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On the Reduction of *N*-Alkoxypyridinium Ions

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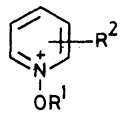
The reduction of 1-ethoxy-2-methylpyridinium (EMP^+) ions in aqueous solution at room temperature by e_{aq}^- and $\cdot CO_2^-$ was investigated in a pulse radiolysis study (irradiation with 10 ns pulses of 45 MeV electrons). For comparison, experiments with 1-methylpyridinium (MP^+) and unsubstituted pyridinium (PH^+) ions were carried out. With MP^+ and PH^+ the spectra of pyridinyl radicals were observed at the end of the pulse. In the case of EMP^+ the spectrum of the pyridinyl radical was not detectable. However, a new absorption band at 340 nm was formed with a significant delay after the reduction. Therefore, it was concluded that pyridinyl radicals formed by reduction of EMP^+ decompose very quickly into picoline and ethoxyl radicals. The latter add to EMP^+ with a rate constant $k=6\times10^7$ dm^3 mol^{-1} s^{-1}. The transient absorption band at 340 nm is ascribed to the adduct.

Recently, it was reported[1] that certain *N*-alkoxypyridinium salts of the general structure



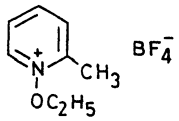
are quite appropriate to act as photoinitiators in free radical polymerizations of compounds possessing ethylenic double bonds. Since these pyridinium salts do not absorb light at $\lambda>300$ nm their utilization as photoinitiators in technical processes is possible only in conjunction with sensitizers. In Ref. 1 amino-substituted 3-ketocoumarins that absorb light at $\lambda>300$ nm were described as highly effective sensitizers. Although the mechanism of the interaction of excited sensitizers with pyridinium ions has not yet been disclosed, it appears probable that pyridinium ions are reduced by electron transfer according to the following mechanism:

$$S \longrightarrow S^* \quad (1)$$

$$S^* + Pyr^+ \longrightarrow S^{\ddagger} + Pyr\cdot \quad (2)$$

Here, the following denotations are used:
S: sensitizer, S*: electronically excited sensitizer, $S^{\ddagger}$: sensitizer radical cation, Pyr^+: pyridinium ion, Pyr·: pyridinyl radical.

With respect to the initiation of free radical polymerization the question arises as to whether the pyridinyl radicals formed according to Reaction 2 are capable of reacting effectively with the monomer or Reaction 2 is followed by a rapid decomposition of the pyridinyl radicals yielding highly reactive species. In order to elucidate the reaction mechanism, the reduction of a typical *N*-alkoxypyridinium salt, namely 1-ethoxy-2-methylpyridinium tetrafluoroborate (EMP^+ BF_4^-) and of related compounds have been studied by means of pulse radiolysis. In this connection earlier work devoted to pyridinyl radicals is notable.[2-8] It was found, for instance, that the absorption spectra of pyridinyl radicals are characterized by rather strong maxima around 280 nm.



(EMP^+)

Experimental

Materials. 1-Ethoxy-2-methylpyridinium tetrafluoroborate (EMP^+ BF_4^-) was prepared according to a procedure described by Reichardt.[9] 1-Methylpyridinium tetrafluoroborate (MP^+ BF_4^-) was synthesized in the laboratory of Prof. H. Shirahama, Hokkaido University, and pyridinium chloride (PH^+ Cl^-) was a commercially available product (Wako Junyaku).

Irradiation of Sample Solutions. The pyridinium salts were dissolved in triply distilled water and irradiated in rectangular quartz cells with 10 ns pulses of 45 MeV electrons generated by a linear accelerator. As required samples were bubbled with argon or N_2O prior to irradiation. The absorbed dose was determined with the aid of the potassium thiocyanate dosimeter. Absorbed doses ranging from 20 to 130 Gy were applied to the solutions.

Results

(a) Experiments with 1-Ethoxy-2-methylpyridinium Tetrafluoroborate ($EMP^+BF_4^-$). (a-1) Reactions of Hydrated Electrons with EMP^+ Ions. The rate constant of the reaction of EMP^+ ions with hydrated electrons was measured by recording the decay of the optical absorption at 700 nm as a function of time after the pulse. Upon application of pseudo-first-order kinetic treatment $k(e_{aq}^- + EMP^+)=4.2\times10^{10}$ dm^3 mol^{-1} s^{-1} was obtained indicating that EMP^+ ions are reduced in a diffusion controlled reaction by hydrated electrons. In these experiments Ar-saturated aqueous solutions containing t-butyl alcohol (0.1 mol dm^{-3}) were used. The absorbed dose was 24 Gy. The decay of the absorption of the hydrated electrons was not accompanied by the formation of the absorption of the reduction product.

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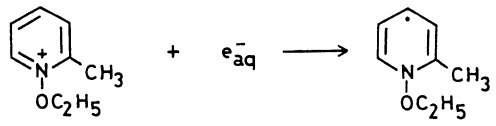
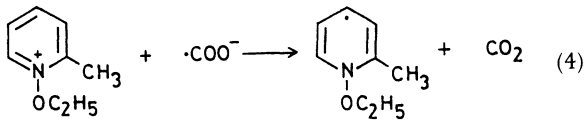
If pyridinyl radicals having a lifetime longer than the pulse length, were generated according to Reaction 3 a



(3)

transient absorption at $\lambda<300$ nm should be formed simultaneously with the decay of the absorption of hydrated electrons. As can be seen from Fig. 1 a new absorption band was formed, however, with a formation lifetime definitely longer than that of the decay of hydrated electrons. Inset (a) in Fig. 1 shows the decay of the absorption of hydrated electrons at $[EMP^+BF_4^-]=1.12\times10^{-3}$ mol dm^{-3} and inset (b) shows the increase in the absorption at 340 nm at $[EMP^+ BF_4^-]=1.12\times10^{-3}$, 3.37×10^{-3} and 8.92×10^{-3} mol dm^{-3}. Obviously, the build-up rate increased with increasing concentration of pyridinium ions. Application of pseudo-first-order kinetic treatment yielded a bimolecular rate constant $k_2=6\times10^7$ dm^3 mol^{-1} s^{-1}.

(a-2) Reactions of $\cdot CO_2^-$ with EMP^+ Ions. The reduction of EMP^+ ions was also accomplished according to Reaction 4 by formate radical anions which were generated by reaction of hydroxyl radicals with formate ions according to Reaction 5.



(4)

$$\cdot OH + HCOO^- \longrightarrow H_2O + \cdot COO^- \quad (5)$$

Upon irradiation of N_2O-saturated $EMP^+BF_4^-$ solutions containig 0.05 mol dm^{-3} sodium formate the optical absorption spectrum (a) in Fig. 2 was formed during the pulse. It possesses a rather strong absorption band with a peak below 280 nm. The decay rate of this absorption band was found to be accelerated by increasing the pyridinium salt concentration. Actually, a similar rather strong absorption was also observed in the absence of pyridinium salt. Therefore, it is concluded that the absorption around 280 nm is due to $\cdot CO_2^-$ radical anions which are capable of reacting with pyridinium ions. The absorption peak of $\cdot CO_2^-$ radical anions has been reported to be located at about 250 nm, in aqueous solution.[10] In the present work, the ground state absorption of EMP^+ was very strong at wavelength below about 275 nm, making the solution almost opaque. Therefore, measurements of changes in the optical density below 280 nm were impossible. The decay of the absorption around 280 nm was followed up by the build-up of a new absorption band with a maximum at about 340 nm (spectrum (c) in Fig. 2). The rate of the reduction of EMP^+ ions by $\cdot CO_2^-$ ions was not correlated to the formation of the new absorption band as is demonstrated by typical kinetic traces shown in Fig. 3(a). Notably, the product of the reaction of $\cdot CO_2^-$ with EMP^+ could not be evidenced spectroscopically. Therefore, the reduction product must be very short-lived. In this respect, these findings correspond to results obtained with the reaction of hydrated electrons with EMP^+ (vide ante). In that case, quite similarly, the rate of decay of hydrated electrons did not correspond to the rate of formation of the new absorption band peaked at 340 nm. From the dependence of the lifetime of the absorption at 280 nm on the pyridinium salt concentration $k(\cdot CO_2^- + EMP^+)=2.1\times10^8$ dm^3 mol^{-1} s^{-1} was obtained. The rate of formation of the transient absorbing at 340 nm increased with increasing pyridinium salt concentra-

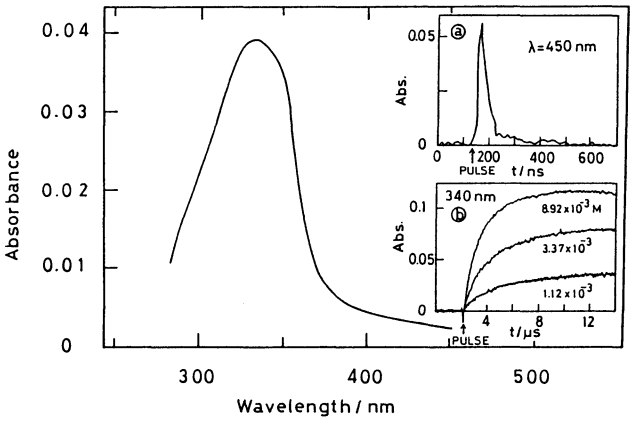


Fig. 1. Irradiation of $EMP^+BF_4^-$ (1.12×10^{-3} mol dm^{-3}) in Ar-saturated aqueous solution containing 0.1 mol dm^{-3} *t*-butyl alcohol with a 10 ns pulse of 45 MeV electrons. D_{abs}=140 Gy. Optical absorption spectrum recorded 20 μs after the pulse. Insets: kinetic traces illustrating the decay of the absorption at 450 nm due to hydrated electrons (a) and the formation of the transient absorption at 340 nm at various concentrations of $EMP^+BF_4^-$ as indicated in the graph (b). D_{abs}=110 Gy.

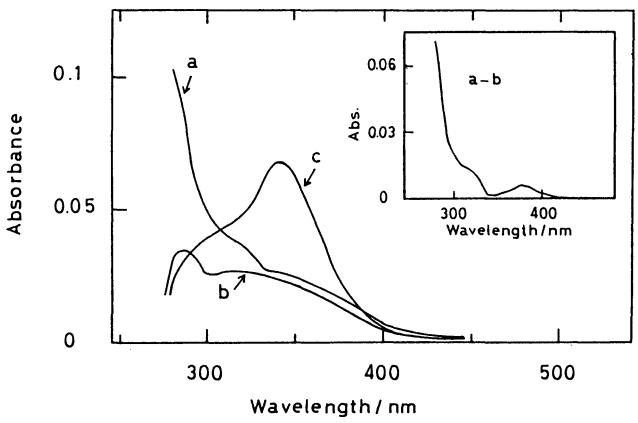


Fig. 2. Irradiation of $EMP^+BF_4^-$ (1.12×10^{-3} mol dm^{-3}) in N_2O-saturated aqueous solution containing 0.05 mol dm^{-3} sodium formate with a 10 ns pulse of 45 MeV electrons. D_{abs}=140 Gy. Optical absorption spectra recorded at the end of the pulse (a) and at 5 μs (b) and 80 μs (c) after the pulse. Inset: difference of spectra (a) and (b).

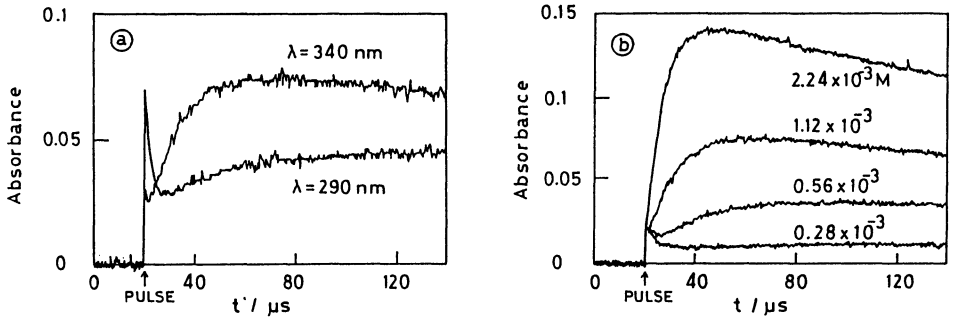


Fig. 3. Kinetic traces illustrating changes in the optical density after the pulse at λ=340 nm and 290 nm at [EMP$^+$BF$_4^-$]=1.12×10^{-3} mol dm^{-3} (a) and at 340 nm at various concentrations of EMP$^+$BF$_4^-$ as indicated in the graph (b). For other conditions refer to legend to Fig. 2.

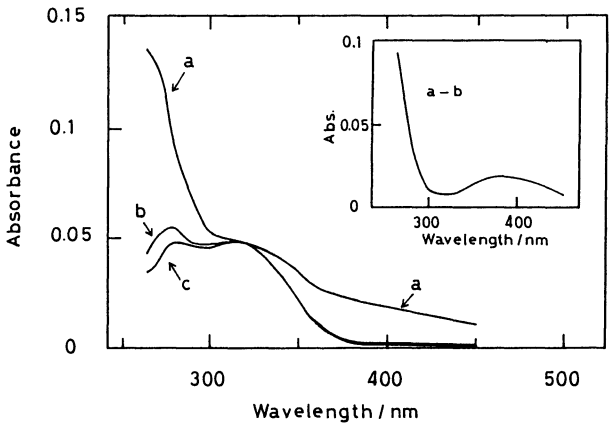


Fig. 4. Irradiation of MP$^+$BF$_4^-$ (1×10^{-3} mol dm^{-3}) in Ar-saturated aqueous solution containing *t*-butyl alcohol (0.1 mol dm^{-3}) with a 10 ns pulse of 45 MeV electrons. D_{abs}=140 Gy. Optical absorption spectra recorded at the end of the pulse (a) and 80 μs (b) and 160 μs (c) after the pulse. Inset: difference spectrum (a)—(b).

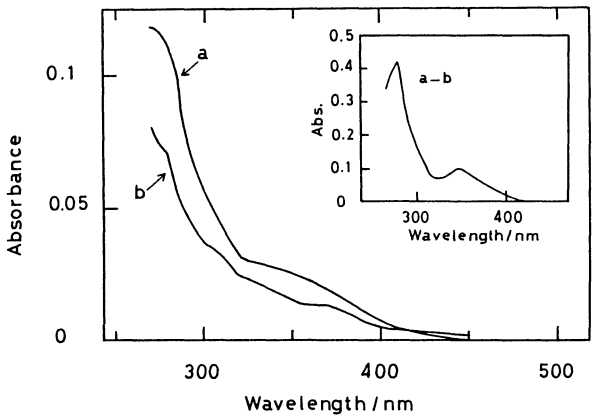


Fig. 5. Irradiation of PH$^+$Cl$^-$ (6.1×10^{-4} mol dm^{-3}) in N_2O-saturated aqueous solution containing sodium formate (0.025 mol dm^{-3}) with a 10 ns pulse of 45 MeV electrons. D_{abs}=160 Gy. Optical absorption spectra recorded 500 ns (a) and 8 μs (b) after the pulse. Inset: difference spectrum (a)—(b).

tion yielding a bimolecular rate constant k_2=8.2×10^7 dm^3 mol^{-1} s^{-1}.

(b) Experiments with 1-Methylpyridinium Tetrafluoroborate (MP$^+$BF$_4^-$). Upon reaction of hydrated electrons with MP$^+$ ions, i.e. upon irradiation of an Ar-saturated MP$^+$BF$_4^-$ solution containing *t*-butyl alcohol (0.1 mol dm^{-3}) the transient spectrum (a) in Fig. 4 was obtained. It possesses a strong absorption band with a maximum at λ<280 nm, which could not be disclosed due to the strong absorption of the 1-methylpyridinium salt in this wavelength range, and a weak band peaked at about 310 nm. The low wavelength portion of this spectrum decayed with a rate constant k=4×10^4 s^{-1} leaving a long lasting spectrum with a broad maximum around 300 nm. Quite similar results were obtained with a N_2O-saturated solution containing sodium formate (0.05 mol dm^{-3}), i.e. in the case of the reaction of $\cdot CO_2^-$ with MP$^+$. Therefore, it is concluded that both hydrated electrons and $\cdot CO_2^-$ radical anions reduce MP$^+$ ions forming pyridinyl radicals. The rate of decay of hydrated electrons correlated with the rate of formation of the transient spectrum which is, therefore, assigned to the pyridinyl radical.

(c) Experiments with Pyridinium Chloride (PH$^+$Cl$^-$). Figure 5 shows a transient absorption spectrum (a) formed upon the reaction of $\cdot CO_2^-$ with PH$^+$, i.e. upon irradiation of a N_2O-saturated solution of PH$^+$Cl$^-$ containing sodium formate (0.025 mol dm^{-3}). This spectrum possesses a maximum at about 270 nm. A quite similar spectrum was observed when hydrated electrons reacted with PH$^+$, i.e. when an Ar-saturated solution containing *t*-butyl alcohol (0.1 mol dm^{-3}) was irradiated. Also in this case, the rate of decay of hydrated electrons correlated with the rate of formation of the transient absorption spectrum as can be seen from Fig. 6, where the decay of the absorption at 450 nm (due to hydrated electrons) and the build-up of the absorption at 265 nm is shown. The latter absorption is, therefore, assigned to the pyridinyl radical. It should pointed out that the transient absorption spec-

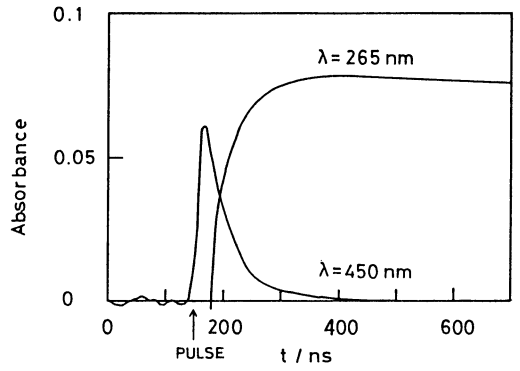
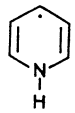


Fig. 6. Irradiation of PH^+Cl^- (8.15×10^{-4} mol dm^{-3}) in Ar-saturated aqueous solution containing *t*-butyl alcohol (0.1 mol dm^{-3}) with a 10 ns pulse of 45 MeV electrons. D_{abs}=140 Gy. Kinetic traces illustrating the decay of the optical absorption at 450 nm due to hydrated electrons and the formation of the optical absorption at 265 nm due to pyridinyl radicals.

trum observed here is quite similar to the spectrum of the pyridinyl radical reported by Cercek and Ebert.[4]

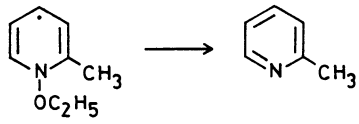
In conclusion, both $\cdot CO_2^-$ and e_{aq}^- were found to react with PH^+ forming the pyridinyl radical



which was detected by its characteristic absorption spectrum.

Discussion

The results show clearly, that, on reduction, the *N*-alkoxypyridinium ion EMP^+ exhibits a behavior quite different from that observed with *N*-methylpyridinium, MP^+, and pyridinium, PH^+. From the transient absorption spectra recorded after the pulse it is inferred that the latter two ions are converted to rather long-lived pyridinyl radicals upon reacting with hydrated electrons or $\cdot CO_2^-$ radical anions. In contrast, in the case of EMP^+ ions, the absorption of the corresponding pyridinyl radical was not observable, although EMP^+ reacts in a diffusion-controlled reaction with e_{aq}^-. From the fact that a new transient absorption band at 340 nm was formed a rather long time after the hydrated electron had reacted with EMP^+, it is concluded that the reduction product decomposes very rapidly, and that the resulting fragments are capable of reacting with EMP^+ ions. Upon studying the reduction of EMP^+ ions by $\cdot CO_2^-$ radical anions the same conclusion was arrived at. Also in this case pyridinyl radicals were not detectable spectroscopically, and the rate of decay of the radical anions did not correspond to the formation rate of a product absorbing at 340 nm. Consequently, it has to be assumed that the lifetime of the reduction product, the pyridinyl radical, is very short, probably shorter than one ns. The decomposition of the pyridinyl radicals leads to products which do not possess absorption bands in the wavelength range inspected (down to 260 nm) differing from that of EMP^+ or do not absorb at all at $\lambda>260$ nm. This conclusion is consistent with a decomposition mechanism according to Reaction 6, a process being comparable to dissociative electron capture processes occurring, e. g., with halogenated hydrocarbons:



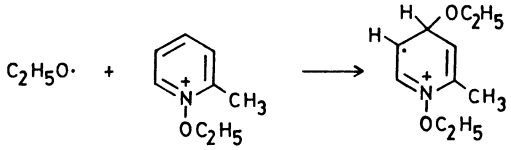
(6)

$$e^- + RCl \longrightarrow R\cdot + Cl^-$$

Ethoxyl radicals are not expected to absorb light markedly above 260 nm and the absorption spectrum of the other reaction product, 2-methylpyridine, is almost identical to that of EMP^+. According to this mechanism ethoxyl radicals are formed as reactive species capable of reacting, e.g., with olefinic compounds when *N*-alkoxypyridinium compounds are used as photoinitiators. In the present case, ethoxyl radicals are expected to undergo a self reaction according to Reaction 7, at sufficiently high $C_2H_5O\cdot$ concentration:

$$2\,C_2H_5O\cdot \longrightarrow \text{Products} \qquad (7)$$

Ethoxyl radicals can also react with EMP^+ ions. They can, for example, add to EMP^+ according to Reaction 8:



(8)

Reaction 8 is thought to give rise to the formation of the transient absorption peaked at 340 nm which is assigned to the adduct of ethoxyl radical to EMP^+. In accordance with this assignment, the formation rate of the transient absorption at 340 nm increased with inceasing EMP^+ concentration yielding the rate constant $k(C_2H_5O\cdot+EMP^+)=(6—8)\times10^7$ dm^3 mol^{-1} s^{-1}.

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