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Journal of Photochemistry and Photobiology A: Chemistry 153 (2002) 33–40

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Laser flash photolysis study of nicotinic acid in water

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Received 7 February 2002; received in revised form 13 May 2002; accepted 13 June 2002

Abstract

The photochemical reactions of the three forms of nicotinic acid ($pK_{a_1} = 2.09$ and $pK_{a_2} = 4.85$) were studied by laser flash photolysis and product studies. Irradiation at pH = 1 yielded a pulse end transient ($\lambda_{max} = 310/440$ nm) assigned to the protonated triplet. Oxygen quenching experiments showed that this triplet is involved in the formation of 2-hydroxy-nicotinic acid. No transient absorptions were detected at pH = 2. Irradiation at $pH > 2.8$ yielded a transient species ($\lambda_{max} = 290/375$ nm) assigned to the anionic triplet. We demonstrated that this latter yielded bipyridine derivatives by reaction with nicotinic acid. Photoionisation of the anionic singlet excited state was also observed. This reaction is likely to be responsible for the phototransformation occurring in oxygenated basic solutions.

Keywords: Pyridine-3-carboxylic acid; Laser flash photolysis; Steady-state irradiation; Triplet; Photoionisation

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1. Introduction

Pyridine and methylpyridine were shown to undergo photoisomerisations and photosubstitutions in organic solvents [1]. This interesting photoreactivity was explained by the intermediary formation of diradicals [2,3]. In aqueous medium, pyridine was proved to undergo ring opening with production of 5-amino-2,4-pentadienal ($\phi = 0.07$) [4,5]. It was established that this compound is formed by hydrolysis of the Dewar pyridine [5]. Substitution of pyridine by CO_2H affects strongly the photoreactivity. Indeed, nicotinic acid (pyridine-3-carboxylic acid) was found to be photolysed into 2-hydroxy-nicotinic acid in very acidic medium and into 2-(3-pyridyl)-pyridine-5-carboxylic acid in the pH range 4–6 while photostability was observed in basic solution [6]. On the basis of oxygen quenching experiments, photo-hydroxylation was ascribed as a triplet excited state reaction [6]. Using the fact that 2-, 3- and 4-pyridylacetic acid undergo efficient photodecarboxylation [7], Takeuchi and co-workers proposed that the formation of carboxybipyridine resulted from the attack of pyridyl carbanion formed by photodecarboxylation on the ground state nicotinate. However, such a mechanism cannot explain the photostability of nicotinic acid in basic medium. Moreover, it is inconsistent with the non-formation of pyridine that should be produced by protonation of pyridyl carbanion in acidic and neutral medium.

To get a better insight into the mechanism of the reaction and in particular into the carboxybipyridine formation, we undertook a detailed study by means of laser flash photolysis and steady-state irradiation. We photolysed the three forms of nicotinic acid ($pK_{a_1} = 2.09$ and $pK_{a_2} = 4.85$) [8].

2. Experimental

2.1. Material and methods

Nicotinic acid was purchased from Fluka and used as-received. 2-Hydroxynicotinic acid (Lancaster), 6-hydroxynicotinic acid (Aldrich) and pyridine (Lancaster) were of the highest purity grade available. Water was purified with a Milli-Q (Millipore) device. ^{1}H NMR spectra were recorded on a Bruker AC400 spectrometer. HPLC–ESI–MS spectrometry analyses were performed by the Service Central d'analyse of CNRS, Solaize, France. A Hewlett-Packard model HP 1100-MSD was used to obtain the mass spectra. Products were separated on a column Waters X terra MS C_{18} (3.5 μm) (2.1 mm × 150 mm). The temperature of the column was maintained at 50 °C. A mixture of $HClO_4$–acidified water (pH = 3.0)–acetonitrile (95–5%) was used as eluent at a flow of 0.3 ml/min. Nitrogen was used as shealth gas at 13 l/min and the spray voltage was 3 kV.

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PII: S1010-6030(02)00238-1

UV–visible spectra were recorded on a Cary 3 (Varian) spectrophotometer. Analytical HPLC was carried out using a Waters apparatus equipped with a photodiode array detector and a column Waters X terra RP_{18} (5 μm) (4.6 mm × 250 mm). The mobile phase was a mixture of H_3PO_4–acidified water (pH = 3.0)–acetonitrile (95–5%).

2.2. *Laser flash photolysis*

Transient absorption experiments were carried out using a frequency-quadrupled Nd:YAG laser (Quanta-Ray GCR-130, 266 nm, pulse duration 9 ns). The procedures used for transient absorption spectroscopy measurements have been described previously [9]. Potassium peroxodisulphate was used for chemical actinometry.

2.3. *Steady-state irradiations*

Aqueous nicotinic acid (10^{-3} M) was irradiated at 254 nm using a device equipped with six germicide lamps. Uranyl oxalate was used as a chemical actinometer. Solutions were deoxygenated by nitrogen bubbling for 20 min prior to irradiation and were suroxygenated by oxygen bubbling. pH was adjusted using $HClO_4$ or NaOH.

2.4. *Identification of photoproducts*

2- and 6-Hydroxynicotinic acid and pyridine were identified by reference to authentics. 2-(3-Pyridyl)-pyridine-5-carboxylic acid was identified using the following procedure. A deoxygenated solution of nicotinic acid (30 ml, 10^{-3} M, pH = 5.0) was irradiated at 254 nm for 1 h to get a conversion extent equal to 50%. The reaction mixture was then evaporated to dryness and analysed by ^{1}H NMR and HPLC–ESI–MS. The main photoproduct had the following characteristics:

$\lambda_{max} = 246$ and 284 nm in H_2O at pH = 3.0; ^{1}H NMR ($CDCl_3$, δ ppm): 9.38 (d, 1H, $J = 2.0$ Hz), 9.25 (d, 1H, $J = 2.0$ Hz), 8.80 (dd, 1H, $J = 5.0$ and 2.0 Hz), 8.66 (dt, 1H, $J = 7.9$ and 2.0 Hz), 8.58 (dd, 1H, $J = 8.0$ and 2.0 Hz), 8.15 (d, 1H, $J = 8.0$ Hz), 7.77 (ddd, 1H, $J = 7.9$, 5.0 and 2.0 Hz); HPLC–ESI–MS: retention time = 6.4 min, $m/z = 201$ corresponding to $[M + H]^+$.

In order to determine the value of the molar extinction coefficient at 284 nm, we used nicotinic acid as an internal reference. By comparing the ^{1}H NMR area obtained for 2-(3-pyridyl)pyridine-5-carboxylic acid and nicotinic acid in the mixture with the HPLC area at 284 nm of the two compounds, we computed $\varepsilon = 5000 \pm 800\,M^{-1}\,cm^{-1}$ at 284 nm for 2-(3-pyridyl)-pyridine-5-carboxylic acid.

Bipyridine and dicarboxybipyridine were also detected in traces in the pH range 4–6 for the former and in basic medium for the latter:

Bipyridine. $\lambda_{max} = 227$ and 277 nm in H_2O at pH = 3.0; HPLC–ESI–MS: retention time = 5.5 min, $m/z = 157$ corresponding to $[M + H]^+$.

Dicarboxybipyridine. $\lambda_{max} = 275$ nm in H_2O at pH = 3.0; HPLC–ESI–MS: retention time = 3.9 min, $m/z = 245$ corresponding to $[M + H]^+$ with a fragment at $m/z = 201$ corresponding to $[M–CO_2 + H]^+$.

3. Results

3.1. *Laser flash photolysis*

The laser flash photolysis of a deoxygenated solution of protonated nicotinic acid (8×10^{-4} M, pH = 1) yielded at pulse end a transient absorption exhibiting two

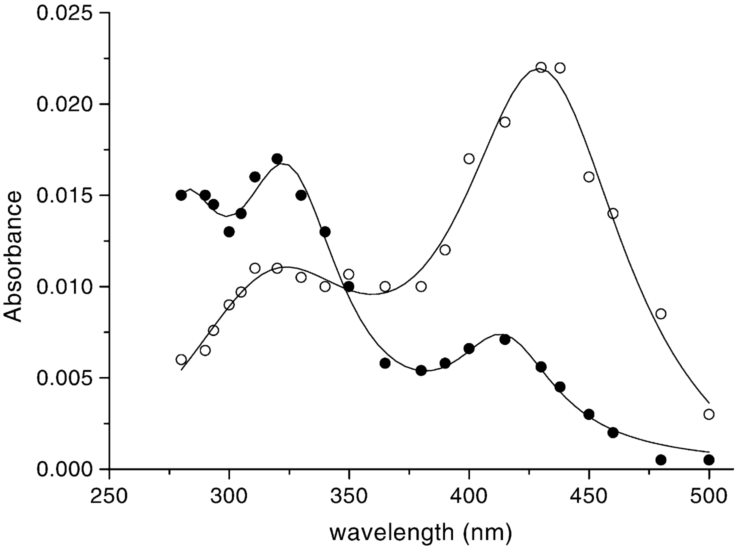


Fig. 1. Transient absorption spectrum from deoxygenated nicotinic acid (8×10^{-4} M); A (266) = 1.50 and pH = 1.0. (○) Pulse end extrapolated absorbance; (●) absorbance measured 4 μs after the pulse end.

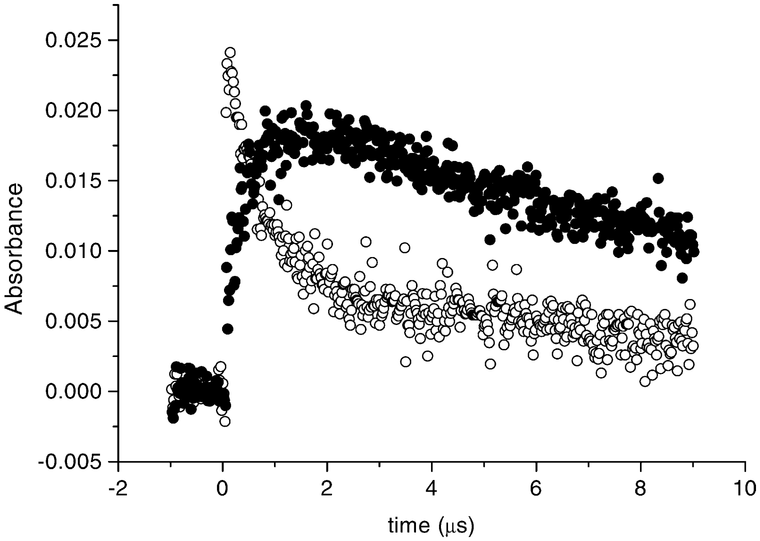


Fig. 2. Time course absorbances from a deoxygenated solution of nicotinic acid (8×10^{-4} M); A (266) = 1.50 and pH = 1.0 at (○) 440 nm and (●) 290 nm.

maxima at 310 and 440 nm (Fig. 1). The decay obeyed a first-order kinetics (Fig. 2). The rate constant k_1 was equal to $1.2 \times 10^6\,\mathrm{s}^{-1}$ and was independent of the nicotinic concentration. The pulse end species was produced by a monophotonic process as proved by the linear increase of the 440 nm absorbance with P, the energy pulse. Using a chemical actinometry, we found for the $\varepsilon \times \phi$ product at 440 nm a value of $90 \pm 20\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$. An other absorption with maxima at 320 and 420 nm was observed 4 μs after the pulse end (Fig. 1). The kinetics of formation of this latter transient was obtained by monitoring the absorbance at 290 nm (Fig. 2). We found a first-order rate constant of formation close to k_1 indicating that the secondary absorption arises from the pulse end transient. In line, oxygen was found to accelerate the disappearance of the pulse end absorption ($6.2 \times 10^6\,\mathrm{s}^{-1}$) and to significantly reduce the intensity of the secondary absorption. Based on this oxygen effect the pulse end transient is likely to be a triplet excited state. In very acidic ethanol, a similar species was obtained.

No transient absorptions were observed by photolysing nicotinic acid at pH = 2. The laser flash photolysis of nicotinate (2×10^{-4} M, pH = 8) yielded two species. A broad absorption band with a maximum around 720 nm characteristic of solvated electrons was observed at pulse end. As shown in Fig. 3, the ratio of the 725 nm extrapolated absorbance over P increased linearly with P. From the intercept (0.00040 ± 0.00005) that is related to the monophotonic formation we found $150 \pm 20\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ for the $\varepsilon \times \phi$ prod-

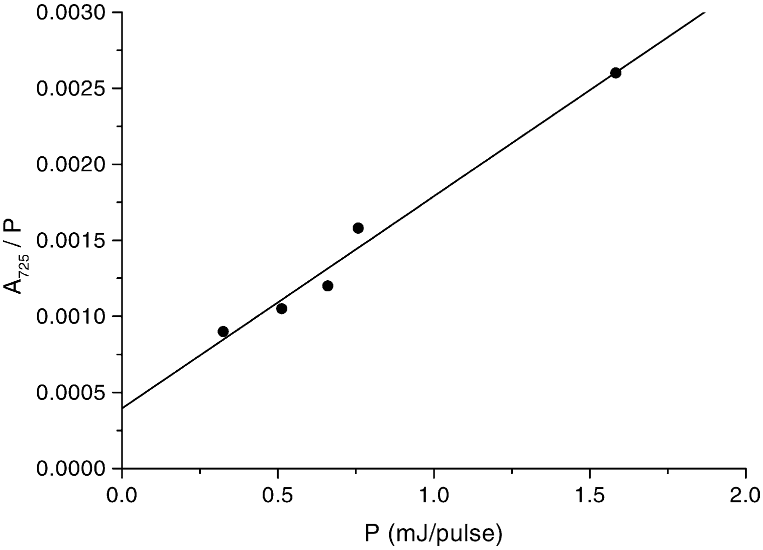


Fig. 3. Dependence of A_{725}/P on P; A is the 725 nm absorbance extrapolated at pulse end and P the energy pulse; A (266) = 0.54 and pH = 6.0.

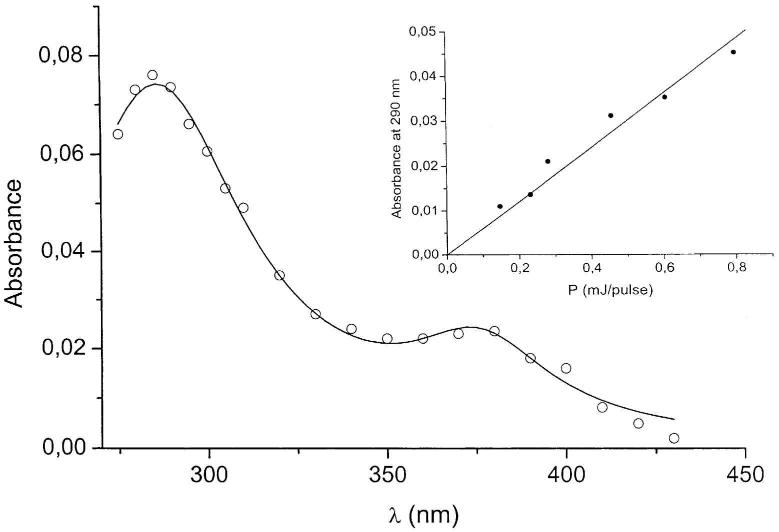


Fig. 4. Transient absorption spectrum from deoxygenated nicotinate (2×10^{-4} M); A (266) = 0.50 and pH = 8.0. Difference between absorbances measured at pulse end and 10 μs after. Insert shows the dependence of the difference of absorbance at 290 nm on P.

uct at 725 nm. Taking for the hydrated electrons a molar extinction coefficient equal to 18 500 M^{-1} cm^{-1}, we obtained that the quantum yield of the monophotonic formation of hydrated electrons was equal to 0.008 ± 0.002.

Another transient absorption exhibiting two maxima at 290 and 375 nm was observed at pulse end (see Fig. 4). This species was produced by a monophotonic process as shown by the linear increase of the 290 nm absorbance with P (insert of Fig. 4) and decayed within the first 20 μs following the pulse by a first-order kinetics with $k_2 = 2.7 \times 10^5\ s^{-1}$ (see Fig. 5). It was quenched very efficiently by oxygen and methyl acrylate ($k = 3.2 \times 10^9$ and $2.0 \times 10^{10}\ M^{-1}\ s^{-1}$, respectively) (Fig. 5). We concluded that it was a T–T absorption.

We measured the $\varepsilon \times \phi$ product at 290 nm for various pH values ranging from 2.9 to 11.2. The values of $\varepsilon \times \phi$ products were obtained from the slopes of linear regressions between the 290 nm absorbance and P using a chemical actinometry. They were found to increase with pH from 160 M^{-1} cm^{-1} at pH = 2.8 to around 3000 M^{-1} cm^{-1} at pH = 7 (see Fig. 6). The increase with pH showed a shape very similar to that of the ionisation curve (ratio [3-pyr-CO_2^-]/[pyr-3-CO_2H] on pH) and the inflection point was close to the second pK_a of nicotinic acid (4.85). It can be concluded that the observed transient derives from the anionic form of nicotinic acid and it should be the anionic triplet excited state.

To confirm this hypothesis, we followed the decay of the 290 nm absorption in acidic medium. As expected, the

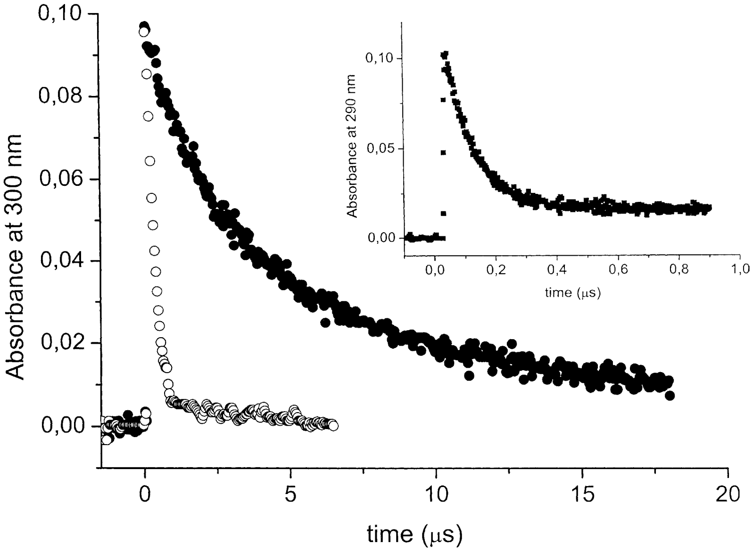


Fig. 5. Time course absorbance at 300 nm from a solution of nicotinate (2×10^{-4} M); A (266) = 0.50 and pH = 8.6. (●) Deoxygenated medium; (○) oxygen-saturated medium. Insert: (■) deoxygenated solution containing methyl acrylate (5×10^{-3} M).

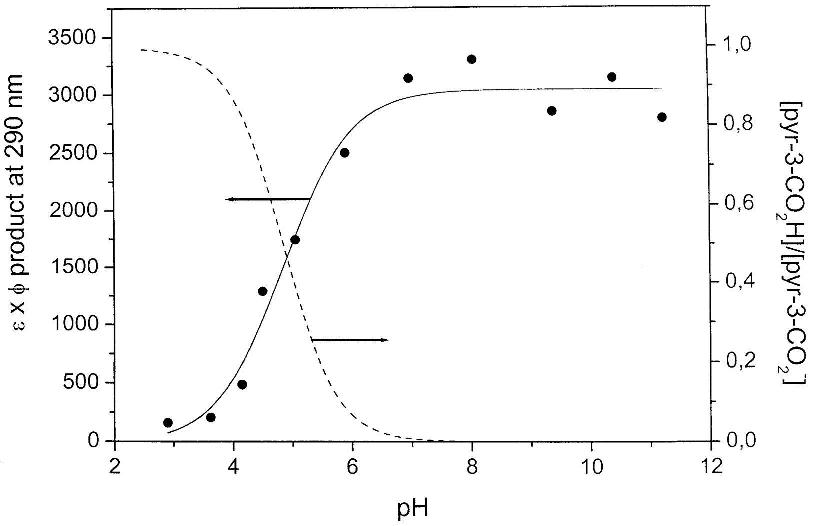


Fig. 6. Dependence of the $\varepsilon \times \phi$ product at 290 nm ([nicotinic acid] $= 2 \times 10^{-4}$ M) and of the ratio [3-pyr-CO_2H]/[pyr-3-CO_2^-] on pH.

decay rate increased linearly with the H^+ concentration (see Fig. 7a). Directly from the slope we deduced a value of $4.7 \times 10^9\,M^{-1}\,s^{-1}$ for the bimolecular rate constant of protonation k_{H^+}.

We also investigated the reactivity of the anionic triplet with nicotinic acid. As shown in Fig. 7b, k_2 increased linearly with the initial concentration of nicotinic acid at both pH = 4.9 and 10.9. However, the slope was higher in the former than in the latter case showing that the triplet reacts more readily with molecular than with anionic nicotinic acid.

Considering all these results, the apparent rate constant of decay can be expressed as

$$k_2 = k_d + k_{H^+}[H^+] + k_{rm}[3\text{-pyr-}CO_2H] + k_{ra}[3\text{-pyr-}CO_2^-]$$

where k_{rm} and k_{ra} are the reaction rate constants between triplet and molecular and anionic nicotinic acid, respectively, and [3-pyr-CO_2H] and [3-pyr-CO_2^-] are the concentration of molecular and anionic nicotinic acid. At pH = 10.9, [H^+] and [3-pyr-CO_2H] are very small and k_2 can be written as $k_2 = k_d + k_{ra}[3\text{-pyr-}CO_2^-]$. From the intercept and slope of the linear regression obtained at pH = 10.9, we get $k_d = 1.6 \times 10^5\,s^{-1}$ and $k_{ra} = 5.8 \times 10^8\,M^{-1}\,s^{-1}$. At pH = 4.9, the ratio [3-pyr-CO_2H]/[3-pyr-CO_2^-] is equal to 0.89 and k_2 is expressed as

$$k_2 = k_d + k_{H^+}[H^+] + \left(k_{rm}\frac{0.89}{1.89} + k_{ra}\frac{1}{1.89}\right)([3\text{-pyr-}CO_2H] + [\text{pyr-}3\text{-}CO_2^-])$$

From the slope of the linear regression obtained at pH = 4.9 and using the value of k_{ra} obtained at pH = 10.9, we get $k_{rm} = 1.1 \times 10^9\,M^{-1}\,s^{-1}$.

At pH = 8.5 the apparent rate constant of triplet decay in suroxygenated medium can be written as $k_2 = k_d + k_{ra}[3\text{-pyr-}CO_2^-] + k_{O_2}[O_2]$. Taking $[3\text{-pyr-}CO_2^-] = 2 \times 10^{-4}$ M and $[O_2] = 1.3 \times 10^{-3}$ M, we obtain $k_{O_2} = 2.9 \times 10^9\,M^{-1}\,s^{-1}$.

3.2. *Product studies*

The quantum yields of nicotinic acid (9.0×10^{-4} M) photolysis were found to be small showing a maximum around pH = 5 (0.0067, see Table 1). Oxygen had an inhibiting effect in acidic medium, especially around pH = 5, while an accelerating influence in basic solution. In the presence of methyl acrylate (5.0×10^{-3} M) and at pH = 5.4, the quantum yield of nicotinic acid consumption was reduced to 0.0016.

The irradiation of the protonated form (pH = 1) led mainly to 2-hydroxynicotinic acid as shown by Takeuchi et al. [6]. Oxygen had an inhibiting influence on its formation: the quantum yield was found to be equal to 1.7×10^{-3} and 0.36×10^{-4} in the absence and presence of oxygen, respectively. Traces of 6-hydroxynicotinic acid were also observed. Within the pH range 2.8–7.5, the carboxybipyridine (2-(3-pyridyl)pyridine-5-carboxylic acid) was the main photoproduct as mentioned by Takeuchi too [6]. The formation of carboxybipyridine was significantly inhibited by oxygen at pH = 4.83 ($\phi_{N_2} = 0.69 \times 10^{-3}$ and $\phi_{O_2} = 0.18 \times 10^{-3}$) and by methyl acrylate. In deoxygenated medium, it accounted for 26% of converted nicotinic acid considering that it is produced from two starting molecules. Traces of unsubstituted bipyridine and pyridine were observed too. In basic and oxygenated medium, 2- and 6-hydroxynicotinic acids and dicarboxybipyridine were produced in small amounts.

4. Discussion

Laser flash photolysis experiments allowed the detection of two triplet–triplet absorptions. The first (λ_{max} = 310/440 nm), observed at pH = 1, is likely to be that of the protonated triplet while the second (λ_{max} = 290/375 nm), observed at pH > 2.8, can be firmly assigned to the anionic

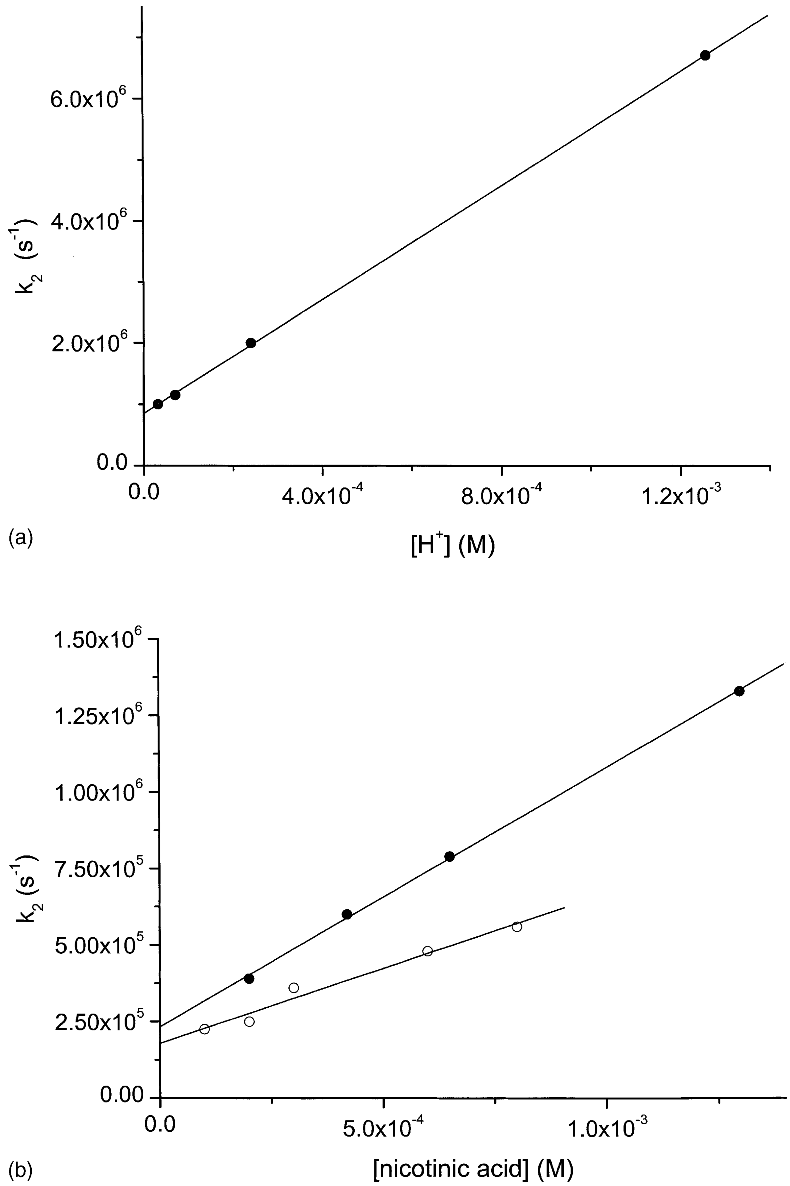


Fig. 7. Dependence of the rate constant of disappearance measured at 290 nm: (a) on [H^+], [nicotinic acid] = 2×10^{-4} M; (b) on the [nicotinic acid]; (●) pH = 4.9; (○) pH = 10.9.

Table 1
Quantum yields of nicotinic acid (1×10^{-3} M) disappearance in deoxygenated (ϕ_{N_2}) and oxygen-saturated (ϕ_{O_2}) solutions

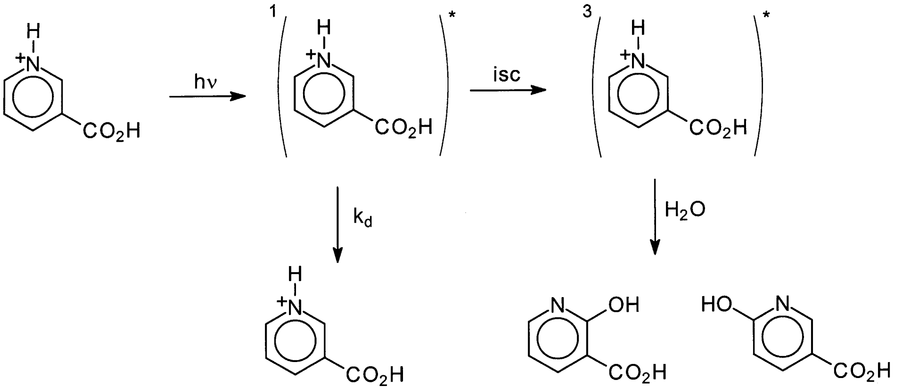
pH	ϕ_{N_2} [a]	ϕ_{O_2} [a]
1.0	0.0043	0.0036
2.80	0.00083	
4.83	0.0053	0.0020
5.14	0.0066	0.0033
5.40	0.0067	
7.66	0.00043	0.0028
9.80	0.00020	0.0024
5.40 + methyl acrylate (5×10^{-3} M)	0.0016	

[a] Average uncertainty is 12%.

triplet. The 310/440 nm absorption was not detected at pH = 2 although about 50% of ground state nicotinic acid is protonated. This result may indicate that the first pK^* of singlet excited state is lower than the first pK_a of ground state (2.08) allowing fast deprotonation of protonated excited molecules.

The two triplets showed distinct reactivities. The protonated triplet was transformed into a secondary transient in a reaction independent of nicotinic acid concentration while the anionic triplet disappeared by reaction with starting nicotinic acid. In line, products distribution depends strongly on the pH.

In the pH conditions where the protonated triplet was observed, 2-hydroxynicotinic acid was formed. The formation



Scheme 1.

was inhibited by oxygen and the ratio ϕ_{N_2}/ϕ_{O_2} measured by steady-state irradiation (0.21) was in a very good agreement with the ratio of the rate constants of triplet decay measured in deoxygenated and oxygenated media (0.19). It can be concluded that 2-hydroxynicotinic acid is produced via the protonated triplet (see Scheme 1). However, the mechanism of the reaction is not clear. First, the secondary transient observed in laser flash photolysis is not assigned. Second, if we make the hypothesis that the initial reaction is the nucleophilic addition of water onto the protonated triplet, the final formation of hydroxylated compounds requires the subsequent elimination of two H atoms. Reduction products should be therefore produced along with hydroxylated products that accounted for only 40% of converted nicotinic acid. However, they were not detected by UV-HPLC.

Experimental data bring evidence that carboxybipyridine is produced via the anionic triplet. First, oxygen and methyl acrylate that readily trapped the triplet inhibited the carboxybipyridine formation too. Second, the anionic triplet state was shown to react with the nicotinic acid ground state. Lastly, the formation of carboxybipyridine was observed between pH = 2.8 and 7.5, i.e. in the pH conditions where the formation of anionic triplet was observed too. At pH > 7.5, carboxybipyridine was not produced indicating that its formation involves the anionic triplet and molecular nicotinic acid only. The mechanism of the addition reaction is not fully understood. A concerted reaction producing both carboxybipyridine and formic acid may occur. (Scheme 2). The reaction between the anionic triplet state and nicotinate ground state is only a deactivation as a result, nicotinic acid is photostable in basic deoxygenated medium.

To resume, the anionic triplet can either be deactivated, undergo protonation or react with nicotinic acid and nicotinate ground states. The quantum yield of 2-(3-pyridyl)pyridine-5-carboxylic acid formation in deoxygenated medium can be expressed as

$$\phi_{N_2} = \frac{\phi_{\mathrm{isc}} \times \alpha \times k_{\mathrm{rm}}[\text{3-pyr-CO}_2\text{H}]}{k_{\mathrm{d}} + k_{\mathrm{H^+}}[\mathrm{H^+}] + k_{\mathrm{rm}}[\text{3-pyr-CO}_2\text{H}] + k_{\mathrm{ra}}[\text{3-pyr-CO}_2{}^-]}$$

where ϕ_{isc} is the quantum yield of inter-system crossing and α the efficiency of bipyridine formation from the complex. In the presence of oxygen, the relationship becomes

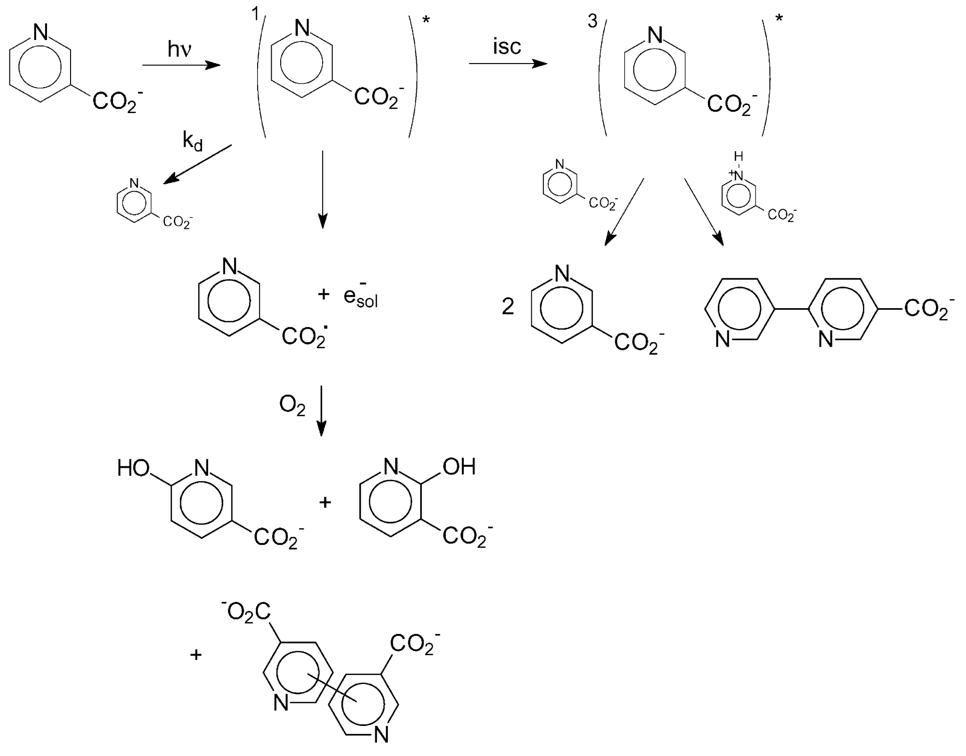
$$\phi_{O_2} = \frac{\phi_{\mathrm{isc}} \times \alpha \times k_{\mathrm{rm}}[\text{3-pyr-CO}_2\text{H}]}{\begin{array}{c} k_{\mathrm{d}} + k_{\mathrm{H^+}}[\mathrm{H^+}] + k_{\mathrm{rm}}[\text{3-pyr-CO}_2\text{H}] \\ + k_{\mathrm{ra}}[\text{3-pyr-CO}_2{}^-] + k_{O_2}[\mathrm{O_2}] \end{array}}$$

Using the rate constants measured by laser flash photolysis, we compute $\phi_{N_2}/\phi_{O_2} = 4.5$ at pH = 4.83 in a good agreement with the experimental value deduced from data of Table 1 (3.8). In contrast, the inhibiting effect of methyl acrylate on nicotinic acid consumption is smaller than excepted on the basis of a rate constant of reaction between anionic triplet and methyl acrylate equal to $2.0 \times 10^{10}\ \mathrm{M^{-1}\,s^{-1}}$. It can be deduced than methyl acrylate both deactivates the anionic triplet and reacts with it.

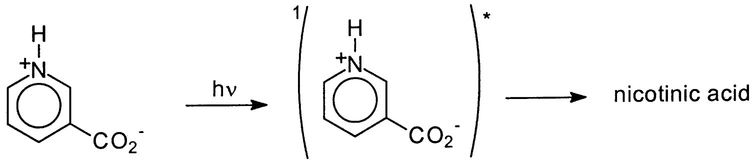
In neutral and basic medium, addition of oxygen was found to accelerate the consumption of nicotinate instead to inhibit it. The mechanism of reaction is therefore, different from that observed at lower pH. Photoionisation of anionic singlet that was shown to occur with a low yield (0.008 ± 0.002) may explain the formation of 2- and 6-hydroxynicotinic acids and dicarboxybipyridine in neutral and basic oxygenated medium.

Neutral nicotinic acid exhibited a low photoreactivity ($\phi = 8.3 \times 10^{-4}$ at pH = 2.8) and no transient species were observed around pH = 2. These results are consistent with a fast deactivation of singlet excited state. Since neutral nicotinic acid was shown to exist in zwitterionic form in water [7,10,11] the deactivation might be promoted by internal proton transfer (Scheme 3). It must be stressed that neutral pyridylacetic acids were found to undergo efficient photodecarboxylation ($\phi = 0.46$ at pH = 4) with formation of methylpyridine [7]. By irradiation of nicotinic acid only traces of pyridine were found and it can be concluded that photodecarboxylation of nicotinic acid is a very minor pathway.

In conclusion, the three forms of nicotinic acid show very different photoreactivities. Triplet–triplet absorptions were detected and the involvement of the triplet excited states in the transformations was proved. The mechanism of hydroxylation in very acidic medium needs to be clarified and



Scheme 2.



Scheme 3.

secondary transients arising from the protonated triplet to be assigned. The anionic triplet state reacts with molecular ground state nicotinic acid to yield carboxybipyridine while it is only quenched by nicotinate. This latter reaction explains the photostability of nicotinic acid in basic and deoxygenated medium. At last, nicotinate was found to undergo photoionisation that seems responsible for the phototransformation observed in oxygenated neutral and basic medium.

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