Photoionization

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Counterintuitive Influence of Protonation on Radical-Anion Photoionization

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The long-standing interest in photoionization has recently received a boost by the recognition that prehydrated electrons (that is, electronically excited states of hydrated electrons $e_{aq}^{\bullet-}$, which are precursors to $e_{aq}^{\bullet-}$ in photoionizations, live for several hundreds of fs, and possess energies of about 160 kJ mol^{-1} above that of $e_{aq}^{\bullet-}$)[1] can cause reductive bond breaks in nucleotides[2] as well as reductive strand breaks of DNA.[3] It would have far-reaching implications if these processes could occur by sunlight. "Green-light photoionizations" are very unlikely to be direct, but an indirect reaction sequence via a metastable intermediate, for example a radical anion,[4] produced by one photon and ionized by another strongly reduces both their energy and their intensity demands. The present study was prompted by the surprising observation that in these two-step photoionizations small structural and electronic changes of the intermediate can strongly influence the yield of hydrated electrons; for instance, the ionization efficiency is about an order of magnitude greater for the radical anions of aromatic ketones than for their triplets.[5–7] In this work, we explore the effect of a protonation by comparing the radical anion M$^{\bullet-}$ and the ketyl radical MH$^{\bullet}$ of the model compound 4-chlorobenzophenone. Such a comparison of this easily accessible acid–base pair never seems to have been attempted despite the popularity of benzophenones in photochemistry. Chemical intuition would predict the photoionization of M$^{\bullet-}$ to be much easier than that of MH$^{\bullet}$, but we found the opposite order with green light.

The two-step character of these photoreactions naturally suggests two-flash laser photolysis for their investigation: A first flash prepares the desired intermediate, a second flash of different wavelength then ionizes it. We chose 4-chlorobenzophenone as the substrate because (see Section 2 of the Supporting Information) the absorption maximum of its ground state M perfectly matches the fourth harmonic (266 nm) of an Nd:YAG laser, while for both radical intermediates the visible ($D_0 \rightarrow D_1$) and near-UV ($D_0 \rightarrow D_2$) transitions can be selectively excited with the second (532 nm) and third (355 nm) harmonic of that laser, with very similar extinction coefficients of M$^{\bullet-}$ and MH$^{\bullet}$ at each of these two excitation wavelengths.

Figure 1 displays representative concentration traces in 532 nm photoionizations of these radicals. (Experimental and corroborative details are given in the Supporting Information, Sections 1 and 2). A weak 266 nm flash converts about half of the substrate into the triplet ^{3}M but only negligibly photoionizes that intermediate. To keep conditions as similar as possible, we prepared both M$^{\bullet-}$ and MH$^{\bullet}$ from ^{3}M using the same quencher, isopropanol, but at different pH. Quenching is practically complete at the isopropanol concentration employed (2.7 M). The initially formed radical MH$^{\bullet}$ persists at natural pH (pH ≈ 7), whereas in strongly basic medium (pH > 12) its deprotonation instantaneously and quantitatively yields M$^{\bullet-}$. After a short delay, the respective intermediate is subjected to a second laser flash (532 nm), which is only absorbed by M$^{\bullet-}$ or MH$^{\bullet}$. As is clearly perceived in Figure 1, MH$^{\bullet}$ both affords about ten times the amount of $e_{aq}^{\bullet-}$ and exhibits about ten times the amount of bleaching as does M$^{\bullet-}$, even though only a lower (by 10%) concentration of MH$^{\bullet}$ is available for photolysis owing to its faster decay, which overcompensates its marginally higher (by 6%) extinction coefficient ε_{532}. Hence, the green-light photoionization of MH$^{\bullet}$ is intrinsically more efficient than that of M$^{\bullet-}$ by one order of magnitude. This effect cannot be explained at all by the energetics (see Section 3 of the Supporting Information), which would rather suggest the reverse: The radical anion is a much stronger base than the ground-state ketone, with the difference in their pK_a values making the ionization of M$^{\bullet-}$ more favorable than that of MH$^{\bullet}$ by as much as 90 kJ mol^{-1} (monophotonic) or 50 kJ mol^{-1} (biphotonic).

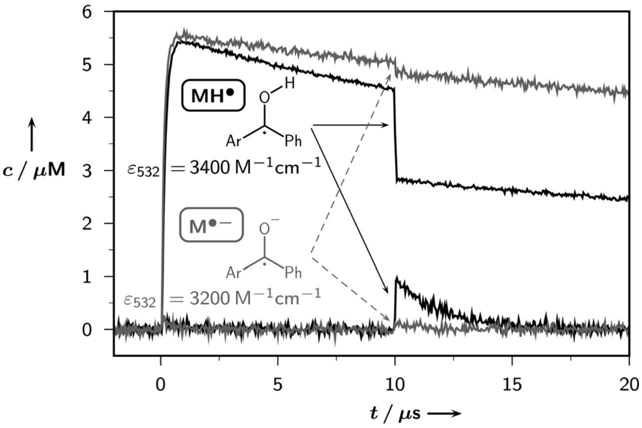

Figure 1. Experimental concentration traces in the green-light photoionizations of 10.8 μM 4-chlorobenzophenone via the ketyl radical MH$^{\bullet}$ (black) and the radical anion M$^{\bullet-}$ (gray). Lower two traces, hydrated electron $e_{aq}^{\bullet-}$; upper two traces, respective radical intermediate. Reaction medium: 2.7 M aqueous isopropanol, pH 7.5 (MH$^{\bullet}$) or 12.5 (M$^{\bullet-}$). Preparing laser flash: 266 nm, 34 mJ cm^{-2}, at 0 μs; photoionizing laser flash: 532 nm, 841 mJ cm^{-2}, at 10 μs. For further details, see the text and Sections 1 and 2 of the Supporting Information.

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More insight is obtained from the intensity dependences in green-light and near-UV photolysis (Figure 2; see also Sections 4 and 5 of the Supporting Information). With the latter, the measurements had to be corrected for radical regeneration from M by the ionizing pulse, and a different quencher had to be used in the case of M$^{\bullet -}$. In contrast to 532 nm, M$^{\bullet -}$ is photoionized efficiently at 355 nm; that ionization is monophotonic. For MH$^{\bullet}$, the ionization is biphotonic at both wavelengths. The energetics provide a natural rationalization of this change in mechanism, as explained in Section 3 of the Supporting Information. In view of its mechanistic disadvantage and its slightly lower extinction coefficient it is significant that at 355 nm MH$^{\bullet}$ still yields more than half the amount of $e_{aq}^{\bullet -}$ than does M$^{\bullet -}$.

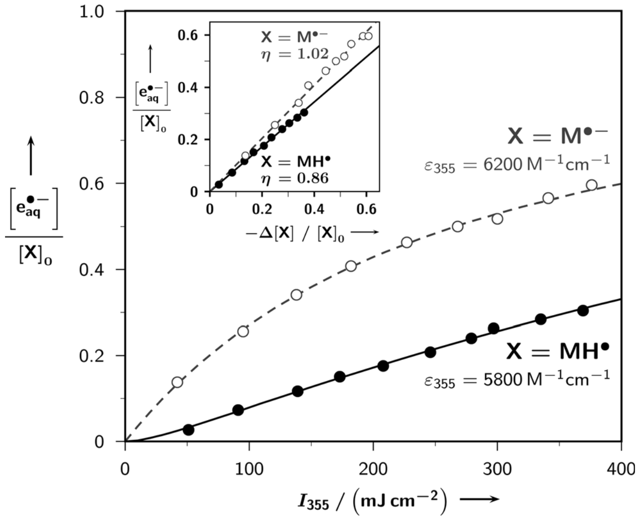

Figure 2. Near-UV photoionizations of the radical anion M$^{\bullet -}$ and the ketyl radical MH$^{\bullet}$. Experimental conditions for M$^{\bullet -}$ (MH$^{\bullet}$): substrate concentration, 10.5 μM (10.0 μM); quencher, 50 mM DABCO (2.7 M isopropanol); first pulse at 266 nm, 32 mJ cm^{-2} (34 mJ cm^{-2}); inter-pulse delay, 2 μs (8 μs). Solvent: 2.7 M aqueous isopropanol; pulse duration: 4 ns. Main plot: intensity dependences of the electron concentration, relative to the concentration of the respective radical X immediately before the photoionizing flash (4.65 μM in both cases), and best-fit functions given in Section 4 of the Supporting Information. Gray dashed curve: M$^{\bullet -}$, monophotonic model, Equations (S6)–(S7); fixed parameter: $\kappa_{01} = 0.13$ cm^2 mJ^{-1} [calculated from Equation (S10)]. Black solid curve: MH$^{\bullet}$, biphotonic model, Equations (S8)–(S9), global fit for photoionization at 532 nm and 355 nm; fixed parameter at 355 nm: $\kappa_{01} = 0.12$ cm^2 mJ^{-1} [Eq. (S10)]. Inset: electron concentrations as functions of radical bleaching. From the slopes, gross photoionization efficiencies η of 1 (M$^{\bullet -}$) and 0.86 (MH$^{\bullet}$) result. For best-fit parameters and further details, see the text.

These intensity dependences give an excited-state (D_1) lifetime of 0.38 ns for MH$^{\bullet}$ in our solvent, almost ten times shorter than in benzene (3.3 ns),[8] which agrees very well with the observation for the unsubstituted diphenyl ketyl radical that hydrogen-bond donating solvents accelerate the non-radiative $D_1 \rightarrow D_0$ decay by an order of magnitude.[9] This involvement of hydrogen bonds also explains our much higher ionization efficiency (η_{532}, 0.64; η_{355}, 0.86) compared to previous results in acetonitrile.[10] For M$^{\bullet -}$, ionization is even seen to be the only chemical deactivation pathway of the upper excited state. The linearity of the plots in the inset of Figure 2 shows that in our system bleaching and electron formation occur in the same upper excited state.

Furthermore, the data for MH$^{\bullet}$ gives the light-dependent rate of the ionization proper, κ_x. If the extinction coefficient of D_1 at the ionization wavelength were known, the quantum yield of the photoionization step would be directly obtained from κ_x. No calibrated spectrum of D_1 is available, but from the published uncalibrated spectrum in benzene,[8] which does not appear to be strongly solvent-dependent,[9] a ratio of extinction coefficients at 532 nm and 355 nm of about 1:3 can be extracted. The observed ratio of κ_x in our experiments is 1:2.6, which seems to indicate that the quantum yield of photoionization proper is very similar at these two wavelengths; it would be slightly higher than 0.01 if the extinction coefficient of D_1 were the same as that of D_0. For M$^{\bullet -}$, the data give a lifetime of the upper excited state of 46 ps, and a photoionization quantum yield of 0.03.

As has emerged, the energy balance of photoionization only controls whether, and by which mechanism, it is basically feasible, but is no help in predicting its efficiency, in particular why green-light photoionization is so much easier for MH$^{\bullet}$ than for M$^{\bullet -}$. A much shorter life of D_1 in the case of M$^{\bullet -}$ might provide an explanation. The excited-state dynamics of radical anions in condensed phase are poorly understood, and widely differing lifetimes have been reported for structurally and electronically similar compounds (benzoquinone, 63 ns;[11] anthraquinone, 70 ps[12]). Although the lifetime of 46 ps that we found for the autoionizing D_2 state of M$^{\bullet -}$ would suggest that the much lower-lying D_1 state is also much longer-lived, a definitive answer is not possible at present. However, all the observed effects can also be explained consistently by another controlling factor, namely the state symmetry of the radical absorbing the ionizing photon.

Quantum-mechanical calculations (for details, see Section 6 of the Supporting Information) show that neither the 4-chloro substituent nor a protonation of the oxygen atom disturbs the symmetry of the orbitals surrounding the SOMO to a significant degree; because the local symmetry of unsubstituted benzophenone is thus retained, an analysis in C_{2v} is permissible.

The photoionization process $D_n \xrightarrow{h\nu} GS + e_{aq}^{\bullet -}$, where D_n is the state of M$^{\bullet -}$ or MH$^{\bullet}$ to be photoionized and GS is the ground state M or MH^{+} accompanying electron formation, is described by the matrix element of Equation (1):

$$\langle \psi(GS)\psi(e_{aq}^{\bullet -})\,|\mu|\,\psi(D_n)\rangle \qquad (1)$$

in which $\psi(X)$ and μ represent the wavefunction of species X and the electrical dipole operator. Both $e_{aq}^{\bullet -}$[13] and the resulting ground state of the substrate, be it protonated or not, possess A_1 symmetry, and the same must thus hold for the autoionizing states of M$^{\bullet -}$ or MH$^{\bullet}$. Hence, for the ionization to be symmetry allowed, the doublet state absorbing the final photon must have the same symmetry as the transition operator μ, that is, A_1, B_1 or B_2. All the molecular orbitals relevant for the visible and near-UV transitions belong to the π system, so can only fall into class A_2 (antiphase linear combinations of the benzene π and π* orbitals, with a node at the C–O group) or B_1 (in-phase linear combinations of those orbitals with the π* orbital of C–O). Photoionizing a state of the former symmetry is forbidden, of the latter allowed.

The doublet ground state D_0 has symmetry B_1 in both cases. However, the solvatochromism shows the electronic nature of D_1, the state to be ionized at 532 nm, to be very different for $M^{\bullet -}$ and $MH^{\bullet}$. The visible absorption band of $M^{\bullet -}$ exhibits a strong blue shift with increasing hydrogen-bond donor strength of the solvent, whereas that of $MH^{\bullet}$ is solvent independent; the former is due to a charge migration away from the C–O moiety into the aromatic rings, whereas the latter indicates that the existing charge on C–O remains.[14] Hence, D_1 is of symmetry A_2 for $M^{\bullet -}$ and of symmetry B_1 for $MH^{\bullet}$, and photoionization is symmetry allowed only for the protonated radical.

The same reasoning predicts both radicals to be photoionizable with 355 nm. The biphotonic 355 nm ionization of $MH^{\bullet}$ proceeds via either D_1 (if radiationless deactivation of the upper excited state is fast on the timescale of our laser pulse) or possibly D_2 (if it is not). The former case has already been discussed, and the absence of solvatochromism for the near-UV absorption band indicates D_2 to possess B_1 symmetry as well. Hence, 355 nm photoionization of $MH^{\bullet}$ is symmetry allowed, regardless of the actual pathway. Finally, for $M^{\bullet -}$ at 355 nm the ionization is monophotonic and for that very reason also symmetry allowed, because in contrast to D_1 the doublet ground state D_0 has symmetry B_1.

In summary, we have demonstrated that green-light photoionization of a ketyl radical is feasible, and much easier than that of the corresponding radical anion, despite equal absorption properties and lower energetic requirements of the latter; in the near-UV range, both types of radicals are photoionizable with a comparable quantum yield. While we cannot yet rule out widely differing excited-state lifetimes as the reason for this counterintuitive ionization behavior, we have presented a novel explanation that consistently accounts for all the observed effects, namely by the state symmetry of the radical species absorbing the ionizing photon. This approach should also be applicable to other chromophores.

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[1] C.-R. Wang, T. Luo, Q.-B. Lu, *Phys. Chem. Chem. Phys.* **2008**, *10*, 4463–4470.
[2] C.-R. Wang, J. Nguyen, Q.-B. Lu, *J. Am. Chem. Soc.* **2009**, *131*, 11320–11322.
[3] J. Nguyen, Y. Ma, T. Luo, R. G. Bristow, D. A. Jaffray, Q.-B. Lu, *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 11778–11783.
[4] V. Zubarev, M. Goez, *Angew. Chem.* **1997**, *109*, 2779–2781; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2664–2666.
[5] M. Goez, B. H. M. Hussein, *Phys. Chem. Chem. Phys.* **2004**, *6*, 5490–5497.
[6] M. Goez, V. Zubarev, *Chem. Phys.* **2004**, *307*, 15–26.
[7] M. Goez, V. Zubarev, *Angew. Chem.* **2006**, *118*, 2189–2193; *Angew. Chem. Int. Ed.* **2006**, *45*, 2135–2138.
[8] M. Sakamoto, X. Cai, M. Hara, S. Tojo, M. Fujitsuka, T. Majima, *J. Phys. Chem. A* **2004**, *108*, 8147–8150.
[9] M. Sakamoto, X. Cai, M. Fujitsuka, T. Majima, *J. Phys. Chem. A* **2006**, *110*, 11800–11808.
[10] R. W. Redmond, J. C. Scaiano, L. J. Johnston, *J. Am. Chem. Soc.* **1990**, *112*, 398–402.
[11] A. R. Cook, L. A. Curtiss, J. R. Miller, *J. Am. Chem. Soc.* **1997**, *119*, 5729–5734.
[12] P. Brodard, A. Sarbach, J.-C. Gumy, T. Bally, E. Vauthey, *J. Phys. Chem. A* **2001**, *105*, 6594–6601.
[13] R. Signorell, F. Merkt, *Mol. Phys.* **1997**, *92*, 793–804.
[14] T. Shida, S. Iwata, M. Imamura, *J. Phys. Chem.* **1974**, *78*, 741–748.