

Formation of radical cations of aziridines generated by laser flash photolysis

Carsten Gaebert,^{a,c} Christian Siegner,^{a,d} Jochen Mattay,^{*a} Marion Toubartz^b and Steen Steenken^{*b}

^a *Organische Chemie I, Universität Bielefeld, Universitätsstraße 25, D-33615, Bielefeld, Germany. E-mail: mattay@uni-bielefeld.de*

^b *Max-Planck-Institut für Bioanorganische Chemie, Stiftstraße 34-36, D-45470, Mülheim/Ruhr, Germany*

^c *Consortium für Elektrochemische Industrie GmbH, Zielstattstraße 20, D-81379, München, Germany*

^d *Plaut Consulting, Im Breitspiel 19, D-69126, Heidelberg, Germany*

Received 8th July 2004, Accepted 22nd September 2004

First published as an Advance Article on the web 7th October 2004

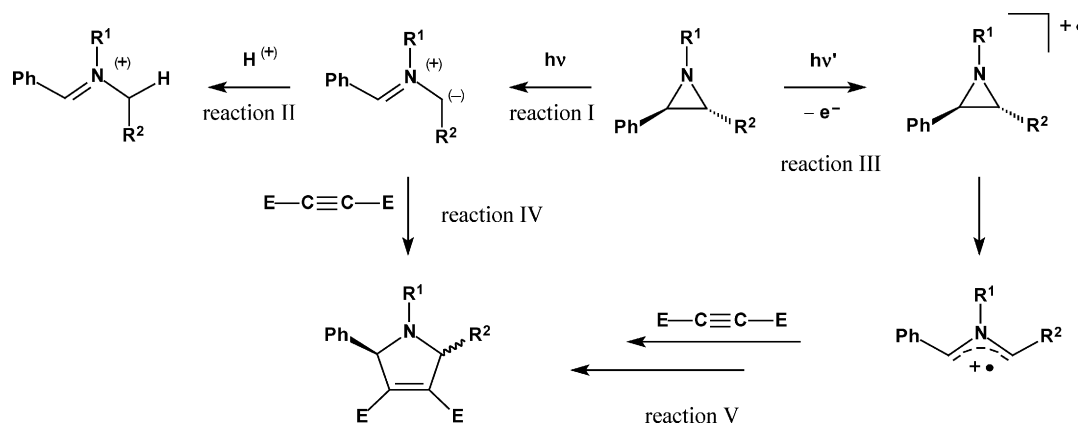
The radical cations of 1-butyl-*trans*-2,3-diphenyl aziridine (1), 1-butyl-2-phenyl aziridine (2), 1,2-diphenyl aziridine (3) and 1-(*p*-methoxyphenyl)-2-phenyl aziridine (4) were generated upon laser flash photolysis in aqueous and aqueous acetonitrile solutions by direct photoionisation as indicated by the broad absorption band of the solvated electron above 550 nm as well.

Aziridines and their reactions are of great interest due to their synthetic and pharmacological importance.^{1,2} On irradiation or on thermal activation aziridines undergo ring opening to the corresponding azomethine ylides (Scheme 1, reaction I) which can be trapped in [3 + 2] cycloadditions with various dipolarophiles, to form nitrogen containing five membered heterocycles (one example is shown in the Scheme 1, reaction IV).³⁻⁵ Under photo-induced electron transfer (PET) conditions the aziridine is oxidized to the corresponding radical cation, which can react in a similar manner (Scheme 1, reaction V).⁶⁻¹⁰ In the course of our investigations aimed at the applications of aziridines in organic synthesis⁵ we became interested in the reactive intermediates of the [3 + 2] cycloadditions, *i.e.* the azomethine ylides and the radical cations of the aziridines, to elucidate the mechanisms of the reactions. A few years ago we reported on studies in which azomethine ylides were generated by laser flash photolysis^{11,12} and recently we published the characterization of aziridine radical cations by short time resolved spectroscopy.¹³ The radical cations were formed on pulse radiolysis or ⁶⁰Co- γ -radiolysis whereas the azomethine ylides were generated upon laser flash photolysis. In this communication we now report on

the formation of aziridine radical cations under the conditions of the laser flash photolysis. The substrates examined in the present study are 1-butyl-*trans*-2,3-diphenyl aziridine (1),¹⁴ 1-butyl-2-phenyl aziridine (2),¹⁵ 1,2-diphenyl aziridine (3),¹⁶ and 1-(*p*-methoxyphenyl)-2-phenyl aziridine (4).¹⁶ In the case of aziridine 2 we used the 193 nm laser light because of its weak absorbance at 248 nm. Aziridines 1, 3, and 4 were photolysed with 248 nm light. The fate of aziridine radical cations, especially ring opening to the corresponding radical cations of ylides and its dependence on the substitution pattern will be discussed in detail separately.

Laser flash photolysis¹⁷ of aziridine 1 in a 1 : 1 mixture of acetonitrile and water leads to an absorption band at 280 nm and an overlapping system at 430 and 500 nm. At 500 nm we detect the azomethine ylide formed *via* reaction I (see Scheme 1). With the same kinetics the azomethine ylide at 500 nm decays and the corresponding iminium ion at 280 nm is formed (Scheme 1, reaction II).^{11,12} The shoulder at 430 nm is best assigned as radical cation of aziridine 1 (Scheme 1, reaction III).¹³ Increasing the content of water to 80% (Fig. 1, spectrum 1) the decay of the azomethine ylide at 500 nm is accelerated, whereas the radical cation at 430 nm seems to be more stabilized.¹⁸ 33 μ s after the laser pulse the azomethine ylide is completely quenched. Only the aziridine radical cation at 430 nm is observed besides the iminium ion at 280 nm. Measurements in pure water were impossible due to the low solubility of aziridine 1.

In the case of aziridines 2, 3 and 4 measurements in a mixture of acetonitrile and water leads to the absorption bands of the corresponding radical cations at 380, 440 and 470 nm, respectively. The azomethine ylides could not be detected. Probably, the



Scheme 1 Photoreactions of aziridines to azomethine ylides and iminium cations (left) and radical cations (by PET sensitization or direct photoionisation $h\nu'$, right side); for trapping experiments (reaction IV and reaction V) see ref. 8–12.

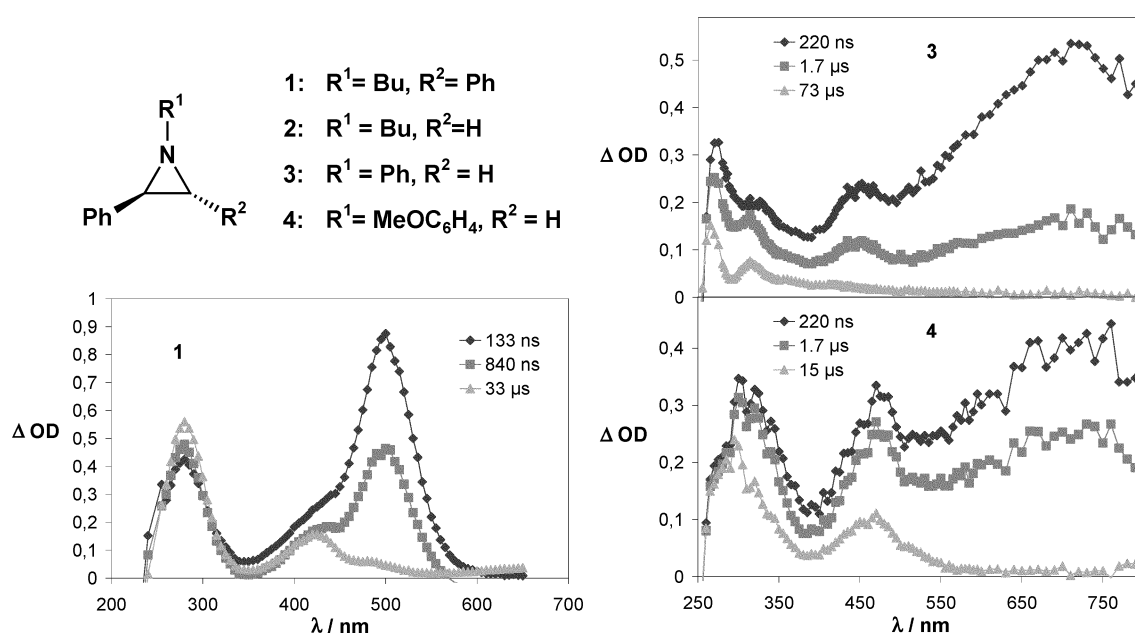


Fig. 1 Laser flash photolysis of 0.25 mM of aziridine **1** in an argon-saturated mixture of 80% water and 20% acetonitrile; laser flash photolysis of 0.1 mM of aziridine **3** and of 0.3 mM of aziridine **4** in argon-saturated water.

decay of the azomethine ylides and the simultaneous formation of the iminium ions are completed within the laser pulse. In order to prove the formation of the radical cations on direct photolysis we irradiate solutions of aziridines **2**, **3** and **4** in pure water. In all three cases we observe the absorption bands of the corresponding aziridine radical cations besides the broad, intensive absorbance of the solvated electron above 550 nm. The spectra of the laser flash photolysis of aziridines **3** and **4** in pure water are given in Fig. 1 (spectra 3 and 4).

In conclusion, we provide a further access to aziridine radical cations upon photolysing aqueous solutions of aziridines with an excimer laser beside pulse radiolysis or ^{60}Co - γ -radiolysis.¹³ This photoionization procedure is important especially for mechanistic studies since the alternative photochemical PET sensitization suffers from strong absorbance of the sensitizer and its radical cation, respectively.

The support provided by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. C. G. thanks the Studienstiftung des deutschen Volkes for a predoctoral scholarship.

Notes and references

- 1 J. Backes, in *Methoden der Organischen Chemie (Houben-Weyl)*, ed. D. Klamann, Thieme, Stuttgart, 1992, vol. E 16c, pp. 370–677.
- 2 J. A. Deyrup, in *Small Ring Heterocycles*, ed. A. Hassner, John Wiley & Sons, New York, 1983, vol. 1, pp. 1–214.
- 3 (a) R. Huisgen, 1,3-Dipolare Cycloadditionen, *Angew. Chem.*, 1963, **75**, 604–637; (b) R. Huisgen, in *1,3 Dipolar Cycloaddition Chemistry*, ed. A. Padwa, John Wiley & Sons, New York, 1984, vol. 1, pp. 1–176.
- 4 J. W. Lown, Recent Developments in Aziridine Chemistry. Synthetic Applications of Cycloaddition Reactions, *Rec. Chem. Prog.*, 1971, **32**, 51–83.
- 5 C. Gaebert and J. Mattay, [3 + 2] Cycloadditions and Nucleophilic Additions of Aziridines under C–C- and C–N-Bond Cleavage, *Tetrahedron*, 1997, **53**, 14297–14316.
- 6 V. Caer, A. Laurent, E. Laurent, R. Tardevil, Z. Cebulka and R. Bartnik, Cycloadditions induites par Transfert Electronique a partir de la Butyl-1-Diphenyl-2,3-*cis*-aziridine, *New J. Chem.*, 1987, **11**, 351–356.
- 7 T. Brigaud, E. Laurent, R. Tardevil, Z. Cebulka and R. Bartnik, Photosensitized Cycloaddition of *cis*-1-Butyl-2,3-diphenylaziridine with Methyl Maleate and Fumarate, *J. Chem. Res. (S)*, 1994, **8**, 330–331.
- 8 (a) C. Gaebert, Diploma Thesis, Westfälische Wilhelms-Universität, Münster, 1994; (b) C. Gaebert, PhD Thesis, Westfälische Wilhelms-Universität, Münster, 1997.
- 9 C. Siegner, PhD Thesis, Christian-Albrechts-Universität, Kiel, 1999.
- 10 C. Gaebert and J. Mattay, [3 + 2] Cycloadditions of Aziridines. Mechanistic Studies, *J. Inf. Record*, 1996, **23**, 3–6.
- 11 C. Gaebert, C. Siegner, J. Mattay, M. Toubartz and S. Steenken, Laser Flash Photolysis of Aziridines. Spectroscopic and Kinetic Characterization of Azomethine Ylides and their Reaction with Alcohols to Yield Iminium Ions, *J. Chem. Soc., Perkin Trans. 2*, 1998, **12**, 2735–2740.
- 12 C. Siegner, C. Gaebert, J. Mattay and S. Steenken, Laser Flash Photolysis of some Phenylaziridines, *J. Inf. Record*, 1998, **24**, 253–256.
- 13 C. Gaebert, J. Mattay, M. Toubartz, S. Steenken, B. Müller, T. Bally, Radical Cations of Phenyl-Substituted Aziridines: What are the Conditions for Ring-Opening?, *Chem. Eur. J.*, in press.
- 14 Using *trans*-stilbene as starting material epoxidation with MCPBA formed the corresponding *trans*-stilbene oxide in yields of 84%. Following the procedure of J. A. Deyrup and C. L. Moyer, *J. Org. Chem.*, 1969, **34**, 175–179, 1-butyl-*trans*-2,3-diphenyl aziridine **1** was formed with a yield of 58% (ref. 5). The cyclization, as described by; I. Okada, K. Ichimura and R. Sudo, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 1185–1189, formed 1-butyl-*trans*-2,3-diphenyl aziridine **1** in a yield of 58% (ref. 5).
- 15 Starting with commercially available styrol oxide, the corresponding β -amino alcohol was prepared according to the procedure of N. B. Chapman and D. J. Trigg, *J. Chem. Soc.*, 1963, 1385–1400. The formation of 1-butyl-2-phenyl aziridine **2** occurred as described above (ref. 5).
- 16 V. Franzen and H. E. Driesen, Umsetzung von Sulfonium-Yliden mit polaren Doppelbindungen, *Chem. Ber.*, 1963, **96**, 1881–1890.
- 17 For the photolysis a 20 ns pulsed laser LAMBDA Physics EMG 103MSC ($\lambda = 193$ and 248 nm) was used at intensities of 20–100 mJ per pulse. Argon- or oxygen-saturated solutions were allowed to flow through a quartz cell (4 mm path length) that was irradiated with laser light in a right-angle geometry with respect to the analyzing light. At least for the aziridine **1** the photoionization is monophotonic due to linear dependence of radical cation yield on laser intensity—see ref. 10, page 58.
- 18 The azomethine ylide is protonated by water leading to the iminium cation. Consequently the lifetime of the azomethine ylide decreases with increasing water concentration, see ref. 11.