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On the Photochemical Behaviour of 1-Methyl-4-Ethoxycarbonylpyridinium Iodide

Short Communication

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The effect of ultraviolet light on a methanol-water solution of 1-methyl-4-ethoxycarbonylpyridinium iodide has been studied. It has been established that the 225 nm irradiation of air-saturated solution initiates the formation of species which absorb at 358 nm. The 280 nm irradiation of a solution containing newly formed particles causes a reverse process of a gradual diminuation of the concentration of the complex formed.

(Keywords: 1-Methyl-4-ethoxycarbonylpyridinium iodide; Reversible photochemistry)

Über das photochemische Verhalten von 1-Methyl-4-ethoxycarbonylpyridiniumjodid (Kurze Mitteilung)

Die Wirkung des Ultraviolettlichtes auf eine methanolisch-wäßrige Lösung von 1-Methyl-4-ethoxycarbonylpyridiniumjodid wurde studiert. Es wurde festgestellt, daß die Belichtung der luftgesättigten Lösung bei 225 nm eine Bildung von Spezies, die bei 358 nm absorbieren, hervorruft. Die Belichtung einer Lösung, die die neugebildeten Partikel enthält, verursacht bei 280 nm einen Rückgang bzw. eine allmähliche Abnahme der Konzentration des gebildeten Komplexes.

Until recently no information concerning the effect of ultraviolet light on alkylpyridinium iodides was available. This communication deals with the preliminary results found in the course of the study of the excited state properties of 1-Methyl-4-ethoxycarbonylpyridinium iodide (*MEPI*). Its UV spectrum is shown in Fig. 1.

The various aspects of the reversible photochemical behaviour of *MEPI* visualised in the respective changes of its UV spectrum are presented in Fig. 2.

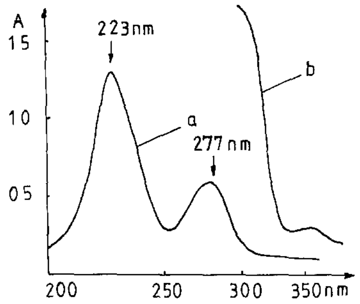

Fig. 1. UV spectrum of *MEPI* in 80% methanol (ca. $1 \cdot 10^{-3} Ml^{-1}$); curve a: $l = 0.1$ cm; curve b: $l = 2.0$ cm

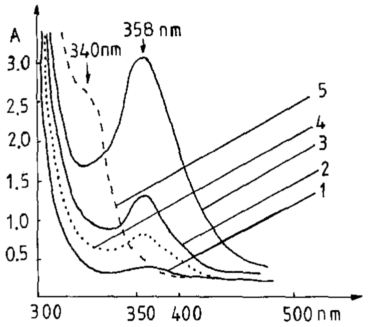

Fig. 2. UV spectra of *MEPI* in 80% methanol (ca. $1 \cdot 10^{-3} Ml^{-1}$); light intensity: $0.59 \cdot 10^{16}$ quanta/cm^3 s; curve 1: before the 225 nm irradiation; curve 2: 10 min 225 nm irradiation in the presence of oxygen in the irradiated solution; curve 3: 96 hours after the end of 225 nm irradiation; curve 4: 120 min 280 nm irradiation of a sample under atmosphere of purified argon; curve 5: 60 min 225 nm irradiation of a sample under atmosphere of purified argon

The 225 nm ultraviolet light irradiation of air-saturated methanol-water solution of *MEPI* leads to the formation of species, which absorb at 358 nm (Fig. 2, curve 2). However, the presence of traces of oxygen in the solution is practically sufficient for the start of the phototransformation. It was proved that the intensity of the absorption band at 358 nm increases after the end of the irradiation (curve 3) with a rate which is proportional to the duration of the irradiation. In fact the 225 nm irradiation initiates a dark process leading to further increases of the concentration of the newly formed particles. Conversely, the 280 nm irradiation of the pale yellow solution (its spectrum is presented by curve 3) results in a diminuation of the concentration (curve 4). An analogous effect was found when the temperature of the solution was raised from 20° to 50 °C.

In an atmosphere of purified argon the irradiation with 225 nm ultraviolet light causes a different effect manifested by an appearance of absorption at 340 nm (curve 5).

Iodide ion in water has two absorption bands in the accessible ultraviolet region at 225.9 and 193 nm [1–3]. Consequently, one can conclude that the intensive band at 223 nm in the UV spectrum of *MEPI* (Fig. 1, curve a) is due to the absorption of the iodide ion. It is obvious that the photochemistry of 1-methyl-4-ethoxycarbonylpyridinium iodide ensues from the photoexcitation of the iodide ion component of the molecule. According to the literature [4] the light absorption by iodide ion leads to an excited state containing an iodine atom. The inference is that absorption is equivalent to photoionization. The act of the light absorption is pictured as transfer of an electron from the p-orbital of iodide ion to a solvent molecule. The *Franck-Platzman* theory [5] of the potential well formed by oriented molecules serves as an adequate description of the location of the electron after the excitation:

$$I^- \xrightarrow{h\nu} I^{\cdot} + e_{(solv)}$$

In the case of pyridinium iodide salts the charge transfer from the iodide ion is believed to be directed to the pyridinium ring [6]:

$$RPy^+I^- \xrightarrow{h\nu} RPy^{\cdot}I^{\cdot}$$

The arising electron absorption band is located in the 330–440 nm region. In nonpolar solvents a second CT-band at shorter wavelength than the first one is observed and has been ascribed to the first excited state of the iodine atom ($^2P_{1/2}$) [7]. Some experimental results indicate that the second band may result from charge transfer to the second vacant molecular orbital of the pyridinium ion [8, 9].

The basic assumption in these considerations undoubtedly is the photoinduced formation of iodine atoms as a result of an electron transfer to the solvent molecule or to the pyridinium ion. This prompted us to check the concentration of the iodide ion. The potentiometric assay of the solutions was carried out by iodide selective electrode technique and indicated that there is no change of the actual concentration of the iodide ion during the irradiation (up to 3 hours) and in the time after the end of ultraviolet irradiation. The implication is strong that for our experimental conditions the appearance of the new absorption band at 358 nm is not related to the formation of iodine atoms and triiodide ions which absorb in the 350–360 nm spectral region.

It is as yet difficult to rationalize the effect of UV light on *MEPI*. The available experimental data do not allow to explain the intrinsic mechanism of the process involved. A special attention has to be paid to the role of oxygen as well as to the nature of the reverse process, caused by the 280 nm irradiation. However, the results reveal that, depending on the presence or absence of oxygen, the 225 nm light causes the formation of two different type of particles—absorbing at 358 and 340 nm respectively. It is instructive to note that the position of the last absorption band is nearly the same as this reported by *Kosower* [6] and attributed to the charge-transfer complex of 1-ethyl-4-methoxycarbonylpyridinium iodide.

The most striking feature of the photochemical properties of *MEPI* is the existence of a dark process resulting in increase of the concentration of the species which absorb at 358 nm.

The study of the kinetics of the photoinitiated transformations of *MEPI*, its emission properties as well as the thermodynamic characteristics of the complex formed is in progress.

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