation contains H-N and B=N bonds.

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