2BPh_4: A THF/CH_2Cl_2 solution (1/1; 3 mL) of $NaBPh_4$ (42 mg, 0.12 mmol) was added to a THF/CH_2Cl_2 solution (1/1; 10 mL) of **2**BF_4 (100 mg, 0.06 mmol) and the mixture was stirred for 20 min. After concentration to ca. 6 mL hexane (8 mL) was added to form precipitates, which were collected by filtration. The solid was dissolved in CH_2Cl_2 (1.5 mL). Hexane (1 mL) was added and purple **2**BPh_4 (80 mg, 0.045 mmol, 75% yield) was obtained by crystallization at $-20\,^{\circ}C$.

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Double Photoionization of Dimethylaminobenzonitrile in Solution: A Three-Quantum Process with Intervening Chemical Step**

Martin Goez* and Valentin Zubarev

Photoionization in solution is a compelling subject of investigation because of the vast importance of the hydrated electron e^-_{aq} for chemical and biological processes.[1] At wavelengths greater than about 300 nm, more than one photon is usually needed to eject an electron from a stable molecule. This is normally realized by an absorption–absorption sequence (two consecutive absorption steps), where the second photon ionizes an electronically excited state of the substrate.

As we recently demonstrated, the insertion of an electron-transfer step between the two absorption processes can greatly facilitate two-photon ionization.[2] With this variant, the second photon ionizes the radical anion resulting from electron-transfer quenching of the excited substrate. Experimental evidence obtained so far seems to indicate that at least for aromatic ketones and quinones the actual photoionization step is intrinsically more efficient by an order of magnitude or more for the radical anion than for the excited $n\pi^*$ triplet state.[2d, 3]

Up to now, this mechanistic variant has only been explored with intermolecular quenching. When both absorption steps are to occur during the same laser flash, that is, typically within a few nanoseconds, this puts considerable constraints on the chemical system: even in the case of a diffusion-controlled electron transfer disproportionately high quencher concentrations must still be employed.[2d] The use of *intra*molecular charge transfer (ICT) is an obvious approach to overcome this difficulty. On the basis of the above experimental observation, one would expect photoionization of an excited state to be the more facile the greater its charge transfer (CT) character is.

Dimethylaminobenzonitrile (DMABN) is a classical ICT compound as far as its first excited singlet state is concerned. However, with regard to the lowest triplet state T_1 the situation is less clear. From an analysis of its deactivation pathways[4] and from the absence of an appreciable volume change in laser-induced optoacoustic spectroscopy[5] it was inferred that T_1 does not possess a pronounced CT character. In contrast, the results of time-resolved infrared measurements indicate that in T_1 a substantial negative charge is located on the cyano group, and it was proposed that there might be two closely lying triplet states, a CT and a non-CT one, with an equilibrium between them.[6]

DMABN can be photoionized in liquid solution at 266 and 308 nm; from a quadratic intensity dependence of the yield of

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$e^{\bullet}_{aq}$ at low light levels this was concluded to occur by a consecutive two-photon process.[4, 7] The starting point of the present work was our observation, made when we attempted to determine the absolute quantum yields of this photoionization to obtain some evidence as to the CT character of T_1, that this photoreaction must be considerably more complex than previously thought.

Because DMABN is hardly soluble in water, most of the measurements were carried out in micellar solutions (sodium dodecyl sulfate, SDS) with a neutral pH in the aqueous phase. As a positive side effect, this microheterogeneous environment also slows down charge recombination considerably; compared to homogeneous phase (water/methanol), we typically observed an increase of the life of $e^{\bullet}_{aq}$ by an order of magnitude. The solutions were degassed, and oxygen was excluded. Nanosecond laser-flash photolysis (excimer laser and/or Nd:YAG laser) with UV/Vis detection was used. Our setup[2b] allows one- and two-pulse (i.e., two-color) experiments.

By scavenging experiments with N_2O it was ascertained that in our system no other species besides $e^{\bullet}_{aq}$ absorbs at 830 nm. The experimentally observed optical density at that wavelength thus directly yields the electron concentration.[8] Figure 1 a shows the dependence of this concentration, relative to the starting concentration c_0 of DMABN, on the laser intensity in a single-pulse experiment using 308 nm light.

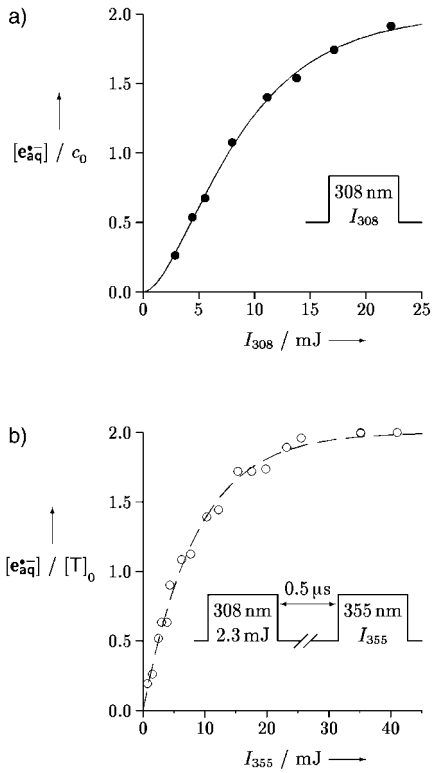

Figure 1. Photoionization of 2.7×10^{-5} M DMABN in aqueous SDS solution (0.031 M). The laser pulse sequences used are displayed as insets. Pulse widths are about 20 ns for 308 nm and about 5 ns for 355 nm. Shown are the concentrations of the hydrated electron $[e^{\bullet}_{aq}]$ relative to the starting concentration of DMABN c_0 in the single-pulse experiment (a), and relative to the starting concentration of the triplet $[T]_0$ in the two-pulse experiment (b) as functions of the laser intensity I_{308} and I_{355}, respectively. The fit curves are explained in the text.

The surprising result is that, quite obviously, *two electrons* are produced from *one substrate molecule*.

At low light levels, where photoionization is negligible, a transient spectrum is obtained under our experimental conditions that is identical to that reported[9] for the lowest triplet state T_1 of DMABN apart from a red-shift by about 30 nm, which we attribute to the different polarity in our case (aqueous micellar environment versus ethanol). The triplet has a half life of 90 µs under these conditions. With increasing laser power, its signal (absorption maximum at 390 nm, which is not obscured by peaks of other species) first increases and then decreases again, indicating that the excited state preceding photoionization in our experiments is T_1 of DMABN.

To gain more information about the photoionization, we carried out two-pulse experiments. The first pulse, at 308 nm, was attenuated so as to produce only a very small amount of electrons (about 1 % of c_0) but a substantial amount of the triplet. The known extinction coefficient[9] of the triplet at its absorption maximum allowed calculation of its absolute concentration $[T]_0$, which was found to be about 12 % of c_0. After a delay of 500 ns, a second pulse was applied, this time at 355 nm. The absorbance of DMABN at this wavelength is about 40 times lower than at 308 nm, and by control experiments it was ensured that even at the highest available laser power only an insignificant amount of $e^{\bullet}_{aq}$ is obtained by the single-pulse scheme at 355 nm. However, in the two-pulse experiment, complete conversion of the triplet into $e^{\bullet}_{aq}$ can be achieved. Figure 1 b depicts the dependence of the electron yield, relative to $[T]_0$, on the intensity of the second pulse. It is clearly seen that, in line with the result of the single-pulse experiment of Figure 1 a, one molecule of the triplet ultimately yields two electrons.

A direct ejection of two electrons from triplet DMABN is very improbable at the wavelengths used because it would lead to a chemical species of rather high energy (a dication). It is much more reasonable to assume two successive ionizations with an intervening chemical step, where the first electron stems from the triplet and the second from another intermediate that is produced by a secondary chemical transformation of the radical cation resulting from ionization of the triplet. The chemical transformation of the radical cation to give an ionizable species must be fast on the timescale of the laser pulses, otherwise complete ionization, as is found in both the single- and the two-pulse experiments, could not occur; for this reason, one would not expect the radical cation to be observable in our experiments but only the subsequent species. Spectra taken at moderate light intensity in N_2O saturated solution (to scavenge the electron) indeed revealed the presence of two other transients, besides the triplet, with absorbance maxima at 370 nm and 495 nm. From the intensity dependences, the former must correspond to an ionizable intermediate and the latter to the final photoproduct. The overall reaction thus proceeds according to Scheme 1, where G, T, C, X, and P are ground state, triplet, (unobservable) radical cation, secondary ionizable species, and final product, respectively.

The three photoreactions can be described as first-order processes with rate constants k_1, k_2, and k_3, because the

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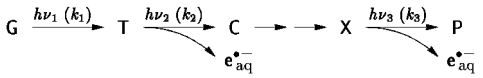


Scheme 1. Overall reaction scheme for the photoionization. For explanation of the symbols, see text.

solutions in our experiments are optically thin. Since C can be ignored in the kinetic equations, the actual shape of the ionizing pulse does not play any role, and the electron yield is completely determined by the total intensity I, with k_1 to k_3 possessing the dimension of a reciprocal energy.[2d] The result for the two-pulse experiment, that is, electron concentration $[e^{\bullet}_{aq}]$ relative to concentration $[T]_0$ of the triplet after the first pulse, is given by Equation (1).

$$\frac{e^{\bullet}_{aq}}{[T]_0} = 2 - \frac{(2k_3 - k_2)\exp(-k_2 I) - k_2 \exp(-k_3 I)}{k_2 - k_3} \quad (1)$$

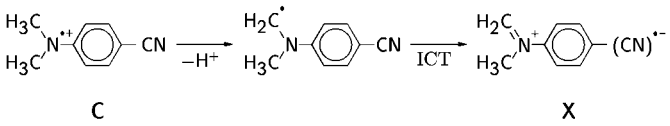
A fit of Equation (1) to the data is shown in Figure 1b. The fit is very well-conditioned, with the initial slope of the curve being determined by k_2 alone. From each of the constants k_i, the quantum yield of the respective photoionization ϕ_{ion} can be calculated if the absolute extinction coefficient at the excitation wavelength λ_{exc} is known.[2d] For triplet DMABN, ε at λ_{exc} was obtained from the spectrum taken at sufficiently low light levels, where the amount of photoionization is negligible, and ε_{max} given in the literature.[9] The extinction coefficient of X at λ_{exc} followed from its observed absorbance and its concentration, which was measured by converting it completely into $e^{\bullet}_{aq}$. With these data, we arrive at a value of ϕ_{ion} for triplet DMABN of 0.48 at 355 nm. The very high efficiency of this ionization seems to indicate considerable charge-transfer character of the DMABN triplet, which would corroborate the conclusions drawn from transient infrared experiments.[6] For the ionization of X, a quantum yield of 0.13 is obtained.

On the basis of Scheme 1, a closed form expression can also be derived for the intensity dependence in the one-pulse experiment [Eq. (2)].

$$\frac{[e^{\bullet}_{aq}]}{c_0} = 2 + \frac{k_2(k_1 - 2k_3)}{(k_1 - k_2)(k_1 - k_3)}\exp(-k_1 I) - \frac{k_1(k_2 - 2k_3)}{(k_1 - k_2)(k_2 - k_3)} \cdot \exp(-k_2 I) - \frac{k_1 k_2}{(k_1 - k_3)(k_2 - k_3)}\exp(-k_3 I) \quad (2)$$

A fit of Equation (2) to the data (compare Figure 1a) was found to be less well-conditioned owing to a pronounced cross correlation between the parameters but gave quantum yields ϕ_{ion} similar to those in the two-pulse experiment. When only low light levels are being used, as in the earlier experiments reported,[4, 7] the mechanism in Scheme 1 is indistinguishable from a usual two-photon ionization: under these conditions, a quadratic intensity dependence of the electron yield is found in both cases because $(k_1 k_2)I^2/2$ is the first nonvanishing term of the respective series expansion (of Equation (2), and of Equation (7) of ref. [2d]). The identical coefficient of I^2 reflects the chemically obvious fact that at low light levels photoionization of X, which is a late intermediate in the reaction sequence of Scheme 1, is negligible, whereas at high levels it contributes as much to the electron yield as does photoionization of the triplet, an early intermediate.

Lastly, we turn to the intriguing question: what species X is ionized in the final step of the reaction? From the findings presented here, and by comparison with related *inter*-molecular photoionizations involving alphatic amines,[2b] we conclude that the reaction C→X proceeds as shown in Scheme 2. The primary result of photoionization of the ICT triplet must be the nitrogen-centered radical cation of



Scheme 2. Intervening chemical reactions in DMABN photoionization.

DMABN.[10] It is known that such aminium radical cations are easily deprotonated at an α carbon to give α-amino alkyl radicals,[11] and that the latter are strongly reducing species.[12] The benzonitrile radical anion moiety that was already contained in the charge-separated triplet is thus regenerated by another ICT process, and is then available for a second photoionization. This mechanism is corroborated by two experimental observations. First, in water/alcohol mixtures, rather than a micellar environment, a slight pH dependence is found: at pH 12 two electrons per molecule of DMABN are formed but at pH 6, where deprotonation of C would be expected to be slower, this limiting value is not quite reached, which would indicate that the deprotonation becomes rate-limiting. Second, with *para*-aminobenzonitrile, where this particular deprotonation is no longer possible, only one electron per substrate molecule is indeed obtained (see also ref. [10]).

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