PERKIN 2

Laser flash photolysis of aziridines. Spectroscopic and kinetic characterization of azomethine ylides. Their [3 + 2] cyclization with alkenes and protonation by water–alcohols to yield iminium ions[1]

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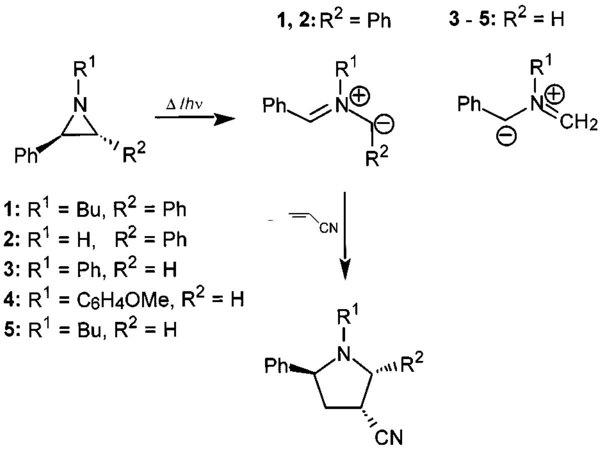
The reactive intermediates generated by laser flash photolysis (λ_{exc} = 248 or 193 nm) of the aziridines (*E*)-1-butyl-2,3-diphenylaziridine **1**, (*E*)-2,3-diphenylaziridine **2**, 1,2-diphenylaziridine **3**, 1-(*p*-methoxyphenyl)-2-phenylaziridine **4** and 1-butyl-2-phenylaziridine **5** in acetonitrile and alcohols as solvents were identified as the corresponding azomethine ylides and spectroscopically and kinetically characterized. The rate constants for the [3 + 2] reaction of the ylides with electron-deficient alkenes to give pyrrolidines are between 10^6 and 10^9 M^{-1} s^{-1}. In the case of **1** and **2** iminium ions are produced by protonation (by H_2O or ROH) of the ylides (also studied by time-resolved conductance). For this reaction, with MeOH as the proton donor, the kinetic isotope effect is *k*(MeO–H)/*k*(MeO–D) = 5–7, from which it is concluded that the transition state for protonation of the carbanionic site of the ylide is linear.

Introduction

Due to their synthetic potential to generate nitrogen-containing five-membered heterocycles,[2] of the reactions of aziridines, the [3 + 2] cycloaddition has been intensively investigated. Upon thermal activation or on photolysis the aziridine ring opens heterolytically to the corresponding azomethine ylide[2,3] (see Scheme 1). The ylide can be trapped in a [3 + 2] cycloaddition with various dipolarophiles, such as, *e.g.*, acrylonitrile, to form the corresponding pyrrolidines.[4] Concerning the intermediates involved in the photochemical reaction, only a few spectroscopic or mechanistic studies have so far been published. For example, on photolysis of 1-aziridinyl-1,2-dibenzoylethylenes,[5] *cis–trans* photoisomerization of the dibenzoylethylene moiety is observed, with the transients absorbing between 300 and 400 nm, whereas in the wavelength range from 550 to 700 nm the azomethine ylides generated absorb. The ylides of 2-aryl-3-benzoylaziridines and 2,3-dibenzoylaziridines[6] absorb between 450 nm and 500 nm. Their lifetimes vary from 1.5 µs to 300 ms, depending on solvent and substituents. In the case of *N*-benzoylaziridines[7] the ylides are characterized by two absorptions, at 280–440 nm and at 560–610 nm. These species are quenchable with oxygen. Recently, aziridinylmaleates and -fumarates were examined.[8] Photoisomerization was observed (signals between 290 and 330 nm) and azomethine ylides detected at 500 to 700 nm. In the course of our investigations directed at applications of aziridines in organic synthesis[4,9] we studied the [3 + 2] cycloaddition of aziridines under direct photolysis in comparison with the transformations upon photo-induced electron transfer (PET). Under PET conditions[10] the aziridine radical cation is generated. In contrast, in *this* study we describe the reactive species from the direct photolysis, the azomethine ylides, using the technique of time resolved flash photolysis with an excimer laser (λ = 193 or 248 nm). The substrates examined in the present study are (*E*)-1-butyl-2,3-diphenylaziridine **1**, (*E*)-2,3-diphenylaziridine **2**, 1,2-diphenylaziridine **3**, 1-(*p*-methoxyphenyl)-2-phenylaziridine **4**, and 1-butyl-2-phenylaziridine **5**. The aziridines **1**–**4** were photolysed with 248 nm light. In the case of **5** we used 193 nm laser light because of the weak absorbance of **5** at 248 nm.



Scheme 1

Results and discussion

(*E*)-1-Butyl-2,3-diphenylaziridine 1

The spectrum after laser excitation of aziridine **1** in argon saturated acetonitrile has two absorption bands, a strong one at 500 nm and a weak one at 280 nm (Fig. 1). Due to the same kinetic behaviour at the two wavelengths, we assign both absorptions to one transient. Within 1 ms, the transient decays to 30% of its original value. This transient is identified as the corresponding azomethine ylide, resulting from the photo-cleavage of the C–C bond of the aziridine ring (see Scheme 1). In order to support this assignment we measured the rate constant of the quenching reaction with acrylonitrile by determining the rate of decay as a function of [acrylonitrile]. The azomethine ylide of aziridine **1** reacts with acrylonitrile in a [3 + 2] cycloaddition.[4] The kinetic plot is presented in the inset of Fig. 1. At both wavelengths we observe the same second-order rate constant ($k = 2.1 \times 10^6$ M^{-1} s^{-1}). The ylide from **1** and

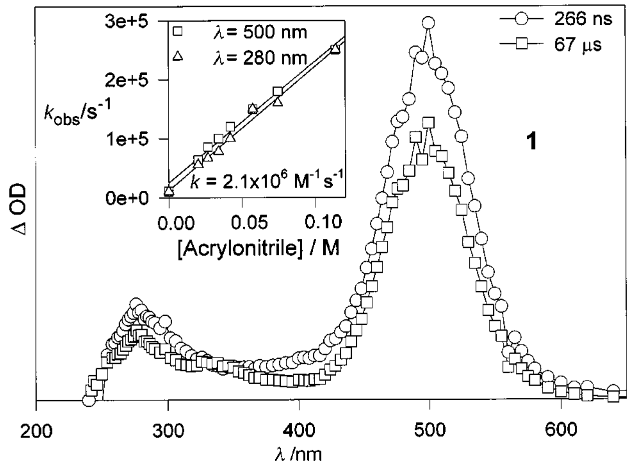
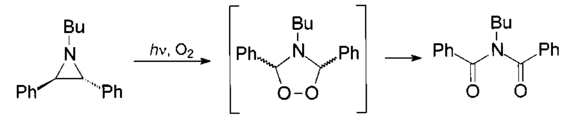


Fig. 1 Absorption spectrum of transient (= ylide) observed on photolysing 0.25 mM of **1** in argon-saturated acetonitrile. The inset shows the quenching reaction of the ylide with acrylonitrile.

those from **2**–**4** (see later) were also reacted with the stronger dipolarophiles $(MeO(O)CC)_2$ and NCCH=CHCN. The data, listed in Table 1, clearly indicate that the reactivity increases with increasing electron deficiency of the dipolarophile. This type of behaviour was also exhibited by the *nitrile* ylides obtained from phenyl*azirines*.[11]

Surprisingly, the ylide is also quenchable with oxygen ($k = 8.8 \times 10^5$ M^{-1} s^{-1}). In this reaction, *N*-benzoyl-*N*-butylbenzamide is the only product (Scheme 2).



Scheme 2

It was found that in protic solvents the lifetime of the azomethine ylide is strongly reduced. This is interpreted in terms of protonation of the ylide to yield the corresponding iminium ion (*cf.* Scheme 3, reaction a). By adding different amounts of the acidic hexafluoro*iso*propanol (HFIP; pK_a = 9.3) to the solution of aziridine **1** in acetonitrile one obtains the rate constant for the protonation of the ylide by this alcohol (Fig. 2, left inset) as $k = 4.2 \times 10^6$ M^{-1} s^{-1}. If the photolysis is performed in neat trifluoroethanol (TFE) as the solvent, at 20 ns after the pulse the ylide, as monitored at 500 nm, is invisible. In its place, an absorption band at 280 nm is detected, which is assigned to the iminium ion, formed by protonation of the ylide (analogously to Scheme 3a). In the less acidic solvent methanol, a rapid decay of the ylide is observed (at 500 nm), and at 280 nm, with the same rate, the iminium ion is seen to 'grow in'. Isosbestic points at 310 nm and 230 nm indicate a simple 1 : 1 reaction (Fig. 2).

In order to support our assignment of the iminium ion at 280 nm we investigated the reaction of this species with OH^- ions. This reaction was monitored at 280 nm, and the rate constant $k = 1.4 \times 10^8$ M^{-1} s^{-1} in methanol and $k = 4.9 \times 10^7$ M^{-1} s^{-1} in ethanol (Fig. 3, B, C) was obtained. (The rate constant for decay of the iminium ion in *neat* methanol is 1.1×10^4 s^{-1}, see Fig. 2, 'inset'). It was found that Cl^- or Br^- have no influence on the lifetime of the iminium ion. Since the halides are *more* nucleophilic than OH^-, they should react *faster* than OH^-. Thus, the observed lack of reactivity is probably only an *apparent* one, caused by very rapid heterolysis of the so-formed halides, due to the very good leaving group properties of the halides, as compared to OH^-. This explanation means that the reaction of the iminium ion with the halides is *reversible*. Such reversible processes in analogous systems have previously been observed.[11,13]

Additional support for the identification of the reaction product of the azomethine ylide as an iminium cation comes from conductivity measurements. Due to the low solubility of aziridine **1** in water we added 20% of acetonitrile to the aqueous solution of **1**. In order to provide for an excess of base, the solution contained 1 mM NaOH. Under this condition, the laser pulse resulted in an *increase* of the conductance of the solution (Fig. 4), whereas in *acidic* solution, a conductance *de*crease was seen (not shown). The reactions initiated by the laser pulse are explained in Scheme 3: the ylide reacts with

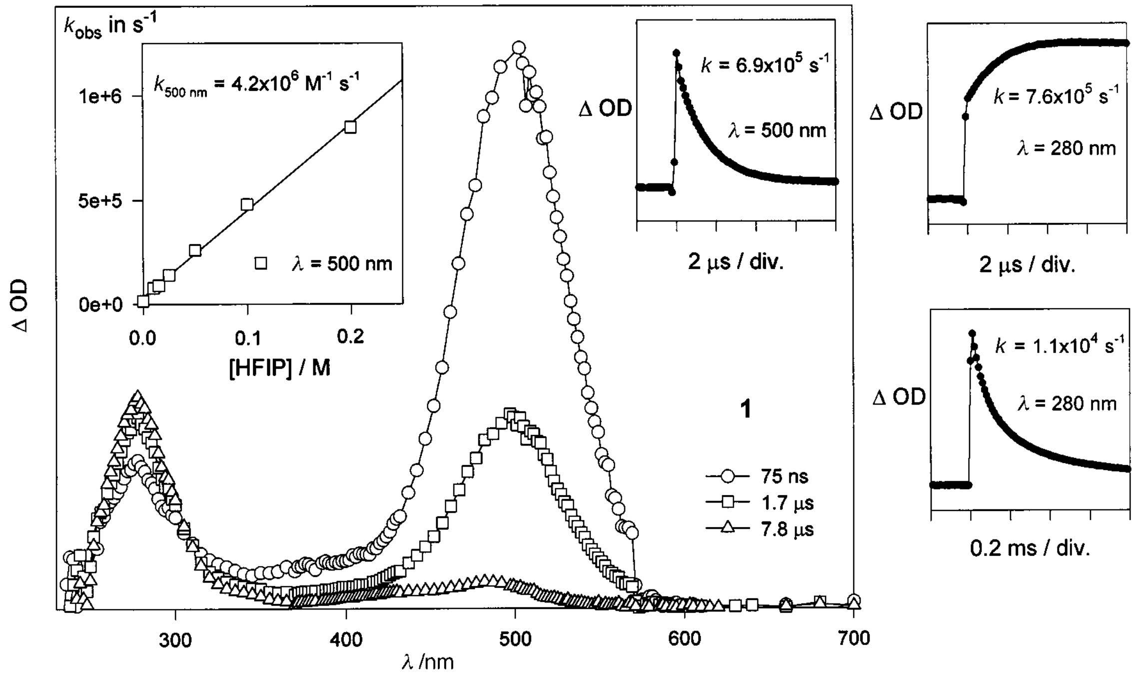


Fig. 2 Absorption spectra of transients observed on photolysing 0.25 mM of **1** in argon-saturated methanol. Insets in the centre and on the right show the decay at 500 nm (= ylide) and the build-up, followed by decay, at 280 nm (= iminium ion). The inset on the left shows the dependence in acetonitrile of the rate of protonation of ylide on [HFIP]. As shown in Fig. 3, A, the rate of decay of the ylide (monitored at 500 nm) correlates with the pK_a value of the solvent,[12] as observed also in the case of *nitrile* ylides.[11]

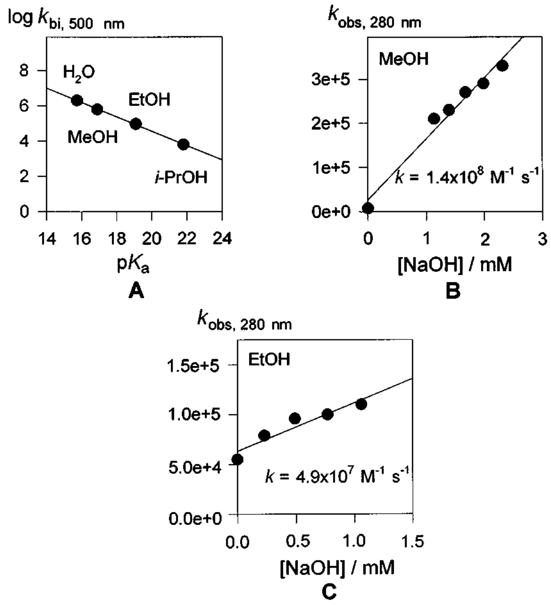


Fig. 3 Aziridine **1**: correlation between the observed rate of protonation and the pK_a value of the solvent (A). Dependence on [OH^-] of the rate of the quenching reaction of the iminium ion from **1** with OH^- in methanol (B) and ethanol (C).

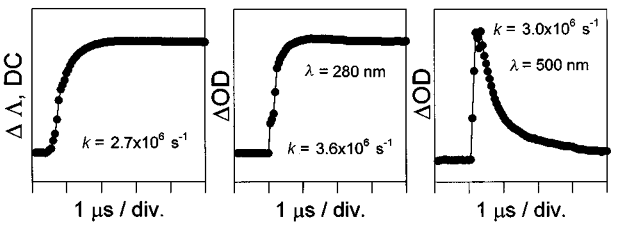


Fig. 4 Photolysis of 0.25 mM **1** in argon-saturated 20% acetonitrile–water containing 1 mM NaOH (protonation of the ylide/formation of the iminium ion, Scheme 3, reaction a). Comparison between the kinetics of the conductance and of the optical changes (at 280 nm and 500 nm).

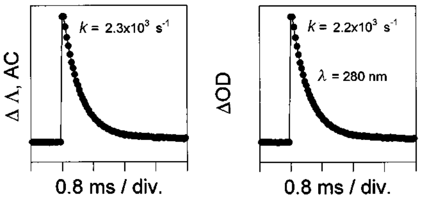
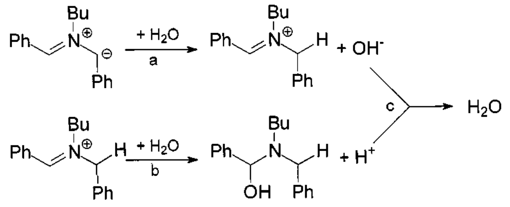


Fig. 5 Photolysis of 0.25 mM **1** in argon-saturated 20% acetonitrile–water containing 1 mM of NaOH (quenching of the iminium ion, Scheme 3, reaction b). Comparison of the kinetics of the conductance (left) with the optical changes at 280 nm (right).

water to form the iminium ion and an OH^- ion (reaction a). The generation of OH^- causes an increase in conductivity (in *acidic* solution the OH^- formed is neutralized by the excess H^+ present, resulting in a decrease of its concentration and thus to a decrease of the conductance). On the basis of the reaction scheme this increase must correlate with the decay of the ylide as monitored optically at 500 nm and the appearance of the iminium ion at 280 nm. That this is the case is shown in Fig. 4. The measured rates have similar values.

On a longer time scale the iminium ion reacts with water to generate a proton which, in basic solution, is rapidly neutralized by an OH^- ion (Scheme 3, reactions b and c). Therefore, the concentration of OH^- decreases, leading to a decrease of the conductance of the solution with $k = 2.3 \times 10^3$ s^{-1}, see Fig. 5. The value is lower by the factor ≈5 than that in pure methanol (1.1×10^4 s^{-1}, see above). This decay of the



Scheme 3

conductance has to correlate (Scheme 3) with the optical decay of the iminium ion at 280 nm, as experimentally observed (Fig. 5). After completion of reactions 3a–c, the conductance level is the same as *before* the pulse (*i.e.*, the generation of the ylide), *i.e.*, the conductance decreases to the zero line.

Furthermore, measurements of the kinetic isotope effect were performed, using *O-deuteriated* methanol as solvent. For the decay of the azomethine ylide, as monitored at 500 nm, to the corresponding iminium ion in MeO–*D*, the rate is considerably smaller (by the factor 5.8), *i.e.*, the isotope effect is $k_H/k_D = 5.8$. This large value, which is similar to that (4.5)[14] for protonation on the *carbon* in cyanide, indicates a linear transition state[15] in the protonation of the ylide carbon by the OH-function of the alcohol, as in reaction (1), as also observed

$$\text{RO–H}\cdots\text{C}^- \longrightarrow \text{RO}^- + \text{HC} \qquad (1)$$

($k_H/k_D = 5.5$)[11] in the case of protonation of *nitrile* ylides. For the decay of the iminium ion only a small kinetic isotope effect is expected[15] and found ($k_H/k_D = 1.5$).

In conclusion, we identified the azomethine ylide of the aziridine **1** as the transient product of the 248 nm laser flash photolysis. The ylide is characterized by a strong absorption band at 500 nm and a weak one at 280 nm. At the same wavelength, 280 nm, the iminium ion is detected as the product of the protonation of the ylide.[16] The ylide is quenchable with acrylonitrile and oxygen whereas the iminium ion can be trapped with OH^-.

(*E*)-2,3-Diphenylaziridine 2

The spectrum observed on photolysing a 0.2 mM solution of the aziridine **2** in acetonitrile is characterized by two transient absorption bands, at 480 and 275 nm (Fig. 6, curve 2), the latter being considerably weaker than the former. Both absorptions show the same kinetic behaviour, so both are due to the same transient. As in the case of aziridine **1** the transient is quenchable with oxygen ($k = 1.5 \times 10^7$ M^{-1} s^{-1}). The reactivity of this intermediate in the [3 + 2] cycloaddition with acrylonitrile is $k = 5.0 \times 10^5$ M^{-1} s^{-1}, *i.e.* four times smaller than that of the azomethine ylide of aziridine **1**. This probably reflects the lower electron density of the ylide from **2**, as compared to the *N*-alkylated **1**. On photolysis of **2** in methanol, the ylide, as monitored at 480 nm, decays rapidly whereas at 250 nm an absorption 'grows in'. An isosbestic point at 260 nm indicates a 1:1 reaction. These observations are interpreted in terms of formation of the azomethine ylide of aziridine **2** and its subsequent protonation to yield the corresponding iminium ion absorbing at 250 nm.[17] The kinetic isotope effect $k_H/k_D = 7.4$, measured for the decay of the ylide at 480 nm by protonation of the ylide by MeOH/MeOD, confirms this assignment.[18]

The similarity of the absorbances of the ylides generated upon laser flash photolysis of the aziridines **1** and **2** shows that the butyl substituent located at the nitrogen of the aziridine ring has only a weak influence on their spectral properties (see Table 1). However, concerning reactivity, without the butyl substituent, the azomethine ylide is more sensitive to oxygen (factor 17) whereas the reactivity with acrylonitrile is diminished (factor 4).

Table 1 Spectroscopic and reactivity properties of the azomethine ylides of **1**–**5**

Aziridine	λ_{max}(ylide)/nm	$k(O_2)/\mathrm{M}^{-1}\,\mathrm{s}^{-1}$	$k[3+2]^{a}/\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ $H_2C{=}CHCN$	$k[3+2]^{b}/\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ $(MeO(O)CC)_2$	$k[3+2]^{c}/\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ $NCCH{=}CHCN$	k_H/k_D for decay of ylide in MeOH/MeOD
1	280, 500	8.8×10^5	2.1×10^6	3.5×10^8	1.0×10^9	at 500 nm: 5.8
2	275, 480	1.5×10^7	5.0×10^5	1.5×10^8	5.2×10^8	at 480 nm: 7.4
3	280, 400	3.6×10^6	8.6×10^6	1.1×10^9	1.3×10^9	
4	270, 410	2.6×10^6	5.9×10^6	1.1×10^9	1.4×10^9	
5	250, 410	7.3×10^6				

[a,b,c] Rate constants for cyclization of ylide (see Scheme 1) with the dipolarophiles indicated.

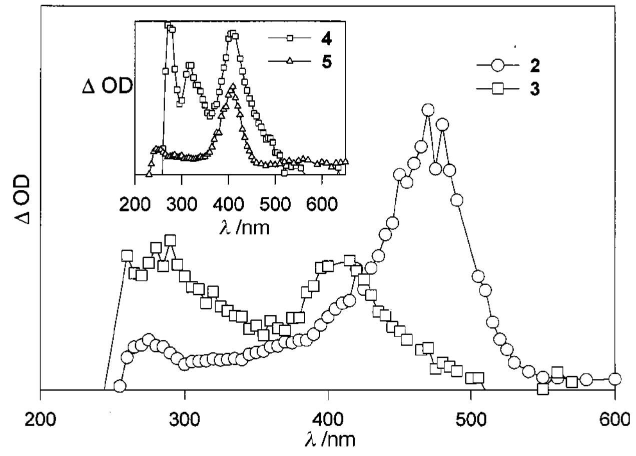


Fig. 6 Transient absorption spectra observed on photolysing 0.2 mM of **2** or 0.1 mM of **3** in argon-saturated acetonitrile. Inset shows the corresponding spectra from the photolysis of 0.1 mM of **4** and 0.05 mM of **5**.

Aziridines 3–5

The spectra obtained on laser flash photolysis of aziridines **3**–**5** in acetonitrile are shown in Fig. 6. In comparison with the aziridines **1** and **2** there is no phenyl group at the second carbon of the aziridine ring, therefore the possibility of charge delocalization is reduced.[19] For this reason the absorption maxima of the azomethine ylides are blue-shifted to ≈400 nm. The spectroscopic data and the rate constants of the azomethine ylides generated from the aziridines **3**–**5** are summarized in Table 1. Due to the insufficient absorption at 248 nm of aziridine **5**, 193 nm laser light had to be used for its excitation. At this wavelength *all* dipolarophiles show absorption, therefore we did not attempt to trap the azomethine ylide of aziridine **5** with acrylonitrile or the other dipolarophiles. The differences in reactivity between **3** and **4** are small and not far from the experimental error range (10–20%). The higher reactivity of **1** relative to **2** for reaction with the electron-deficient dipolarophiles probably reflects the higher electron density of **1**.

In order to study the behaviour of the transients in a protic solvent we again used methanol. In this solvent, the azomethine ylides from aziridines **3** and **4** were not detectable any more. Apparently, methanol is acidic enough for the complete protonation of the ylide within the laser pulse (20 ns). In the case of **3**, the corresponding iminium cation was reacted in MeOH/H_2O 9:1 (in this solvent, the rate constant for decay of the iminium ion is 8.8×10^3, and in neat methanol it is 4.5×10^4 s^{-1}) with the strong nucleophile N_3^-. From the linear plot of k_{obs} as a function of $[N_3^-]$, the rate constant for this reaction is $8.5 \times 10^8\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$, which is clearly less than diffusion-controlled (the accepted value for reaction in H_2O of N_3^- with carbocations is $5 \times 10^9\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$).[20] The difference may indicate partial reversibility of the reaction. Therefore, the reaction of the iminium cation with the weaker nucleophile but also less powerful leaving group OH^- was also studied (in MeOH). The rate constant found for this reaction is a reasonable[21] $8.8 \times 10^8\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$.

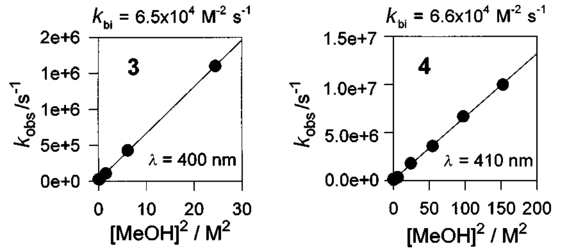


Fig. 7 k_{obs} for the protonation of the transients generated on photolysing 0.1 mM **3** or **4** in acetonitrile as a function of [methanol].

If methanol is added to solutions of **3** or **4** in acetonitrile, it turns out that the *k*(decay of ylide) *vs.* [MeOH] plot (not shown) is 'curved up', *i.e.*, the *reactivity* increases with increasing methanol concentration. As seen in Fig. 7, the dependence is quadratic, *i.e.*, k_{obs} increases with the square of the methanol concentration, which may be taken as indicative of *two* methanol molecules being involved in the reaction. Similar phenomena have previously been reported and discussed.[11,22]

In the case of 1-phenylaziridine[23] and 1-(*p*-cyanophenyl)-2-phenylaziridine[4b] the photolysis in acetonitrile led to only very weak spectra which could not be further analysed.

Summary and conclusions

The azomethine ylides of the aziridines **1**–**5**, formed by laser flash photolysis, were characterized spectroscopically and by their reactivity with O_2, acrylonitrile, and alcohols (MeOH/MeOD). With two phenyl groups present at the carbon centres, the absorption maximum of the ylide is located at about 480–500 nm. In the presence of only one phenyl group the maximum is at 400 nm. In all cases there is an additional absorption at about 270 nm. In the case of aziridines **1** and **2** the large kinetic isotope effects of 5–7 indicate a linear transition state for the ylide protonation. The corresponding iminium ions generated by protonation of the ylide show absorption bands at about 260 nm and can be trapped with OH^-. The reactions of the iminium ions with the stronger nucleophiles but better leaving groups Hal^- appear to be reversible.

Experimental

For the photolysis a LAMBDA Physik EMG 103MSC laser (λ = 193 and 248 nm) was used at intensities of 20–100 mJ per 20 ns pulse. Argon- or oxygen-saturated solutions were flowed through a 2 mm (in the direction of the laser light) by 4 mm (in the direction of the analysing light) quartz cell (4 mm path length). The flow rates were 100–200 ml h^{-1}.

Starting materials

(*E*)-1-Butyl-2,3-diphenylaziridine **1**,[4] (*E*)-2,3-diphenylaziridine **2**,[24] 1,2-diphenylaziridine (**3**),[25] 1-(*p*-methoxyphenyl)-2-phenylaziridine **4**[25] and 1-butyl-2-phenylaziridine **5**[26] were prepared by reported procedures.

Irradiation of aziridine 1 in the presence of oxygen

500 mg (2 mmol) of aziridine **1** were dissolved in 100 ml acetonitrile (LiChrosolv-grade) and irradiated for 18 h with a high pressure mercury lamp (Heraeus TQ 150) while oxygen passed through the solution. Separation by HPLC (10% ethyl acetate–cyclohexane) afforded *N*-benzoyl-*N*-butylbenzamide[27] as the only isolated product.

Acknowledgements

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12 Due to the low solubility of aziridine **1** in water we added 20% acetonitrile to the aqueous solution, but take the pK_a-value of pure water.

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17 The fact that the λ_{max} of this ion is lower than that (280 nm) from **1** may be due to the higher electron density in the latter case.

18 This higher value as compared to **1** may indicate a higher degree of linearity of the transition state.

19 It is likely that the charge distribution in the ylides is different for **1**–**2** as compared to **3**–**5**. With **1** and **2**, the negative charge is localized equally on the equivalent benzylic carbons, whereas in **3**–**5** it is probably located on the single benzylic carbon, as indicated in Scheme 1.

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