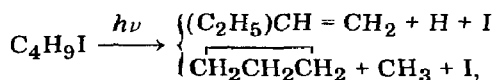


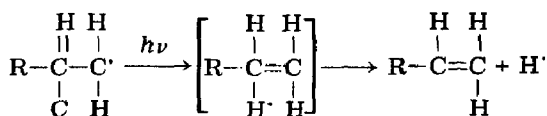
Fig. 1. ESR spectrum of the products of the photolysis of *n*-butyl iodide at 2460 Å in Ar at 4 °K. (a) 15 minutes photolysis; (b) 30 minutes photolysis.

but not the direct photolysis mechanism



in which the concentrations of all products should increase linearly with photolysis time.

It is suggested that the secondary photolysis of alkyl radicals involves the photoexcitation



where the dot denotes the unpaired electron. An empirical molecular orbital calculation involving the bonding orbitals of one of the β -CH bonds and the unpaired electron orbital indicates that this transition has a sizeable oscillator strength and a lower transition energy than is required for photoexcitation of the corresponding saturated hydrocarbon $\text{R}-\text{CH}_2-\text{CH}_3$.

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Ionic Photodissociation of Charge Transfer Complexes

Solute-Solvent Charge-Transfer Complexes

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Tetracyanobenzene (TCNB), pyromellitic dianhydride (PMDA) and tetrachlorophthalic anhydride (TCPA) are typical electron acceptors, forming weak charge-transfer (CT) complexes with donor etherial solvents such as ether, THF and dioxane. Photo-irradiation of these acceptors in the donor solvents give rise to the radical anions of the acceptors. [1, 2] In order to study the mechanism of such photo-induced anion formation, we carried out uv-irradiation with these acceptors in 77 °K glasses of EP (ether and isopentane, 1:1) and MTHF (2-methyltetrahydrofuran).

The formation of the ground-state CT complexes was confirmed by examining spectral changes in absorption band, indicating absorption tails in the longer-wavelength side of the local-excitation (LE) bands of the acceptors or indicating some isosbestic points in the region of the acceptor bands. The CT complex formation was also confirmed by fluorescence measurements.

Using piperylene as a triplet quencher, we studied the process in which the ionic dissociation takes place. The following results were obtained. (1) In MTHF glass, the TCNB and PMDA anions are produced mostly from the lowest excited singlet states (S_1) of the complexes. (2) In EP glass, the anions are formed *via* the lowest excited triplet states (T_1). (3) Fluorescences from the MTHF glasses are much weaker than those from the EP glasses.

Since the T_1 states of the complexes studied here are of the LE character, the ionic dissociation should occur in higher triplet states (T_n) having CT characters. In order to clarify this, we studied the dependences of exciting light intensity on the rate of the anion formation, using a cross illumination technique. We found that the formation of TCNB^- and PMDA^- in EP glass occurs biphotonically *via* the T_1 state. Such biphotonic dissociation of CT complexes has not been reported so far.

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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