

Photoinduced reductive cleavage of some chlorobenzyl compounds. New insights from comparison with electrochemically induced reactions

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The photoinduced reductive cleavage of the carbon–chlorine bond in some chlorobenzyl nitro- and cyano-substituted compounds has been studied by transient absorption spectroscopy. The influence of the nature of the electroattractive group as well as its relative position and of the mixture composition of the solvent were investigated to give new clues into the mechanisms and into the factors that control the concerted or stepwise character of the process. Experimental results have been compared with previous results obtained by electrochemical techniques on the same molecules. Analysis leads to the conclusion that, beside the molecular structure, the solvation conditions and the driving force offered to the reaction, the formation of an excited state may control the reactivity.

1. Introduction

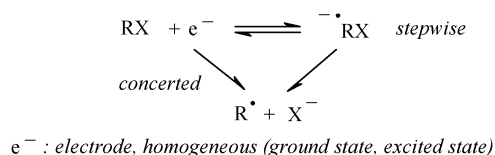
Coupling between electron transfer and dissociation (or formation) of a chemical bond is a key step in numerous chemical and biological processes. Whatever the electron injection mode (thermally, electrochemically, by radiolysis or photolysis), the control and understanding of the parameters influencing the reaction mechanism, such as the solvent nature, the molecular structure of the reactant or the energy of the excess electron (*i.e.* the driving force of the reaction), is an active research field.^{1–3} In particular, the frontier between a concerted (one step, involving the crossing of one single transition state) and a stepwise mechanism (leading to the formation of a transient one electron reduced or oxidised species) is difficult to probe and, even more, to cross under control.^{1d,1e} In the following we will focus on reduction reactions (Scheme 1), although all reasoning could be transposed to oxidation without any difficulty.

In the mechanistic dichotomy (one step *vs.* two steps pathway), the very existence of a transient is a central question. If this transient does not exist (*i.e.* lives for less than a vibration), the process is concerted. Less obvious is the fact that, even if the transient may exist, the process is not necessarily stepwise. The key is the energy required for each reaction path. The reaction will proceed through the less energetic transition state: the more negative the energy of the transient, the more favorable the fully concerted pathway, and *vice versa*. In this connection, a sub-key point is the driving force offered by the electron donor (electrode in electrochemistry, excited state of a molecular donor in photolysis). The more reducing the donor,

the more favored the stepwise pathway.¹ A striking example is offered by the reduction of the 4-cyanobenzylmethylphenyl sulfonium cation, that affords 4-cyanobenzyl radical and methylphenyl sulfide.⁴ While the reaction is fully concerted when taking place at an electrode (low driving force conditions), the process becomes dominated by the sequential pathway, going through the intermediacy of a short lived radical, when the electron donor is the singlet excited state of 2-ethyl-9,10-dimethoxyanthracene (large driving force conditions). Such a mechanistic switch could also be triggered by changing the molecular structure of the substrate being cleaved (as an example, going to a progressively better leaving group by decreasing the strength of the bond being cleaved gives more chance to the concerted pathway to occur).¹ Changing the solvent in order to stabilize the transient intermediate at the expense of the fragmented products may also be another way to induce a mechanistic switch, although an experimental case has yet to be found.

Molecules containing a carbon–halogen chemical bond are good models to approach these reactions and related reactivity concepts,^{1d,1e,5–7} in particular because of the wide range of the C–X bond energy when varying the halogen atom. On a more practical side, aliphatic and ethylenic brominated and chlorinated molecules are known to be widespread organic pollutants of industrial soils and ground water,⁸ while the biotic and abiotic reduction processes designed for depollution remain far from being understood at a molecular level.⁹

One-electron reduction (at an electrode) of nitro-substituted aromatic compounds containing a halogen in benzylic position

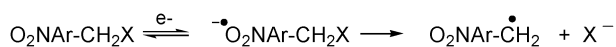


Scheme 1

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Scheme 2

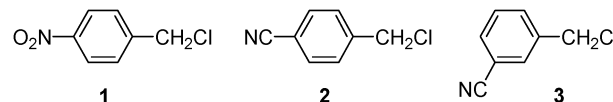
are known to initially produce an anion radical that subsequently dehalogenates according to Scheme 2.^{1d,e,5} The dehalogenation step could be viewed as an intramolecular dissociative electron transfer reaction from the π^* orbital mainly located on the nitro group where the electron temporarily resides, to the σ^* orbital of the C–X bond that breaks.

The rate for dehalogenation greatly depends on the nature of the halogen (the weaker the bond the faster the cleavage), on the relative position of the substituent onto the aromatic ring, and also on the nature of the solvent as well as on the pH.^{2b,5,7,10} As an example of the influence of the relative substituent position, dehalogenation rate constant for 3-nitrobenzylchloride in *N,N*-dimethylformamide (DMF) has been measured to 80 s^{-1} (electrochemical measurement) and to $4 \times 10^6 \text{ s}^{-1}$ with 4-nitrobenzylchloride.⁵ Such a difference is not related to thermodynamic factors but is mainly due to the fact that the mixing between the π^* and σ^* diabatic states is much stronger with the *para* derivative than with the *meta* derivative, thus decreasing the barrier for the C–Cl cleavage. Adding 1 M H_2O into the DMF leads to a decrease by a factor 10 of the cleavage rate constant for the 3-nitrobenzylchloride,¹¹ because of the strong stabilization of the negative charge borne by the transient anion radical (this charge is mainly located onto the nitro group) by the water molecules.^{2b}

With the less electroattractive cyano group, the reactions are faster and the mechanism may eventually change.^{2h} The 3-cyanobenzylchloride cleaves through the intermediacy of a radical anion, and the cleavage rate constant is now too fast to be measured by electrochemical techniques. With the 4-cyanobenzylchloride, the reductive cleavage becomes a purely concerted reaction, with both electron transfer and C–Cl bond breaking occurring simultaneously, through the passage of one single transition state. In this case, the π^* and σ^* diabatic states so strongly mix that the anion radical no longer exists (Scheme 3).^{2h}

The purpose of this paper is to get new insights into these reductive cleavage processes. To do so, we have performed UV-flash photolysis experiments on several benzylic compounds [4-nitrobenzylchloride (**1**), 4- and 3-cyanobenzylchloride,

(**2** and **3** respectively)] in liquid acetonitrile (ACN), in the presence of a sacrificial electron donor (triethylamine, TEA), and with increasing concentrations of water. Comparison of these results to those obtained by electrochemical techniques allowed us to shed new light on the various factors that control the reduction mechanism. The formation of an excited state of the substrate as compared to the ground state reactions involved in electrochemistry will be emphasized.



2. Experimental

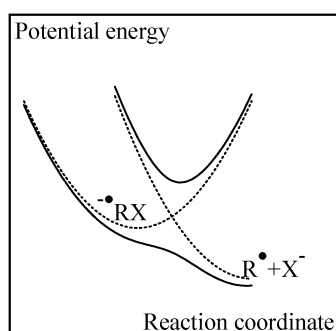
4-nitrotoluene (Acros Organics, 99%), 4-nitrobenzyl chloride (Acros Organics, 99%), 3-cyanobenzyl chloride (Chemstep, pure), ACN (Merck, Uvasol 99,9%) and TEA (Prolabo, 99%) were used as received. 4-cyanobenzyl chloride (Alfa Aesar, 98%) was recrystallized in a 60:40 mixture of pentane and dichloromethane. Water was obtained from a MilliQ system (18.2 M Ω cm).

The initial UV flash (308 nm, 20 ns, $E \sim 100 \text{ mJ}$) coming from an XeCl excimer laser (Lambda Physik ComPex 102) generated the excited form of the aromatic compound that extracted an electron from TEA (not absorbing at 308 nm). The photoreduction of aromatic compounds by aliphatic amines is a well known process,¹² producing the transient anion radical. The sample was illuminated in a Hellma circulating $1 \times 1 \text{ cm}$ quartz cuvette by a Xenon lamp (Ushio, 150 W) perpendicularly to the laser beam. The solution was refreshed after each laser flash, thanks to a peristaltic pump (Gilson Minipuls 3). The signal was collected into a spectrometer (Acton Research SP-150) and then detected either by a CCD camera (Princeton Instruments IRY 700G/RB) or a photomultiplier tube (Hamamatsu R928). Spectral measurements were typically averaged 20 times, and kinetic traces were averaged at least 5 times. Spectral data were directly transferred to a computer, whereas kinetics were acquired by an oscilloscope (Tektronix TDS-694C) before the transfer to the computer. All experiments were conducted at room temperature, *ca.* 25 °C.

3. Results and discussion

3.1 Reductive cleavage of 4-nitrobenzyl chloride

In pure ACN as well as with small concentration of water (Fig. 1, top), the photolysis of a mixture of TEA (0.1 M) and 4-nitrobenzylchloride (**1**) (0.5 mM) shows the growth of an absorption band peaking at 320 nm in one to a couple of microseconds that slowly decreases to give rise to a very weak and broad absorption band, with a maximum around 390 nm. Stability of the TEA/benzylic chlorides mixtures, with and without water, were ensured by UV-Vis steady-state spectroscopic measurement (no thermal reaction was observed). In pure ACN, in the absence of a halogen atom in the molecule, as with 4-nitrotoluene for example, we observed a strong absorption band peaking at 315 nm with a small bump around 440 nm, in good agreement with previous measurements.^{10a,13}



Scheme 3 Reductive cleavage of a substrate RX (X, leaving group, *e.g.* a halogen). Diabatic (dotted lines) and adiabatic (full lines) products' electronic states in the case of a strong coupling.

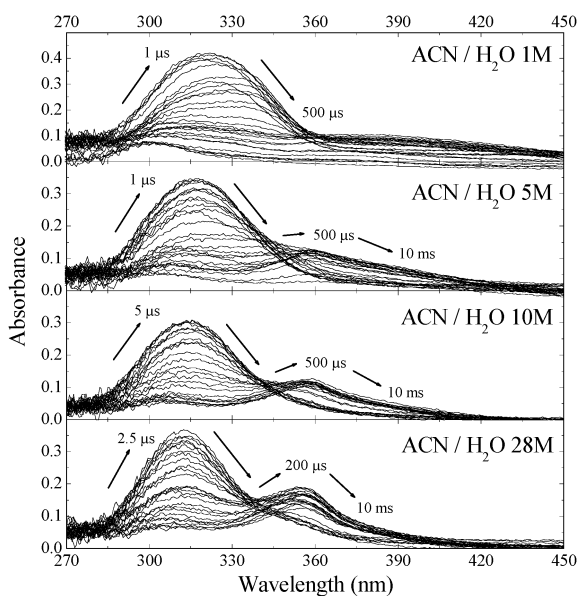


Fig. 1 Transient absorption spectra measured after the UV-photolysis of a 0.5 mM solution of 4-nitrobenzyl chloride (**1**) in the presence a sacrificial electron donor (TEA, 0.1 M) in a mixture of ACN with increasing concentrations of water (from top to bottom: 1 M, 5 M, 10 M and 28 M).

The main peak grows in a couple of microseconds and then decays in tens of microseconds (Fig. 2). Thus, the band at 320 nm could be attributed to the anion radical of the nitroaromatic compound, while the band around 390 nm corresponds to the radical. The reaction mechanism for cleavage is stepwise, as shown on Scheme 4.

With increasing concentrations of water, two main effects are observed. First, a solvatochromic effect gradually narrows both absorption bands of the anion radical and of the radical, thus increasing separation between the two bands. We also noted a slight blue-shift for both bands. In a mixture containing 28 M of water (ACN/water 50 : 50), the anion radical absorption band peaks at 312 nm (compared to 320 nm in pure ACN), while in the same mixture, the radical band is more separated from the first band and is peaking at 355 nm (compare to 390 nm in pure ACN). An isobestic point, around 345 nm,

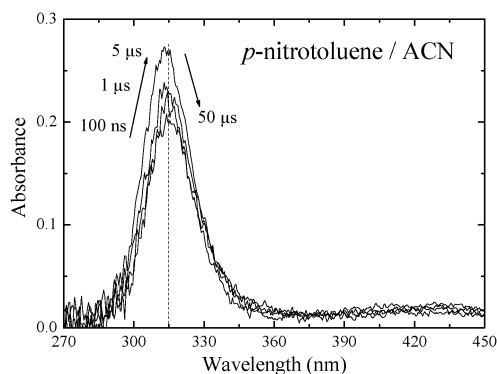
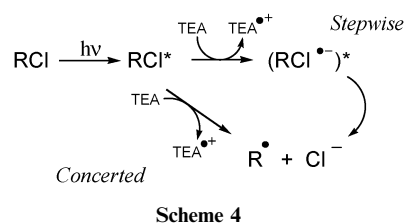


Fig. 2 Transient absorption spectrum, recorded between 10 ns and 50 μ s after the excitation laser pulse, of the 4-nitrotoluene anion radical produced by photoinduced electron transfer of a 0.25 mM solution of 4-nitrotoluene in pure ACN containing 0.1 M of TEA.



becomes clearly observable starting from a water concentration of 5 M. The rate constant for the anion radical decrease is thus directly correlated with the rate constant for radical formation (Fig. 3). One can also note that whatever the concentration of water, the two absorption bands can be observed, indicating that the two species are always formed during the reaction. The second effect is a slowing down of the unimolecular bond-breaking rate constant (Table 1). Passing from pure ACN to a mixture containing 50% of water, the first-order rate constant for the anion radical cleavage decreases from $(2.17 \pm 0.20) \times 10^5$ to $(1.3 \pm 0.2) \times 10^4$ s⁻¹. The rate constant measured by electrochemistry is 4.0×10^6 s⁻¹ in DMF⁵ and 5.7×10^6 s⁻¹ in ACN,¹⁴ whereas it was reported to be 7.6×10^3 s⁻¹ in pure water (pulse radiolysis).^{7g} The influence of water on the bond-breaking rate constant could be explained by the stabilization of the negative charge of the anion radical by the surrounding water molecules, so that the breaking of the C–Cl bond is delayed because of less favorable kinetics.^{2b,11} Water molecules also stabilize the chloride anion released during C–Cl cleavage, which should increase the cleavage rate, but the net effect is a less unstable transient.

The reduction mechanism is the same as in electrochemical experiments, with the formation of an anion radical that quickly expelled a chloride anion, leaving a nitrobenzyl radical. Whereas at very low driving force it has been shown that the mechanism switch to a concerted pathway avoiding the anion radical,¹⁴ the large driving force offered here to the reductive cleavage, thanks to the generation of an excited state of **1**, acts as a boost for the sequential mechanism to occur. In other words, the photochemical reaction is triggered under strong reductive conditions, thus providing favorable energetic conditions for the anion radical to be formed. A striking difference with electrochemical reactions is however that the

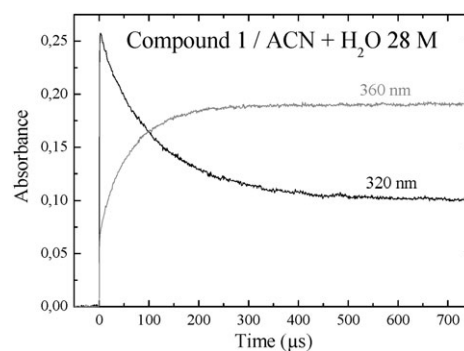


Fig. 3 Transient kinetics measured in a 0.5 mM solution of compound **1** in a mixture of ACN containing 28 M of water and 0.1 M of TEA. Traces at 320 and 360 nm correspond, respectively, to the decrease of the transient anion radical and the correlated formation of the radical issued from C–Cl bond breaking.

Table 1 Unimolecular bond-breaking rate constant, k , for compound **1** in ACN as a function of water concentration (kinetic measurements at 320 nm)

[H ₂ O]/M	0	1	5	10	28
$k/10^5 \text{ s}^{-1}$	2.17 ± 0.2	1.49 ± 0.2	0.77 ± 0.1	0.34 ± 0.05	0.13 ± 0.02

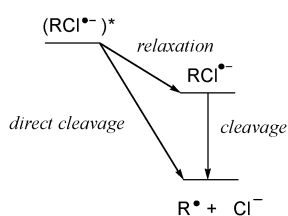
cleavage rate constant for the C–Cl bond is 20 times slower. This indicates that the excited state **1*** leads to an excited anion radical (**1**^{•−})* after electron donation from TEA, that cleaves more slowly than the ground state anion radical generated at an electrode. Cleavage of (**1**^{•−})* may thus be either controlled through relaxation to anion radical ground state or through direct fragmentation of the carbon–chloride bond at the level of the excited state (Scheme 5).

It should be noted that the addition of increasing amounts of water leads to a decrease of the bond-breaking rate constant, as already mentioned, but to a lesser extent than previously measured with similar compounds by electrochemistry. For example, adding 1 M of water into ACN leads to a decrease by a factor 10 of the dehalogenation rate of the anion radical of 3-nitrobenzylchloride (Scheme 6, left).¹¹ A 10 M concentration of water in ACN leads to a slower N–F reductive cleavage by a factor 10³ in a nitro-substituted *N*-fluorosulfonamide (Scheme 6, right),¹¹ for which the charge at the level of the anion radical is essentially located onto the nitro group. At the same time, 1 M and 10 M of added water only lead to a decrease of the C–Cl bond cleavage rate in (**1**^{•−})* by a factor of 1.5 and 6.4, respectively. It could reflect the more delocalized nature of (**1**^{•−})* as compared to the ground state and thus the lesser stabilization of the negative charge by the solvating water molecules. Alternatively, if fragmentation of (**1**^{•−})* is controlled by decay to **1**^{•−}, it would reflect the weak dependence of such deactivation to solvation conditions.

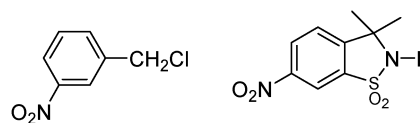
Finally, it is remarkable that depending on the reduction conditions (electrochemical, photoinduced or direct excitation of the substrate followed by a reductive quenching) and on the water content in the polar solvent (ACN, DMF), the lifetime of the anion radical may be controlled and finely tuned over two and a half orders of magnitude.

3.2 Reductive cleavage of 4-cyanobenzyl chloride and 3-cyanobenzyl chloride

4-Cyanobenzylchloride (**2**) is known to follow a concerted mechanism in DMF when reduction is initiated by cyclic voltammetry^{2h} or photochemically (electron donation from the excited state of an aromatic donor).⁴ This fundamental different behaviour from the nitro-substituted derivative could



Scheme 5



Scheme 6

be ascribed, as recalled in the introduction, to the strong electronic coupling between the diabatic states of the products, which makes the cleavage barrier for the anion radical vanish. It is interesting to speculate on the influence on the reductive mechanism of the generation of an excited state of **2**, to which electron transfer will occur, and the possibility that the mechanism may change from a purely concerted process to a sequential one, with the possible formation of an excited anion radical that would be non accessible through electrochemical reduction nor through donation from an aromatic excited donor. 3-cyanobenzylchloride (**3**) was found to follow a stepwise mechanism in DMF when initiated by electrochemical methods.^{2h} Thus, in this case, it is likely that direct excitation of **3** will lead, after one electron reduction by TEA, to the formation of an excited anion radical (**3**^{•−})*.

Pedersen *et al.* characterized the absorption spectrum of 4-cyanotoluene anion radical in DMF generated by flow electrolysis.¹³ The spectrum is very similar to those of 4-nitrotoluene anion radical (Fig. 2): a strong absorption peaking at 316 nm and another weak and large band peaking at 436 nm are present. This result led us to perform measurements at 320, 350 and 380 nm with **2** and **3**, similarly to what we have done with **1**.

Since the absorption coefficients at 308 nm are weaker for compounds **2** and **3**, we used higher concentrations (*ca.* 50 mM) than with compound **1**. However, no direct photolysis of the substrates were observed in the absence of electron donor. The transient kinetics obtained at these wavelengths for a solution of **2** in a mixture of ACN with 28 M H₂O clearly show an unique and homogeneous increase, then decrease of the whole absorption (Fig. 4, top). It should be noted that differences in the absorbance amplitude between substrates are mainly due to slightly different locations of their peak maximum. The same behavior was also observed in pure ACN. When analyzing benzyl and 4-cyanobenzyl radical absorption spectra,^{7c,15} it appears that both absorption bands are located within the same region: typical spectra show an intense absorption around 260 nm with two weaker peaks at 310 and 320 nm, respectively. Thus, there could be an overlap between the anion radical of **2** (if ever formed) and 4-cyanobenzyl radical resulting from bond breaking. In this case, one would observe a kinetic behavior revealing the presence of two different species (typically two kinetic regimes), that we did not observe. Moreover, the increase at 320 nm (Fig. 4, left), as well as at 350 and 380 nm is monoexponential and pretty slow, the maximum being reached after 4 μs whereas referenced anion radical spectra indicate a maximum reached after 1 μs or less. We can conclude that the observed species is the radical resulting from a concerted electron transfer–bond breaking process, as observed during electrochemical measurements. Increasing concentration of water up to 52 M, *i.e.* 95% of the solvent mixture (Fig. 4, bottom), has only a limited effect

on the spectra, with little shift of the whole absorption band and maybe more complex recombination reactions of the radical. The decrease of the absorption band is first-order, with a rate constant of $(2.50 \pm 0.02) \times 10^4 \text{ s}^{-1}$. This may indicate that the radical does not primarily recombine with itself but rather with another molecule such as TEA that is present in high concentration and/or with TEA deprotonated radical or cation radical, thus leading to pseudo-first order kinetics.^{12c} A detailed examination of these reactions stands beyond the scope of this paper.

Going from the 4-nitro-substituted to the 4-cyano-substituted benzyl **2** induces a major change in the reductive mechanism, which passes from a two steps pathway with the former compound to a purely concerted process with the latter. Despite direct excitation of **2**, no transient anion radical is formed, thus reinforcing the conclusions drawn from our previous electrochemical studies, suggesting that strong electronic coupling of the diabatic states of the products lead to a continuously decreasing potential hypersurface, with no locally bounded minima, *en route* to the fragmented final products.

With **3**, kinetic traces present a significant different profile as compared to those measured with **2** (Fig. 5, note also the different timescale between Fig. 4 and 5). After the initial laser flash, a rise of a couple of microseconds, reaching its maximum after roughly 2 μs , precedes a slow and general decrease of the absorption. A primary signal was repeatedly

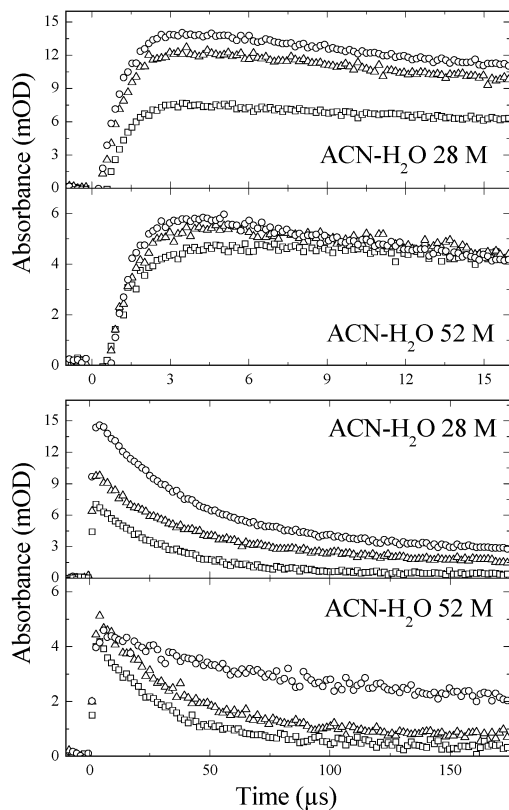


Fig. 4 Transient kinetics measured in a 50 mM solution of 4-cyanobenzylchloride (**2**) in a mixture of ACN containing 28 or 52 M of water and 0.1 M of TEA. Traces are represented, respectively, at 320 nm by open squares, at 350 nm by open circles and at 380 nm by open triangles.

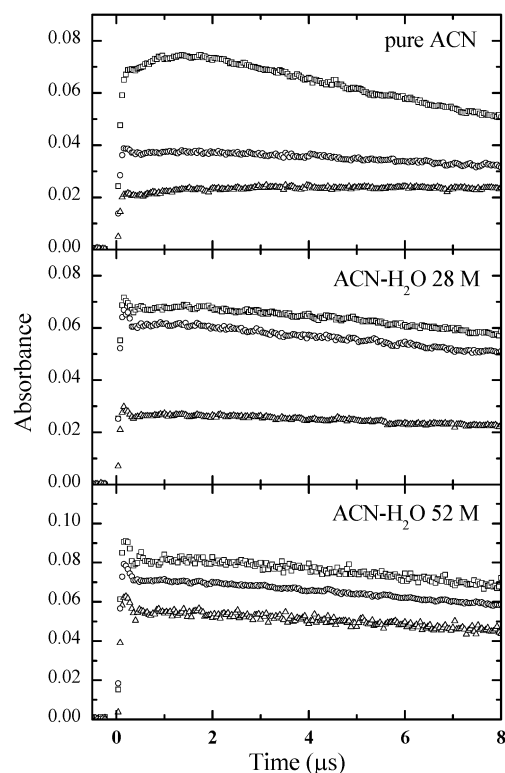


Fig. 5 Transient kinetics measured in a 50 mM solution of 3-cyanobenzylchloride (**3**) in ACN containing 0.1 M of TEA with increasing concentration of water (from top to bottom). Traces are represented, respectively, at 320 nm by open squares, at 350 nm by open circles and at 380 nm by open triangles.

observed at the very beginning of the kinetics, in the first few hundreds of nanoseconds. This signal decreases rapidly after the initial excitation and is then flood into the main, slowly increasing signal of the first microseconds. In solvent mixtures containing a high concentration of water (Fig. 5, center and bottom), all three wavelengths indicate similar time evolution. This is not the case in pure ACN where kinetics at 320 nm shows a stronger absorbance and, after a few microseconds, a slightly faster decrease. This may be due to the overlap between the absorption spectra of the anion radical (if formed) and those of the radical issued from the cleavage reaction. We have indeed seen with **1** that absorption bands are overlapping in neat acetonitrile whereas water induces a separation of the two bands (anion radical and radical).

Moreover, the initial spike is increased tenfold with increasing water concentration. This observation reveals the formation of a short lived anion radical of **3**, that further rapidly proceeds to bond cleavage with the release of a halogen ion and a radical. This primary signal is also observed in pure ACN, indicating the same mechanism is operating. The presence of water only better revealed this signal, thanks to a solvatochromic effect that narrows absorption bands and better defined its components. While **2** is concertedly reduced, the reductive cleavage of **3** thus goes through a sequential, two steps pathway, involving the formation of a very unstable excited anion radical, those lifetimes could not be obtained from our set-up. These conclusions are in agreement with previous

electrochemical experiments.^{2h} Comparing **2** and **3**, one major difference is the smaller coupling of the diabatic states of the products in the latter than in the former,^{2h} thus leaving room for a transient to survive along the reaction pathway, with an activation barrier to cross for cleavage.

4. Conclusions

The photoinduced reductive cleavage of the carbon–chlorine bond in **1** and **3** follows a sequential mechanism. The reaction was initiated by direct excitation of the substrate, and the excited state was then reduced by triethylamine. If the decay of (**3**^{•-})^{*} is too fast to be measured (with our set-up), the decay of (**1**^{•-})^{*} is close to $2.2 \times 10^5 \text{ s}^{-1}$ in pure acetonitrile, 20 times slower than in electrochemistry, illustrating the tuning of the cleavage rate. The dehalogenation reaction also slows down with increasing amounts of water, due to specific solvation of the nitro group that bears most of the negative charge at the level of the anion radical. Going to **2** induces a mechanistic change, the reduction being in this case purely concerted. Despite the large driving force offered to the reaction, no transient anion radical is formed before formation of the benzylic radical and chloride anion. These results are in agreement with electrochemical experiments and confirm previous interpretation. Indeed, they illustrate the strong electronic coupling that exists between the diabatic states of the products in the case of the *para*-cyano derivative **2**, leading to a continuously decreasing potential surface, contrary to what happen with the *meta*-cyano derivative **3**. In the case of the *para*-nitro compound **1**, the electronegativity of the nitro group is strong enough for an anion radical to be transiently formed before cleavage occurs.

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