*versus* molecular elimination processes [1, 3], as well as providing valuable information concerning photophysical processes, *i.e.* intersystem crossing (ISC) and internal conversion (IC).

The vacuum-ultraviolet (VUV) photochemistry of the various isomeric difluoroethylenes and fluoroethylene has been performed in Ar, N_2, Kr, CO, and CO-doped argon matrices between 8 and 24 K. Selective excitation at various frequencies of the broad $\pi^* \leftarrow \pi$ absorptions was performed with N and Br resonance line sources and $\sigma^* \leftarrow \sigma$ and/or Rydberg absorptions were excited with the 1216 Å H-resonance line.

As major processes, all three difluoroethylenes photodissociate into HF and fluoroacetylene,

$$C_2H_2F_2 + h\nu \rightarrow C_2HF + HF \qquad (1)$$
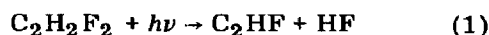
via molecular elimination, and all give rise to the same difluorovinyl free radical,

$$C_2H_2F_2 + h\nu \rightarrow C_2HF_2 + H \qquad (2)$$
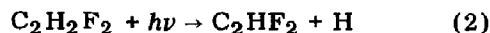
presumably via atomic detachment. No acetylene or difluoroacetylene was observed. Isomerization of the three difluoroacetylenes into each other was observed as minor processes. The results of experiments conducted in CO matrices, wherein almost total quenching of the atomic detachment process and normal occurrence of molecular elimination were observed, strongly suggest that the former occurs via intersystem crossing (ISC) and the latter via internal conversion (IC).

In the case of fluoroethylene, the major elementary processes which occur as a result of photoexcitation are:

$$H_2C=CHF + h\nu \rightarrow C_2H_2 + HF \qquad (3)$$

and
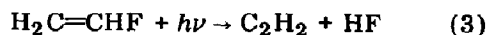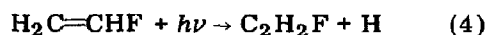
$$H_2C=CHF + h\nu \rightarrow C_2H_2F + H \qquad (4)$$

where again (3) is molecular elimination and (4) a radical producing process. Photoexication with the Br and H resonance sources also produces fluoroacetylene via $H_2C=CHF + h\nu \rightarrow C_2HF + (HH) \qquad (5)$ to a very small extent. Based on relative infrared intensities (3) $\cong$ (4) $\geqslant$ (5) at all the exciting frequencies. The results of the concurrent studies involving the difluoroethylenes suggest that (3) and (4) probably occur via internal conversion and intersystem crossing, respectively.

1 S. G. Thomas and W. A. Guillory, J. Phys. Chem., 77 (1973) 2469.
2 S. G. Thomas and W. A. Guillory, J. Phys. Chem., 78 (1974) 1461.
3 W. A. Guillory and G. H. Andrews, J. Chem. Phys., in press.
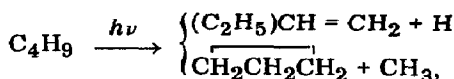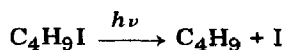4 S. G. Thomas and W. A. Guillory, J. Phys. Chem., 79 (1975).

W10
Wavelength Dependence of Alkyl Iodide Photolysis: Secondary Photolysis of Alkyl Radicals

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The products of the photolysis of alkyl iodides in rare gas matrices at liquid helium temperature, as revealed by electron spin resonance (ESR) spectroscopy, are often too numerous to be explained by simple dissociation of the carbon–iodine bond. The most frequently observed additional products are H atoms and CH_3 radicals. Studies of alkyl iodide photolysis as a function of photon energy have shown that for $\gamma > 2800$ A only the C–I bond dissociation product is observed, but for $\gamma < 2500$ A H atoms and CH_3 radicals are also formed.

The results for the photolysis of n-butyl iodide at 2460 A including the relative growth of the various products as a function of photolysis time are shown in Fig. 1. The n-butyl signal increases linearly and the H atom signal increases quadratically with photolysis time. The weak sharp-line CH_3 spectrum, which is superimposed on the four central lines of the n-butyl spectrum also increases supralinearly with photolysis time. These results are consistent with the photolysis mechanism involving secondary photolysis of n-butyl, as shown below,
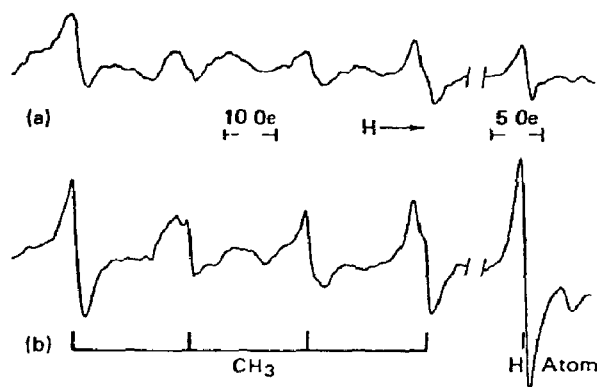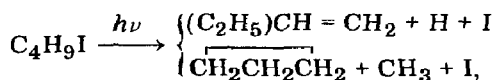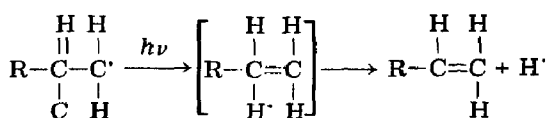
$$C_4H_9I \xrightarrow{h\nu} C_4H_9 + I$$

$$C_4H_9 \xrightarrow{h\nu} \begin{cases} (C_2H_5)CH=CH_2 + H \\ \overline{CH_2CH_2CH_2} + CH_3, \end{cases}$$

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

$$C_4H_9I \xrightarrow{h\nu} \begin{cases} (C_2H_5)CH = CH_2 + H + I \\ \overline{CH_2CH_2CH_2} + CH_3 + I, \end{cases}$$

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

$$\begin{array}{c} H \;\; H \\ \| \;\; | \\ R{-}C{-}C{\cdot} \\ |\;\; | \\ C \;\; H \end{array} \xrightarrow{h\nu} \left[\begin{array}{c} H \;\; H \\ |\;\; | \\ R{-}C{=}C \\ |\;\; | \\ H{\cdot}\; H \end{array} \right] \longrightarrow \begin{array}{c} H \;\; H \\ |\;\; | \\ R{-}C{=}C + H{\cdot} \\ | \\ H \end{array}$$

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 R–CH_2–CH_3.

W11
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 photoinduced 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.