

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.

- 1 Y. Achiba and K. Kimura, *Chem. Phys. Letters*, 19 (1973) 45.
- 2 K. Kimura and Y. Achiba, *J. Phys. Chem.*, 77 (1973) 2520.

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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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