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Photoionization via Absorption/Electron Transfer/ Absorption Studied by Two-Pulse Two-Color Laser Flash Photolysis

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We have recently reported[1] on a new and efficient pathway to hydrated electrons ($e_{aq}^{\bullet-}$) under laser flash photolysis conditions, which is shown in Chart 1. The characteristic feature of this two-photon ionization is that the second photon is not absorbed by an excited singlet or triplet state of the substrate but by a radical ion produced by electron-transfer quenching of that state. One reason for the efficiency of this mechanism is the longer life of radical ions compared to that of excited states. The photophysics and photochemistry of radicals or radical ions in solution have received continuous attention over the last decades.[2]

In the experiments of ref 1, the two photons were absorbed during the same laser flash. It is evident that this puts severe constraints on the chemistry of the systems, above all because rate constants and quencher concentrations must be chosen to yield a sufficient concentration of radical ions within some 20 ns, the duration of a typical excimer laser pulse. Detailed investigation of the ionization proper is impossible in this way because only the combined effect of the whole reaction sequence is observable. Much more specific information is accessible by two-pulse experiments,[2b−e,g,h,l] i.e., when the two excitation steps are separated in time and can be carried out at different wavelengths. This approach is pursued in the present work.

Figure 1 shows experimental examples for the system 4-carboxybenzophenone/triethylamine (CB/TEA) in water at pH 12. For clarity, Table 1 lists the relevant reactions with their rate constants.

The first laser pulse (at 308 nm) excites the ketone. The fast rise of the 650-nm absorption (top trace) following this pulse is due to $CB^{\bullet-}$, which is produced almost quantitatively within 400 ns through electron-transfer[3] quenching of ^3CB by TEA (see reactions 1a and 1b in Table 1). At the pH value of our experiments, the reversible protonation equilibrium between $CB^{\bullet-}$ and the neutral ketyl radical $CBH^{\bullet}$ (reactions 2a and 2b) lies far to the side of $CB^{\bullet-}$. Hence, $CBH^{\bullet}$ need not be considered under our experimental conditions.

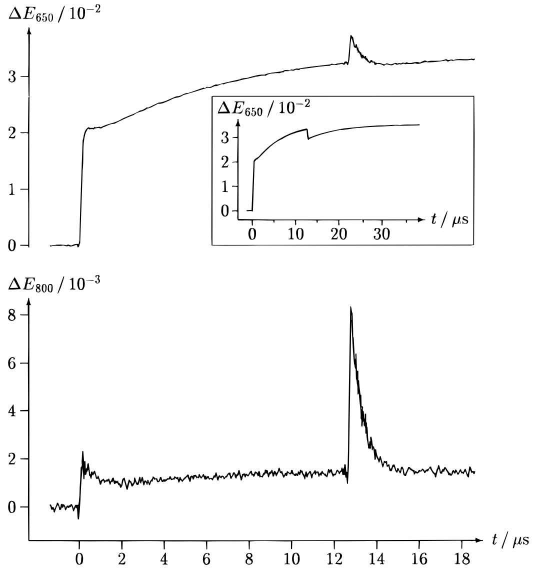

Figure 1. Two-color two-pulse laser flash photolysis in the system 4-carboxybenzophenone/triethylamine (CB/TEA) in aqueous solution. Experimental conditions: $\lambda_1 = 308$ nm, $I_1 = 4.8$ mJ/pulse, $\lambda_2 = 387.5$ nm, $I_2 = 1.6$ mJ/pulse, 12.5 μs delay between the pulses, pulse widths 20 ns, [CB] = 8.13 × 10^{-5} M, [TEA] = 5 × 10^{-3} M, pH 12, 1000 transients averaged. Top: $\lambda_{obs} = 650$ nm. Bottom: $\lambda_{obs} = 800$ nm. The inset at the top shows the outcome of the same experiment ($\lambda_{obs} = 650$ nm) but with the solution saturated with N_2O.

Chart 1

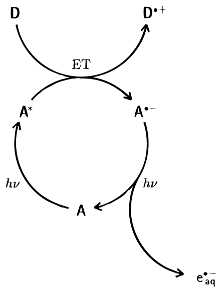

Table 1. Relevant Reactions in the System 4-Carboxybenzophenone/Triethylamine (CB/TEA) and Their Rates

	reaction	rate constant
1a	$^3CB \rightarrow CB$	1/(5.3 μs)
1b	$^3CB + TEA \rightarrow CB^{\bullet-} + TEA^{\bullet+}$	1.1 × 10^9 M^{-1} s^{-1}
2a	$CB^{\bullet-} + H_2O \rightarrow CBH^{\bullet} + HO^-$	2.5 × 10^2 M^{-1} s^{-1} [a]
2b	$CBH^{\bullet} + HO^- \rightarrow CB^{\bullet-} + H_2O$	8.7 × 10^9 M^{-1} s^{-1} [a]
3a	$TEA^{\bullet+} \rightarrow TEA^{\bullet} + H^+$	3.3 × 10^5 s^{-1} [b]
3b	$TEA^{\bullet}$ + CB → iminium cation + $CB^{\bullet-}$	3.4 × 10^9 M^{-1} s^{-1} [b]
4	$e_{aq}^{\bullet-} + CB \rightarrow CB^{\bullet-} + nH_2O$	2.2 × 10^{10} M^{-1} s^{-1}
5a	$e_{aq}^{\bullet-} + N_2O \rightarrow N_2 + HO^{\bullet} + HO^- + (n-1)H_2O$	8.7 × 10^9 M^{-1} s^{-1} [c]
5b	$HO^{\bullet} + TEA \rightarrow H_2O + TEA^{\bullet}$	1.1 × 10^{10} M^{-1} s^{-1} [d]

[a] Bobrowski, K.; Marciniak, B. *Radiat. Phys. Chem.* **1994**, *43*, 361−364. [b] Apparent rate constant, see ref 5. [c] Reference 8, $[N_2O]_{sat} \approx 0.02$ M. [d] Reference 9.

The subsequent slow growth of the 650-nm absorption is caused by secondary reactions of the quencher-based radicals: The initially formed radical cations $TEA^{\bullet+}$ are deprotonated (reaction 3a), yielding α-aminoalkyl radicals $TEA^{\bullet}$; the latter are strongly reducing species,[4] which undergo electron transfer with ground-state CB (reaction 3b) to give $CB^{\bullet-}$ and an iminium cation. Both of these processes take place on a microsecond time scale under the experimental conditions of Figure 1.[5] Neither the iminium

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[2] For instance, see: (a) Fox, M. A. *Chem. Rev.* **1979** *79*, 253−273. (b) Hilinski, E. F.; Huppert, D.; Kelley, D. F.; Milton, S. V.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1984**, *106*, 1951−1957. (c) Nagarajan, V.; Fessenden, R. W. *Chem. Phys. Lett.* **1984**, *112*, 207−211. (d) Nagarajan, V.; Fessenden, R. W. *J. Phys. Chem.* **1985**, *89*, 2330−2335. (e) Scaiano, J. C.; Johnston, L. J.; McGimpsey, W. G.; Weir, D. *Acc. Chem. Res.* **1988**, *21*, 22−29. (f) Eriksen, J. In *Photoinduced Electron Transfer. Part A. Conceptual Basis*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; pp 391−408. (g) Redmont, R. W.; Wayner, D. D. M.; Kanabus-Kaminska, J. M.; Scaiano, J. C. *J. Phys. Chem.* **1989**, *93*, 6397−6401. (h) Redmont, R. W.; Scaiano, J. C.; Johnston, L. J. *J. Am. Chem. Soc.* **1990**, *112*, 398−402. (i) Fujita, M.; Ishada, A.; Majima, T.; Takamuku, S. *J. Phys. Chem.* **1996**, *100*, 5382−5387. (j) Majima, T.; Fukui, M.; Ishada, A.; Takamuku, S. *J. Phys. Chem.* **1996**, *100*, 8913−8919. (k) Cook, A. R.; Curtiss, L. A.; Miller, J. R. *J. Am. Chem. Soc.* **1997**, *119*, 5729−5734. (l) Faria, J. L.; Steenken, S. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1153−1159.

[3] Cohen, S. G.; Ojanpera, S. *J. Am. Chem. Soc.* **1975**, *97*, 5633−5634.

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cation nor its decay product *N*,*N*-diethylvinylamine, which is stable for several seconds,[6] possesses an absorption above 300 nm.[7]

At the moment of the second flash (12.5 μs after the first one), $TEA^{\bullet}$ has thus been consumed almost completely. In any case, the amine-derived species do not absorb significantly at the wavelength chosen for that pulse (387.5 nm); neither does the starting ketone. However, $CB^{\bullet-}$ can be excited by it. The formation of hydrated electrons $e_{aq}^{\bullet-}$ by the second pulse manifests itself by a transient absorption at 800 nm (bottom, Figure 1), and also in the 650-nm trace (top) because $e_{aq}^{\bullet-}$ possesses a larger extinction coefficient at that wavelength than does $CB^{\bullet-}$.

Variation of the reactant concentrations indicates that the subsequent rapid decrease of the electron signal is caused by the reaction between $e_{aq}^{\bullet-}$ and CB (reaction 4), for which a rate constant of 2.2×10^{10} M^{-1} s^{-1} is obtained. That $e_{aq}^{\bullet-}$ decays predominantly through this channel is corroborated by the fact that the 650-nm absorption falls back to exactly the same level as before the second pulse.

The maximum concentration of $e_{aq}^{\bullet-}$ is found to be 2.5×10^{-6} M from the known extinction coefficient ($\epsilon_{800} = 14\,000$ M^{-1} cm^{-1}).[8] The degree of conversion of $CB^{\bullet-}$ into $e_{aq}^{\bullet-}$ can be easily determined by saturating the solution with N_2O, which scavenges $e_{aq}^{\bullet-}$ quantitatively within the duration of the laser pulse (reaction 5a). This experiment is shown as inset at the top of Figure 1. That N_2O does not react with ^3CB, $CB^{\bullet-}$, $TEA^{\bullet+}$, or $TEA^{\bullet}$ follows from the observation that the concentrations of $CB^{\bullet-}$ at any time up to the second laser pulse are identical in the measurements with and without N_2O. From the transient dip in this trace, it can be directly concluded that 13% of the radical anions are photoionized by the second laser pulse despite its small energy. Interestingly, the decay time of this dip is identical within experimental error to the rise time of the above mentioned slow growth of $CB^{\bullet-}$ on a microsecond time scale, and essentially the same final value of the absorbance is reached in the experiments with and without N_2O. This is readily explained when one considers that N_2O converts $e_{aq}^{\bullet-}$ into the radical anion $HO^{\bullet}$ which is immediately scavenged by TEA to give $TEA^{\bullet}$ (see reactions 5a and 5b).[9] As before, the latter then reduces ground-state CB to its radical anion.

As seen in the bottom trace, a small amount of $e_{aq}^{\bullet-}$ is also produced by the first laser pulse, about a fifth of that resulting from the second pulse. Control experiments without TEA bear out that this is not due to photoionization of ^3CB but to photoionization of $CB^{\bullet-}$ formed during the 308-nm pulse. This can occur because at the concentrations employed some 15% of ^3CB are quenched during that pulse, the extinction coefficient of $CB^{\bullet-}$ at 308 nm is more than one-half of that at 387.5 nm and the intensity of the 308-nm pulse is three times higher than that of the 387.5-nm pulse. On the other hand, these results show that photoionization of the radical anion is much more efficient than its photoionization of the triplet despite the fact that at 308 nm the extinction coefficient of ^3CB lies above that of $CB^{\bullet-}$.

Although under our experimental conditions (8×10^{16} photons cm^{-2} at 387.5 nm) every molecule of $CB^{\bullet-}$ is excited about two times on the average during the second laser pulse, no indication of saturation was found. Hence, deactivation of excited $CB^{\bullet-}$ must be considerably faster than 10 ns. From the amount of electrons formed and the amount of light absorbed, the quantum yield of ionization of excited $CB^{\bullet-}$ was estimated to be about 0.05.[10]

The standard electrode potential of the hydrated electron is −2.77 V,[8] and that of the couple ($CB/CB^{\bullet-}$) is −1.13 V.[11] Thermodynamically, ionization of $CB^{\bullet-}$ would thus be feasible up to about 750 nm. To obtain information about which electronic state of $CB^{\bullet-}$ can be ionized, the wavelength of the second laser pulse was varied. No hydrated electrons were observed when the long-wave absorption band (maximum at 650 nm) was excited at 580 nm, although $\epsilon_{387.5}$ and ϵ_{580} of $CB^{\bullet-}$ differ by less than 10% and the laser intensity at 580 nm was higher than at 387.5 nm. When the second laser was operated at 480 nm, which is the onset of that absorption band, no electrons were detected either; this experiment, however, had a lower sensitivity because for $CB^{\bullet-}$ ϵ_{480} is only about one-fifth of $\epsilon_{387.5}$. On the other hand, 387.5 nm, where photoionization is pronounced, is practically the edge of the short-wave absorption band of $CB^{\bullet-}$. These findings seem to indicate that ionization cannot occur from the first excited doublet state of $CB^{\bullet-}$, whereas it is feasible from the second one.

Photoionization of the quencher-derived radical $TEA^{\bullet}$ must be even easier thermodynamically because $\Delta G°$ for electron transfer from $TEA^{\bullet}$ to CB is negative. Moreover, at 308 nm, the absorption of $TEA^{\bullet}$ is no longer negligible ($\epsilon_{308} = 1300$ M^{-1} cm^{-1}).[9] On these grounds, the question arises whether $TEA^{\bullet}$ can be ionized in addition to $CB^{\bullet-}$. Single-flash measurements, as were performed in ref 1 for systems such as 1,5-anthraquinonedisulfonate/TEA, do not allow a distinction. However, an answer can be obtained with the two-pulse scheme of this work, when both laser pulses are set to 308 nm and the delay between them is varied. With a long delay, no $TEA^{\bullet}$ is present anymore, so $e_{aq}^{\bullet-}$ can only stem from $CB^{\bullet-}$. After 2−3 μs on the other hand, the ratio $[TEA^{\bullet}]:[CB^{\bullet-}]$ has reached its maximum value of 0.2 under the experimental conditions of Figure 1. By control experiments, it was ensured that for given intensity of the second laser pulse the amount of $e_{aq}^{\bullet-}$ is linearly dependent on the concentration of $CB^{\bullet-}$, which holds because the samples are optically thin and saturation effects are absent. Comparison of the traces obtained with long and short delays shows that the intensity ratio of $[e_{aq}^{\bullet-}]$ in these two cases cannot be accounted for by photoionization of $CB^{\bullet-}$ alone; photoionization of $TEA^{\bullet}$ also participates with a quantum yield that is estimated to be about 50% higher.

These examples demonstrate that the two-pulse scheme yields considerably more information about photoionization via the absorption/electron-transfer/absorption pathway than do single-flash measurements. It is obvious that the combination of this method and this mechanism should also provide a convenient tool for the generation of $e_{aq}^{\bullet-}$ in a time-resolved experiment, which can be tailored to a particular application by choosing appropriate quenchers, concentrations, wavelengths, and delay times. Compared to pulse radiolysis, this method possesses the advantages that optical absorption is more specific than is absorption of ionizing radiation, that homogeneous distributions of $e_{aq}^{\bullet-}$ are obtained, and that the large number of potentially reactive intermediates produced by radiolysis is avoided. This should considerably reduce the complexity of reaction systems investigated in this way.

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(5) Fits of the experimental traces to the pertaining reaction scheme gave rate constants of 3.3×10^5 s^{-1} and 3.4×10^9 $M^{-1}s^{-1}$ for the transformation $TEA^{\bullet+} \rightarrow TEA^{\bullet}$ and the reduction of CB by $TEA^{\bullet}$, respectively. As the final absorbance of $CB^{\bullet-}$ is noticeably smaller than twice the value of the absorbance immediately after quenching of ^3CB, additional decay channels of $TEA^{\bullet+}$ or $TEA^{\bullet}$ or both must exist, which are contained in these apparent rate constants.

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