DOI: 10.1002/anie.200504056

Efficient Photoionization of a Norrish II Diradical

Martin Goez* and Valentin Zubarev

The photochemistry of reactive intermediates in solution^[1] is a fascinating subject because of its promise of new mechanisms and applications.^[2] Photoionizations of excited singlet and triplet states are common; examples of photoionizations of radicals^[3] and radical anions^[4] are known. Here, we present the first report on the photoionization of a diradical and show that it is considerably more efficient than that of its precursor triplet.

We performed laser flash photolysis at very high light intensities, where mechanisms involving more than one photon reveal themselves much more clearly than under the usual conditions. Our setup^[4c] allows two-flash two-color experiments (355 or 266 nm, pulse width 6 ns; 308 nm, pulse width 30 ns; freely adjustable interpulse delay) and homogeneously illuminates a well-defined reaction volume, thus permitting quantitative determinations of absolute concentrations of transients. As the primary observable, the concentration of the hydrated electron e_{aq}^{-} directly at the end of a laser pulse was measured through its optical absorbance.^[5]

Alkyl phenyl ketones M can be ionized with 308 nm light.^[4d,6] The usual mechanism is a sequential two-photon process as displayed in Scheme 1. Absorption of the first

$$M \xrightarrow{h\nu_1} \overset{\text{dark}}{\underset{\text{reaction}(s)}{\longrightarrow}} *M \xrightarrow{h\nu_2} M^{\bullet+}$$

Scheme 1. Sequential two-photon ionization of a ketone, M.

photon leads to an intermediate *M, normally the triplet state, which is then ionized by the second photon. Even at our high light intensities, the rate of the first step is limited by the excitation of M because of the small extinction coefficient at 308 nm; the subsequent dark reactions to give *M, such as intersystem crossing, are much faster.

When the ketone bears a hydrogen atom in the γ position, its triplet is rapidly transformed into a 1,4-diradical by an intramolecular hydrogen abstraction (the Norrish II reaction).^[7] We were interested in how this classic photoreaction influences the photoionization. Figure 1 compares the electron yields, as functions of the laser intensity in single-flash experiments at 308 nm, for two model compounds in degassed aqueous base (nominal concentration of KOH, 0.4 M), γ methylvalerophenone as an efficient Norrish II substrate,^[8]

[*] Prof. Dr. M. Goez, V. Zubarev
Fachbereich Chemie
Martin-Luther-Universität Halle-Wittenberg
Kurt-Mothes-Strasse 2, 06120 Halle/Saale (Germany)
Fax: (+49) 345-552-7657
E-mail: goez@chemie.uni-halle.de



Figure 1. Electron concentrations relative to the substrate concentration c_0 as functions of the laser intensity *I* at 308 nm for propiophenone (open symbols and dashed line; $c_0 = 1.66 \times 10^{-4}$ M) and γ -methylvalerophenone (filled symbols and solid line; $c_0 = 7.15 \times 10^{-5}$ M) at pH 13.54. The formulas of the substrates are shown at the curves. The fit functions are given by Equation (1). Constant parameter $k_d \tau$: 0 (propiophenone) and 0.41 (γ -methylvalerophenone); best-fit parameters κ_{exc} and κ_{ion} : 1.02×10^{-3} cm² mJ⁻¹ and 9.19×10^{-4} cm² mJ⁻¹ (propiophenone); 1.21×10^{-3} cm² mJ⁻¹ and 1.43×10^{-2} cm² mJ⁻¹ (γ -methylvalerophenone). The ratio of the κ_{exc} was fixed at the ratio of the extinction coefficients of the two ketones at 308 nm (1.19).

and propiophenone as the longest-chain alkyl phenyl ketone that is not yet capable of undergoing this reaction. It is evident that the Norrish II substrate produces substantially more electrons.

The upward curvature of the intensity dependence bears out that the ionization of the Norrish II substrate is still biphotonic. With the mechanism of Scheme 1, the electron yield is determined by the (intensity-dependent) rates of both steps. As expected, the extinction coefficients of the two ground-state ketones, and thus the rates of production of *M for given laser intensity, are very similar. Hence, this step cannot explain the observed effect, and the different yields have to be ascribed to different properties of the photoionizable intermediate *M. It is natural to assume that they reflect the differences between the triplet (for propiophenone) and the Norrish II diradical (for γ -methylvalerophenone) because the latter is formed within less than 5 ns,^[8] in other words, much faster than the duration of the laser pulse.

This is corroborated by the results of pH variation. As Figure 2 shows, the electron yield is independent of pH in the case of propiophenone, whereas a titration curve with a turning point at pH 11.5 is found in the case of γ -methyl-



Figure 2. Dependence of the relative electron concentrations $[e_{aq}^{-}]/c_0$ on the pH (adjusted with KOH and phosphate buffers of variable composition) at 308 nm and constant excitation intensity (392 mJ cm⁻²). Open symbols and dashed line: propiophenone, $c_0 \approx 2.7 \times 10^{-4}$ M; filled symbols and solid line: γ -methylvalerophenone, $c_0 \approx 7.9 \times 10^{-5}$ M. The exact pH and substrate concentration c_0 were determined before each experiment in the solution used.



Communications

valerophenone. Although in neutral solution the NorrishII substrate exhibits a reduced yield, it still produces more than twice the amount of electrons than the simpler ketone does.

The absorption spectrum of M is not influenced by the pH value. Nor can the extinction coefficient and photoionization quantum yield of the triplet change with pH, as the absence of an effect in the propiophenone experiment shows. The difference between the two substrates that persists in neutral solution finally excludes a transition from triplet ionization at low pH to diradical ionization at high pH as the origin of the pH dependence, which would also be difficult to reconcile with the short lifetime of the γ -methylvalerophenone triplet. Instead, a deprotonation of the diradical in basic medium provides a natural explanation.

Except for their intramolecular deactivation steps, NorrishII diradicals are describable as separate alkyl and ketyl radical moieties.^[8] The alkyl radical moiety cannot be deprotonated, so it could only cause a pH-independent contribution to photoionization. Even that is thought very unlikely in our case because of insufficient absorption (the extinction coefficient of the tert-butyl radical at 308 nm is as low as 200 m⁻¹ cm⁻¹).^[9] In contrast, both the ketyl radical and its deprotonated form, the radical anion, have medium to strong absorptions at 308 nm, and their photoionization is much more favorable energetically than alkyl radical photoionization because the by-product is a closed-shell moiety, that is, the regenerated carbonyl group. Of importance for the electron yield is the red shift of the absorption band caused by the deprotonation,^[10] which leads to a considerable increase of the extinction coefficient at 308 nm.

Definitive evidence that the Norrish II diradical is responsible for the difference in the electron yields was obtained by two-pulse experiments. They allow the separation of groundstate excitation and the actual photoionization, which provides a twofold advantage. First, the weak absorption of the ground-state ketone M at 308 nm can be overcome by the choice of a different wavelength, 266 nm, for the first pulse; when the second pulse is left at 308 nm, the small extinction coefficient of M is turned into an asset because that pulse now predominantly excites the intermediate. Second, the lifetime of the photoionizable intermediate can be determined by varying the interpulse delay.

With both ketones studied, the extinction coefficient of M is about 16 times higher at 266 nm than at 308 nm. However, this is not paralleled by a similar increase of the extinction coefficients of the photoionizable intermediates: at 266 nm, the electron yield is even slightly smaller than at 308 nm. With a suitably attenuated 266-nm pulse, about 30% of the substrate can be converted into *M with negligible electron generation. By the second pulse, at 308 nm, the respective intermediate is photoionized after a delay Δt .

In Figure 3 the electron yields relative to the maximum in each system have been plotted as functions of Δt , allowing a direct comparison of the lifetimes of the electron precursors. With propiophenone one observes a slow decrease on a timescale of a few microseconds, as expected for the photo-ionization of the triplet state. However, with γ -methylvalerophenone the decrease is much more rapid; a fit by a monoexponential decay curve gave a time constant of 74 ns.



Figure 3. Two-pulse experiments with the pulse sequence represented in the inset; pulse intensities: 35 mJ cm⁻² (266 nm) and 400 mJ cm⁻² (308 nm). Shown are the electron yields scaled to maximum, $[e_{aa}]_{rel}$, as functions of the interpulse delay Δt for propiophenone (open symbols and dashed line; $c_0 = 1.66 \times 10^{-4}$ m) and γ -methylvalerophenone (filled symbols and solid line; $c_0 = 8.68 \times 10^{-5}$ m), both at pH 13.5.

It is well known^[8] that Norrish II diradicals cleave on that timescale to give an alkene and an enol (or, in the case of a deprotonated diradical, an enolate). These diamagnetic products are not expected to be photoionized as efficiently as the diradical, if at all, so the two-pulse experiment monitors the diradical decay. For final confirmation, we omitted the second pulse and observed the decay of the diradical directly, using its characteristic absorption at 440 nm. The diradical lifetime obtained in this way (76 ns) and the decay time constant in the two-pulse experiment were identical within experimental error. A very similar lifetime (84 ns) was found in neutral solution.

We determined the pK_a of the γ -methylvalerophenone ketyl radical to be 9.7 by generating hydrated electrons from 8-amino-2-naphthalenesulfonic acid with 355-nm light at different pH values, scavenging them with our ketone, which does not absorb at that wavelength, and observing the ketyl radical or its anion at 308 nm. The obtained value agrees very well with that for the acetophenone ketyl radical ($pK_a = 10.0$).^[10] The significantly higher turning point of the titration curve in Figure 2, at pH 11.5, presents a discrepancy that might seem to contradict the paradigm of independent ketyl and alkyl radical moieties in the NorrishII diradical.

An apparent pK_a in methanol/water of 11.8 was also reported for the diradical of γ -phenylbutyrophenone, a very close analogue to our diradical, and ascribed to a solvent effect.^[11] In our experiments, however, an apparent pK_a that is shifted to a higher value is most likely due to a rate effect: Regardless of pH, direct formation of the diradical with the deprotonated ketyl moiety is impossible, because it is the product of an intramolecular hydrogen abstraction by the carbonyl group. At pH values higher than the true pK_a , the ketyl moiety will subsequently be deprotonated, resulting in a higher photoionization probability, but our experiment only responds to those deprotonated diradicals that are formed within the duration of the laser pulse. When the pH is increased, the concentration of proton acceptors rises, the deprotonation becomes faster, and the fraction of deprotonated diradicals available within the kinetic window increases. Experiments with different buffer concentrations might support this hypothesis, but the feasible range of variation is rather limited at that high pH.

Scheme 2 summarizes the mechanism of the photoionization of γ -methylvalerophenone as inferred from these experiments. After excitation of the substrate by the first photon and intersystem crossing on a subnanosecond timescale,^[6] the



Scheme 2. Photoionization of γ -methylvalerophenone via its diradical.

first species potentially capable of absorbing the second photon is the triplet. However, the probability of its photoionization is low because it is converted into a Norrish II diradical within a few nanoseconds,^[8] which is still fast compared to the duration of the ionizing laser pulse. In basic solution, the ketyl moiety of the diradical is deprotonated. Both the unmodified and the deprotonated ketyl moiety can be photoionized, the latter yielding more electrons, and this ionization competes with chemical deactivation of the diradical.

An approximate kinetic treatment is possible for the limiting cases of very high or very low pH, where the diradical is present exclusively in either of its two forms (see Figure 2). Photoionization of the short-lived precursor triplet and of the ketone formed by diradical cleavage are neglected, the latter because its concentration during the pulse is low and its structure precludes another Norrish II reaction, so its ionization must be less efficient than that of the parent compound. The mechanism is thus that of Scheme 1 enhanced by an additional light-independent deactivation pathway of *M (with rate constant k_d). With the assumption of a rectangular laser pulse of duration τ , diradical formation occurs with a rate constant $\kappa_{exc} I / \tau$ and photoionization with a rate constant $\kappa_{ion} I/\tau$, where each parameter κ is proportional to the product of the extinction coefficient of the species absorbing the photon and the quantum yield of the resulting process.^[4e] The intensity dependence of the electron yield at the pulse end is given by Equation (1). When k_d is set to zero, Equation (1) can also be applied to the photoionization of propiophenone.

$$\begin{split} [\mathbf{e}_{\mathrm{aq}}^{-}]/c_{0} &= \frac{\kappa_{\mathrm{ion}}I}{\kappa_{\mathrm{ion}}I + k_{\mathrm{d}}\tau} \left(1 - \frac{\kappa_{\mathrm{exc}}I}{\kappa_{\mathrm{exc}}I - (\kappa_{\mathrm{ion}}I + k_{\mathrm{d}}\tau)} \exp[-(\kappa_{\mathrm{ion}}I + k_{\mathrm{d}}\tau)] \right. \\ &\left. + \frac{\kappa_{\mathrm{ion}}I + k_{\mathrm{d}}\tau}{\kappa_{\mathrm{exc}}I - (\kappa_{\mathrm{ion}}I + k_{\mathrm{d}}\tau)} \exp[-\kappa_{\mathrm{exc}}I] \right) \end{split}$$
(1)

Fitting Equation (1) to the data (see the legend of Figure 1) shows that for the deprotonated diradical the constant κ_{ion} is larger by a factor 15.6 compared to that of the triplet; in neutral solution, in other words, for the initially formed diradical, this factor is found to be only 2.1. The scavenging experiment described above gave extinction

coefficients of the γ -methylvalerophenone ketyl radical and radical anion at 308 nm of 1900 and $15100 \,\mathrm{M^{-1}\,cm^{-1}}$, the ratio of which closely parallels the ratio of $\kappa_{\rm ion}$ in neutral and basic solution. Hence, we conclude that deprotonation of the ketyl moiety does not influence the photoionization quantum yield, and that the different electron yield (Figure 2) is solely due to the change of the extinction coefficient. The extinction coefficient of the γ -methylvalerophenone triplet should practically be identical to that of the propiophenone triplet, $4400 \,\mathrm{M^{-1}\,cm^{-1}}$ at 308 nm.^[4d] The same comparison thus reveals that the quantum yield of photoionization of the diradical is almost five times higher than that of the triplet, which is in good agreement with the previously obtained^[4d] ratio for the propiophenone triplet and radical anion.

Our results for other systems^[4b-e] suggest that the conversion of a triplet state into the corresponding radical or radical anion, as can be achieved by the addition of a suitable quencher, is a general method to increase the photoionization quantum yield, presumably because this transformation suppresses reverse intersystem crossing of the upper excited state. The diradical studied here represents an intramolecular application of that principle.

Received: November 15, 2005 Published online: February 24, 2006

Keywords: diradicals · ketones · laser chemistry · photoionization · photolysis

- a) J. C. Scaiano in *Kinetics and Spectroscopy of Carbenes and Biradicals* (Ed.: M. S. Platz), Plenum, New York, **1990**, pp. 353–368; b) L. J. Johnston, *Chem. Rev.* **1993**, *93*, 251–266; c) W. G. McGimpsey in *Molecular and Supramolecular Photochemistry*, *Vol. 2* (Eds.: V. Ramamurthy, K. S. Schanze), Marcel Dekker, New York, **1998**, pp. 249–306; d) A. Natarajan, L. S. Kaanumalle, V. Ramamurthy in *CRC Handbook of Organic Photochemistry and Photobiology*, 2nd ed. (Eds.: W. Horspool, F. Lenci), CRC, Boca Raton, FL, **2004**, pp. 107/1–107/24.
- [2] a) I. A. Shkrob, M. C. Sauer, Jr., A. D. Liu, R. A. Crowell, A. D. Trifunac, J. Phys. Chem. A 1998, 102, 4976-4989; b) C. R. Lambert, I. E. Kochevar, R. W. Redmond, J. Phys. Chem. B 1999, 103, 3737-3741; c) V. V. Jarikov, A. V. Nikolaitchik, D. C. Neckers, J. Phys. Chem. A 2000, 104, 5131-5140; d) M. Goez, V. Zubarev, Angew. Chem. 2001, 113, 2948-2951; Angew. Chem. Int. Ed. 2001, 40, 2867-2869; e) M. Goez, M. Schiewek, M. H. O. Musa, Angew. Chem. 2002, 114, 1606-1609; Angew. Chem. Int. Ed. 2002, 41, 1535-1538; f) M. Goez, B. H. M. Hussein, Angew. Chem. 2003, 115, 1697-1700; Angew. Chem. Int. Ed. 2003, 42, 1659-1661; g) M. Goez, D. von Ramin-Marro, M. H. O. Musa, M. Schiewek, J. Phys. Chem. A 2004, 108, 1090-1100; h) X. Cai, M. Sakamoto, M. Hara, S. Tojo, A. Ouchi, A. Sugimoto, K. Kawai, M. Endo, M. Fujitsuka, T. Majima, J. Phys. Chem. A 2005, 109, 3797-3802.
- [3] a) R. W. Redmont, J. C. Scaiano, L. J. Johnston, J. Am. Chem. Soc. 1990, 112, 398-402; b) J. L. Faria, S. Steenken, J. Am. Chem. Soc. 1990, 112, 1277-1279; c) J. L. Faria, S. Steenken, J. Phys. Chem. 1993, 97, 1924-1930; d) J. L. Faria, S. Steenken, J. Chem. Soc. Perkin Trans. 2 1997, 1153-1159.
- [4] a) P. Natarajan, R. W. Fessenden, J. Phys. Chem. 1989, 93, 6095 6100; b) V. Zubarev, M. Goez, Angew. Chem. 1997, 109, 2779 2781; Angew. Chem. Int. Ed. Engl. 1997, 36, 2664–2666; c) M. Goez, V. Zubarev, G. Eckert, J. Am. Chem. Soc. 1998, 120, 5347 –

Communications

5348; d) M. Goez, V. Zubarev, *Chem. Phys.* **2004**, *307*, 15–26; e) M. Goez, B. H. M. Hussein, *Phys. Chem. Chem. Phys.* **2004**, *6*, 5490–5497.

- [5] For better sensitivity, e_{aq}^- was not observed at its absorption maximum (720 nm) but at 829 nm; see, Ref. [4d], footnote 9. By control experiments (saturation of the solutions with the electron scavenger N₂O) it was ascertained that no other species absorbs at 829 nm. The extinction coefficient of e_{aq}^- at 829 nm, 13750 m⁻¹ cm⁻¹, was determined by comparison with the maximum extinction coefficient at 720 nm.^[4e]
- [6] R. Boch, M. K. Whittlesey, J. C. Scaiano, J. Phys. Chem. 1994, 98, 7854–7857.
- [7] P. J. Wagner, Acc. Chem. Res. 1971, 4, 168-177.
- [8] J. C. Scaiano, *Acc. Chem. Res.* **1982**, *15*, 252–258, and references therein.
- [9] C. Huggenberger, H. Fischer, *Helv. Chim. Acta* 1981, 64, 338– 353.
- [10] E. Hayon, T. Ibata, N. N. Lichtin, M. Simic, J. Phys. Chem. 1972, 76, 2072–2078.
- [11] R. A. Caldwell, S. N. Dhawan, D. E. Moore, J. Am. Chem. Soc. 1985, 107, 5163–5166.