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Photoisomerization of *p*-nitrobenzaldehyde to *p*-nitrosobenzoic acid in aqueous solution

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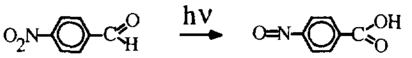
Abstract

Evidence is presented by nanosecond laser photolysis, coupled with conductometric detection, that in aqueous solution the photoisomerization of *p*-nitrobenzaldehyde to *p*-nitrosobenzoic acid occurs via rapid formation of an aci-nitroketene intermediate and its rearrangement. © 1998 Elsevier Science S.A.

Keywords: Photoisomerization; Rearrangement; Aci-nitroketene; Aqueous solution

1. Introduction

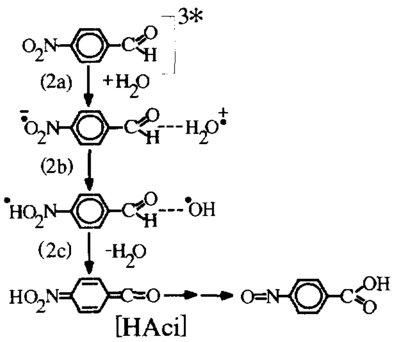
The photoisomerization of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid has long been known [1–8]. A corresponding photoisomerization of *p*-nitrobenzaldehyde to *p*-nitrosobenzoic acid



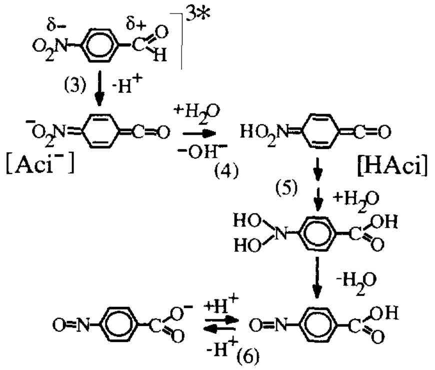
(1)

has been reported only recently [9–11]. Wubbels et al. [11] have shown that the reactive electronic state is the lowest triplet and that reaction (1) requires water as medium. The quantum yield is 0.04 at pH 0–10 and no photoreaction was found in pure acetic acid or acetonitrile. The key step in the proposed mechanism [11] is electron transfer from water to triplet *p*-nitrobenzaldehyde, Eq. (2a, Scheme 1) followed by proton transfer, Eq. (2b). The thereby formed (geminate) OH radical should abstract the formyl hydrogen, Eq. (2c), to form the aci-nitroketene (**HAci**), which then rearranges into *p*-nitrosobenzoic acid [11]. Involvement of **HAci** was indicated by *p*-nitrosobenzamide as photoproduct in the presence of ammonia.

Evidence is now presented that the photoisomerization of *p*-nitrobenzaldehyde to *p*-nitrosobenzoic acid occurs via **Aci**$^-$, the conjugate base of the above aci-nitro species (reaction 3). **Aci**$^-$ is observed by flash photolysis of *p*-nitrobenzaldehyde in aqueous solution concomitant with formation of H$^+$ at the end of the laser pulse. Subsequently, formation



Scheme 1.



Scheme 2.

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of OH^- (reaction 4), rearomatization (reaction 5) and eventually neutralization occur (Scheme 2).

2. Experimental details

p-Nitrobenzaldehyde (EGA) was used as received, water was purified by a millipore (milli-Q) system. The experimental setup (248-nm laser pulses) and the procedures were as described previously [12–14]. The measurements refer to 24 ± 2°C.

3. Results

Excitation of *p*-nitrobenzaldehyde in neutral aqueous solution by 248-nm laser pulses yields a transient with $\lambda_{max} = 350$ nm (inset of Fig. 1). The 350-nm transient is formed within the pulse width (20 ns) and decays by first-order kinetics; its spectrum remains virtually unchanged in the pH range 2.5–10 (Table 1). The rate constant ($1/\tau_{350}$) increases with decreasing pH (Fig. 1), the lifetime varies from ≈ 1.3 μs in the neutral or alkaline pH range to 20 ns at pH 2.8. The results are described in terms of a protonation reaction,

$$1/\tau_{350} = k_o + k_+[H^+]$$

where $k_+ = 4 \times 10^{10}\ M^{-1}\ s^{-1}$ is the rate constant for reaction of the transient with H^+ and k_o a limiting rate constant ($7 \times 10^5\ s^{-1}$ at pH 4.6). Due to these findings the observed transient is assigned to **Aci**$^-$. The presence of air has no effect on τ_{350} but addition of NH_3 enhances the decay; the observed rate constant at pH 10 is about $1 \times 10^8\ M^{-1}\ s^{-1}$.

Table 1
Absorption maximum and lifetime of the optical transient and half-life for decay of the transient conductivity [a]

pH	λ_{max} (nm)	τ_{350} (μs)	$t_{1/2}(\Delta\kappa)$ (μs)
p-nitrobenzaldehyde			
2.5	350	< 0.02	
3.0	355	0.028	< 0.03
3.5		0.07	0.07
4.0	350	0.25	0.3
5.0	355	1.2	≥ 2
7.0	356	1.3	
10	350	1.0	
p-nitrophenylglyoxylic acid [b]			
2.5	350	< 0.018	
3.0	350	0.025	< 0.03
3.5	351	0.07	0.06
4.0	352	0.23	0.18
5.0	352	1.3	> 0.5
7.0	350	1.3	
10	352	1.6	
12	355	1.4	

[a] In argon-saturated aqueous solution, $\lambda_{exc} = 248$ nm.
[b] Taken from Ref. [13].

The conductivity signals increase concomitantly with the pulse in the whole pH range of 3.0–11.0 (Figs. 2 and 3), the amplitude then either decreases (pH 3.2–4.0), increases further (pH 4.2–8.4) or decreases (pH 8.5–11). The decreasing $\Delta\kappa$ component within a few μs is due to neutralization $H^+ + OH^- \rightarrow H_2O$. The net result after a few μs in the neutral and acidic pH range is proton release via reaction (6). *p*-nitrosobenzoic-acid, the stable photoisomer of *p*-nitro-

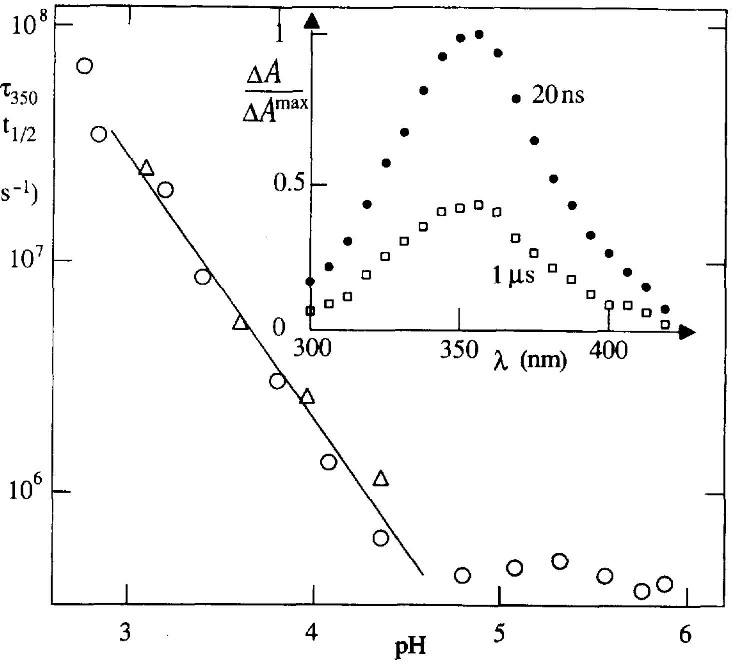


Fig. 1. Semilogarithmic plot of $1/\tau_{350}$ (○) and $1/t_{1/2}(\Delta\kappa)$ (Δ) vs. pH for *p*-nitrobenzaldehyde (0.2 mM) in argon-saturated aqueous solution. Inset: Transient absorption spectrum at 20 ns (●) and 1 μs (□) at pH 7.

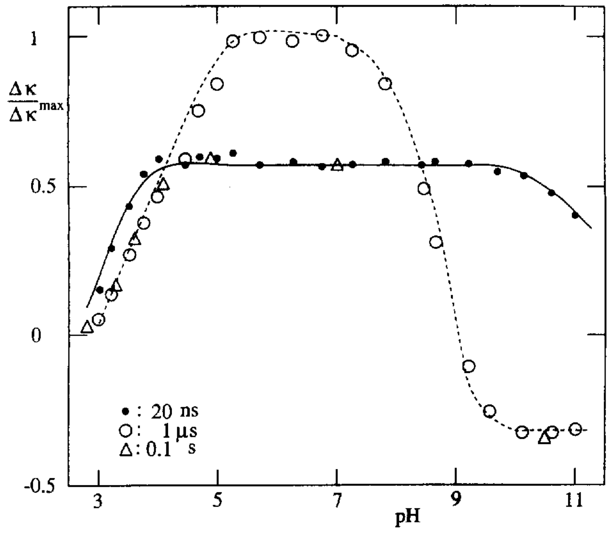


Fig. 2. Changes of the conductivity amplitude vs. pH for *p*-nitrobenzaldehyde (0.2 mM) in argon-saturated aqueous solution at 20 ns (●), 1 µs (○) and 0.1 s (Δ) after the pulse.

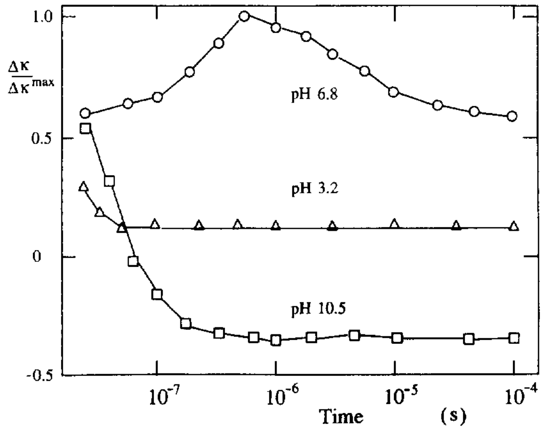


Fig. 3. Conductivity signals as a function of time (log scale) at pH 3.2 (Δ), pH 6.8 (○),and pH 10.5 (□).

benzaldehyde, is present as anion, $pK_a = 3.3$ [15]. Proton formation is further supported by the result that addition of phosphate buffer at pH7 reduces $\Delta\kappa$; its relative amplitude at 0.1 ms for 0.1 mM KH_2PO_4/K_2HPO_4 is less than 3% with respect to the value in the absence of buffer and its half-concentration is as low as 5 μM. At pH 3.0–3.5 the signal increases concomitantly with the pulse and then rapidly decreases (Figs. 2 and 3). The inverse half-life, $1/t_{1/2}(\Delta\kappa)$, obtained from conductivity and $1/\tau_{350}$ from optical detection show virtually the same pH dependence in the range 3–5 (Fig. 1). This is in agreement with protonation of **Aci**$^-$ to yield *p*-nitrosobenzoic acid. On the other hand, the kinetics at pH > 9 are determined by the removal of OH^- from the bulk of solution within 1 μs (Figs. 2 and 3). On a long time scale after the above reaction steps, e.g., between 0.1 ms and 0.1 s, the conductivity signal remains essentially constant.

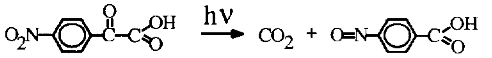
4. Discussion

Reaction sequence (3)–(6) is essentially based on the conductivity changes after the pulse. The conductivity behavior on a short time scale is interpreted as follows. The increase in $\Delta\kappa$ within 20 ns is due to pulse-induced proton formation according to Eq. (3). The second increasing $\Delta\kappa$ component within ≤ 1 μs in neutral solution (Fig. 3) is explained by formation of OH^- after reaction of **Aci**$^-$ with water according to Eq. (4). Thus, the following ionic mechanism is proposed: The key step after excitation into the triplet state of *p*-nitrobenzaldehyde is a charge separation due to the strong electron accepting power of the nitro group. The postulated zwitterion deprotonates instantaneously at the formyl group, Eq. (3), thereby generating intermediate **Aci**$^-$. Reaction of **Aci**$^-$ with water yields OH^- and **HAci**, Eq. (4). The rearomatization, Eq. (5), occurs by addition of water to the electrophilic carbon of the ketene side of **HAci** followed by dehydration at the $(HO)_2N$ side to give the nitroso group (cf. reactions 10 and 11 in Ref. [13]).

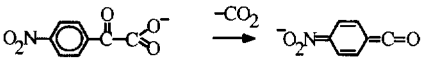
The long-lived conductivity component is explained by proton formation according to forward reaction (6). The signal is positive at pH 4–8 and negative at pH 9–11, the latter is due to the removal of OH^- from the bulk of solution. The ratio of the amplitudes at these pH's is about 1:0.6, in agreement with the ion mobilities of H^+ and OH^- (350 and 190 Ω^{-1} cm^2 mol^{-1}, respectively). The amplitude decreases with decreasing pH, the inflection point is pH 3.7, due to equilibrium (6). A comparison of the amplitudes at 20 ns and 0.1 ms or 0.1 s demonstrates that the charged species at the end of the pulse has to be a proton, in agreement with reaction (3).

Aci$^-$ cannot be the excited singlet or a triplet state of *p*-nitrobenzaldehyde, the former because of the too long lifetime of the 350-nm transient and the latter because of the insensitivity towards oxygen. A very similar 356-nm transient has been detected in the photodecarboxylation of *p*-nitrophenyl acetate; it has been assigned to the *p*-nitrobenzyl anion which has a tautomeric aci structure [16]. Absorption maxima at 350–400 nm have been reported for aci-type structures of various nitro-aromatics [17]. Since the quantum yield of isomerization in aqueous solution is rather small [11], other deactivation pathways of excited *p*-nitrobenzaldehyde are presumably also involved. They are radiationless since neither fluorescence or phosphorescence could be detected [12]. In the presence of 2-propanol the α-hydroxy-(*p*-nitrobenzyl) radical is formed [12]. Photodeuteriation in acetone/D_2O (3:1, vol), as found for several substituted benzaldehydes having an n,π triplet state, does not occur [18]. The suggested reason is the too short lifetime of the *p*-nitrobenzaldehyde triplet state [12,18], due to fast deprotonation via step (3) and no subsequent possibility for H/D exchange.

The nature of the 350-nm transient as **Aci**$^-$ is supported by observation of the same intermediate in photoreaction (7) of *p*-nitrophenylglyoxylic acid in aqueous solution [13].


(7)

At pH > 1 p-nitrophenylglyoxylic acid is present as anion, pK_a = 1.1. The suggested decarboxylation step is reaction (8), which is initiated by fast electron transfer to the nitro group in an excited state, probably the triplet state (of the anion).


(8)

Decay of **Aci**$^-$ was found to be accelerated by protonation [13] and once the aci-species is formed, the pathways from p-nitrophenylglyoxylic acid to p-nitrosobenzoic acid and the photoisomerization of p-nitrobenzaldehyde are suggested to be the same. The mechanism for p-nitrophenylglyoxylic acid was likely based on conductivity changes, the amplitude of $\Delta\kappa$ depending on time and pH [13]. The main differences in $\Delta\kappa$ are (i) formation of a permanent proton in the case of p-nitrobenzaldehyde and no conductivity change after neutralization for p-nitrophenylglyoxylic acid and (ii) a negative component on a prolonged time scale for p-nitrophenylglyoxylic acid at pH > 9 due to bicarbonate formation from CO_2. This is in line with sequence (8) plus (4)–(6).

The $t_{1/2}(\Delta\kappa)$ and τ_{350} values are very similar at pH 3–5 for either p-nitrobenzaldehyde or p-nitrophenylglyoxylic acid and they have the same pH dependence (8). Apart from this acid-catalyzed (and possibly a base-catalyzed) reaction, **Aci**$^-$ reacts with NH_3 and decays via **HAci** into p-nitrosobenzoic acid. The postulated zwitterionic nature in the (initial) pathway from triplet p-nitrobenzaldehyde towards **Aci**$^-$ makes it plausible that the quantum yield of reaction (1) is lower than that of reaction (7), ≈0.04 [11] and 0.28 at pH 2–12 [13], respectively. In the latter case, triplet p-nitrophenylglyoxylic acid (as anion), due to the CO_2^- group, should exhibit a more efficient electron transfer to the nitro group and should thus yield more **Aci**$^-$.

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