

TABLE 1

Ionic photodissociation of n- π type CT complexes*

Acceptor	Donor**	Mechanism	Character of S ₁	Character of T ₁
TCNB } PMDA }	MTHF	S ₁ (+ T _n)***	CT	LE
TCPA	MTHF	T _n [Two-photon]	LE	LE
TCNB } PMDA } TCPA }	Ether (EP)	T _n [Two-photon]	LE	LE

* At 77 °K.

** Solvent.

*** Minor contributions from the T_n.

Some results obtained here from the photo-irradiation experiments are summarized in Table 1, suggesting an interesting rule that when the S₁ state is of CT character the singlet-state ionic photodissociation largely occurs, whereas when the S₁ state is of LE character the anion formation is attributed to the biphotonic process via the T₁ state.

Furthermore, the PMDA-THF complex was excited in the CT band by laser 347-nm pulse at room temperature, three kinds of solvents (THF, 1:2 THF-ether and 1:2 THF-acetonitrile) being used. In each case, the ionic dissociation was found to occur *via* both the singlet and triplet states.

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Physical and Chemical Quenching of the Excited Uranyl Ion

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Physical and chemical quenching of the excited UO₂²⁺ ion have been monitored in aqueous acidic media by directly observing the decay of the excited state absorption of UO₂²⁺ at 590 nm using ns laser flash photolysis ($\lambda_{\text{excitation}} = 347 \text{ nm}$).

(UO₂²⁺)* is quenched by

(i) Temperature (over the range 275 - 355 K, $t_{1/2}$ falls from 2 μs to 100 ns).

(ii) UO₂²⁺ (*i.e.* self-quenching).

(iii) Alkyl halides (I > Br > Cl > F). The quenching constants approach the diffusion-control figure for I, but the effect is not one of perturbation by spin-orbit coupling, for Xe exerts no quenching whatsoever. Electron-transfer is regarded as the main contributor.

(iv) Alkenes. The mechanism here, which parallels that of alkene quenching of benzene fluorescence, is thought to be due to exciplex formation.

(v) Carboxylic acids. Effects of substitution are quite subtle here — a 2-alkoxy group increased the quenching rate by a factor of 10². Aromatic acids quench very effectively, the substituent effects here following a good Hammett plot.

(vi) Ethers. Unexpectedly, these prove to be considerably more potent chemical quenchers than analogous alcohols.

Possible mechanisms of the quenching processes are discussed in the light of our finding that (UO₂²⁺)* is subject to almost as universal quenching as the excited Hg atom.

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Photodecomposition in the Solid State of Uranyl Formate Monohydrate

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It has previously been shown in our laboratory that photodecomposition in the solid state of $\text{UO}_2(\text{HCCO})_2$, H_2O yields uranium IV and CO_2 and H_2O 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 U^{VI} to U^{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 U^{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 U^{IV} . The curves giving the numbers of moles of U^{V} and U^{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 (4×10^{-4} at 298 K). Thus, the photoexcitation of UO_2^{2+} in the first electronically excited state [3] is followed by a chemical quenching step leading to U^{V} .

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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 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 B_2O_3 , HBO and a H-bonded species believed to be a dimer of HBO_2 . Photolysis of borane-amine (BH_3NH_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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