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FLASH PHOTOLYSIS OF A PYRIDINIUM IODIDE THROUGH THE CHARGE-TRANSFER BAND

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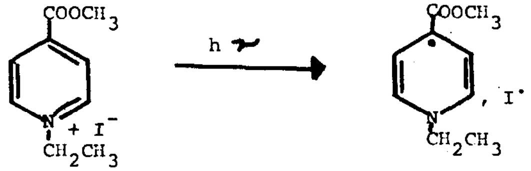
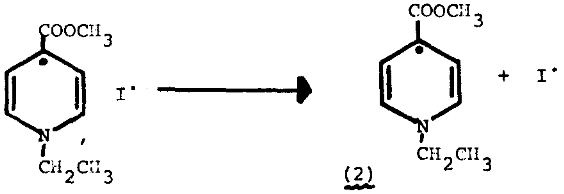
Flash photolysis of 1-ethyl-4-carbomethoxypyridinium iodide (1) offers an excellent opportunity for the study of the chemical consequences of photoexcitation because the spectra of the expected initial products have been reported previously. (1,2) The primary photoreaction is Py$^+$ I$^-$ → Py$^\cdot$I$^\cdot$ (eq. 1) which might be followed by dissociation (eq. 2) if charge-transfer is complete.

(1)



(1)

(2)



(2)

Iodine atoms in a number of solvents have been examined by Strong and coworkers (3,4) and 1-ethyl-4-carbomethoxypyridinyl (2) has been isolated in pure form.(5) We have found that the radical 2 is formed after a flash; however, the iodide 1 is rapidly regenerated, accounting for the observed stability of the salt to light.

Solutions of 1 (1-15μM) in benzene (Eastman Spectro Grade) were carefully degassed (saturation with argon was effected after each freezing) and flashed in a 20cm fused silica cell using a sodium nitrile filter (cutoff 4000 A). A flash unit with a maximum energy of 3750 joules and a flash duration of 4μsec. was used. The transmission of a xenon lamp through a pyrex filter and through the solution was monitored with a system similar to that already described by Lindqvist.(6).

Immediately after the flash a strong absorption band (λ_{max} ca. 3980 A) is observed (Fig. 1) identified as the pyridinyl radical 2 (λ_{max} 3950A, ε_{max} 4700 $M^{-1}cm.^{-1}$ in acetonitrile). (5) The radical concentration is estimated from this absorption coefficient, corresponding to ca. 20% photodissociation at 1000 joules. Iodine atoms in benzene absorb weakly in the visible, with a broad maximum at 5000 A. (4) In this wavelength region, 1 also has a weak absorption maximum (the charge-transfer band).[a] The absorption increase due to iodine atoms matches the decrease due to depletion of pyridinium iodide (Fig. 1).

The transient absorption band disappeared in a two-step process as shown in the oscillogram (Fig. 2). Results from runs at different concentrations and different degrees of excitation showed that both steps were second-order. Since 2 was the only species present with strong absorption at 3980 A (iodine atom absorption was weak) (4), the fast decay step corresponded to con-

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[a] This charge-transfer band has not been previously found, probably because of the low rate of solution and low solubility of the iodide 1 in benzene. These solutions will be the subject of a separate study.

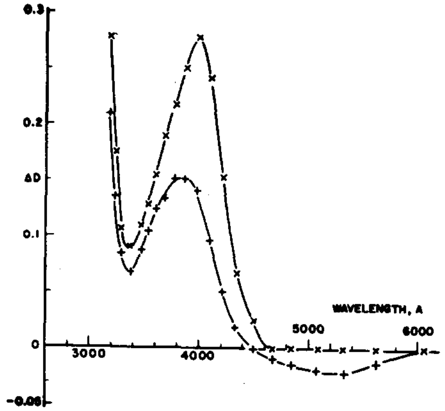


FIG. 1

Transient change in optical density (Δ D) following flash excitation (1000 joules) of a 15 μM solution of pyridinium iodide 1 in degassed benzene, optical path 20 cm. -x-x- immediately after the flash; - + - + - 0.5 msec. after the flash, i.e., after the fast decay step.

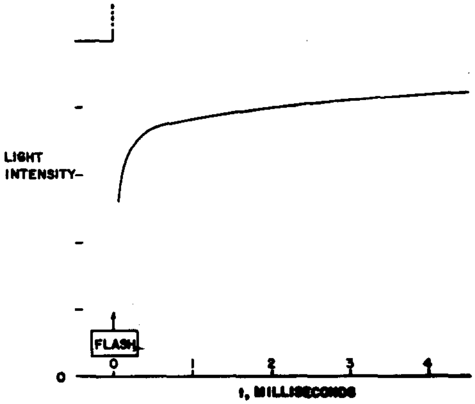
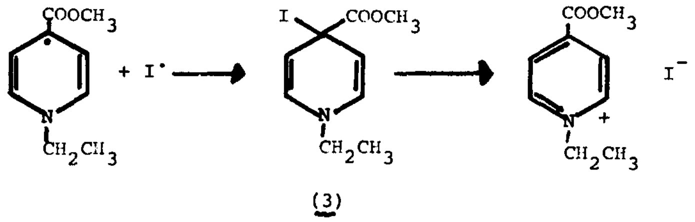


FIG. 2

Oscillogram showing the change in light transmission through a 15 μM solution of pyridinium iodide 1 in degassed benzene, measured as a function of time after flash excitation at 3980 A.

sumption of radical 2, with recombination (eq. 3) as the only

(3)

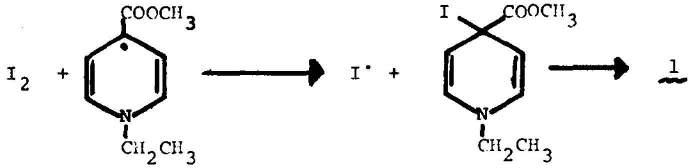


reasonable possibility. (The adduct 3 was written as an intermediate on the basis of studies of the effect of solvent on the rates of reaction of pyridinyl radical 2 with halocarbons.) (8) The abrupt change in the rate of disappearance of 2 (Fig. 2) was explained by the intervention of iodine atom recombination, a very efficient process, (3,4) (eq. 4).

$$(4) \qquad I^\cdot + I^\cdot \rightarrow I_2$$

The slow disappearance step was thus a reaction between radical 2 and molecular iodine. (eq. 5). The transient absorption re-

(5)



maining after the fast decay process (Fig. 1) was consistent with the proposed mechanism, since molecular iodine in benzene (λ_{max} ca. 2900 ε_{max} ca. 15,000 (9)) should diminish markedly the apparent loss in 2 near 3200 Å and cause an increase in transmission near 5000 Å due to weaker absorption by the molecule as compared with iodine atom.

Reactions (3) and (4) had rate constants of about 10^9 - 10^{10} $M^{-1}sec.^{-1}$ and reaction (5) had a rate constant of 10^7 - 10^8 $M^{-1}sec.^{-1}$. Repeated flashes caused a slight loss in pyridinium iodide, possibly due to light absorption by the primary products.

At higher concentrations of **1**, oxygen does not influence the observed reactions. At low concentrations, the presence of oxygen leads to a substantial loss of **1** after flashing. One may thus infer a rate constant for the reaction of oxygen with the radical **2** of $10^6 - 10^7$ M^{-1}Sec.$^{-1}$. Previous work (5) had shown only that the oxygen-radical reaction was rapid.

Flash photolysis studies of pyridinium iodides yield a direct demonstration of the validity of charge-transfer absorption theory (10,11), show that absorption in the charge-transfer band may be important photochemically and illustrate the complexity of apparently straightforword photoexcitation processes.

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