Infrared spectra and UV-induced photochemistry of methyl aziridine-2-carboxylate isolated in argon and xenon matrices

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ABSTRACT

Methyl aziridine-2-carboxylate (MA2C) has been isolated in low temperature argon and xenon matrices and its structure and photochemistry were studied by FTIR spectroscopy. The reactant as well as the main photoproducts were characterized by comparison of their experimental IR spectra with spectra calculated at the DFT(B3LYP)/6-311++G(d,p) level. The theoretical calculations predicted the existence of two low energy MA2C conformers, differing by the orientation of the O=C—C—N dihedral angle. Both conformers were identified in the studied matrices. Both narrowband tunable and broadband UV irradiations of matrix-isolated MA2C yielded isomerization photoproducts resulting from cleavage of the C—C and weakest C—N bonds of the aziridine ring. Irradiation with UV laser-light at $\lambda = 235$ nm resulted in the formation of the *E* isomer of methyl 2-(methylimino)-acetate (MMIA) and the *Z* isomer of methyl 3-iminopropanoate (M3IP). Subsequent irradiation at 290 nm led to observation of new bands resulting from $E \rightarrow Z$ isomerization of MMIA, while bands due to M3IP remained unchanged. The photoproduced *Z* isomer of MMIA could be subsequently consumed upon higher-wavelength irradiation ($\lambda = 330$ nm). The initially produced MMIA conformer was found to obey the nonequilibrium of excited rotamers (NEER) principle. No photoproducts resulting from the cleavage of the strongest C—N bond of the MA2C aziridine ring were observed, nor that of methyl 3-aminoacrylate (M3AA), which could in principle be obtained also by cleavage of the weakest C—N bond of the MA2C aziridine ring, but would imply a different H-atom migration simultaneous with the ring opening process. These results indicate that both the differential electronic characteristics of the C—N bonds of substituted aziridine rings and the type of required H-atom migration are major factors in determining the specific photochemistries of substituted aziridines. Photofragmentation reactions of MA2C were also observed, through identification of various related products, *e.g.*, acetonitrile, methanol, methane, CO and CO_2.

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1. Introduction

Aziridines are saturated three-membered heterocycles containing a nitrogen atom, which occur naturally and have innumerable applications [1,2]. The best known examples of natural products containing an aziridine ring include biologically active compounds such as mitomycins, carzinophilin and azinomycins, which possess strong antibiotic and antitumor properties [3–6]. Aziridines are also extremely versatile compounds used in the synthesis of molecules such as amino acids, nitrogen-containing larger-ring heterocycles and alkaloids, chiral ligands, natural products, pharmaceutical intermediates, *etc.*, *via* ring-opening or ring-expansion reactions [1–18]. In particular, aziridine-2-carboxylates and their derivatives have been used as

intermediates in the synthesis of α- and β-amino acids, both natural and non-natural, by stereospecific ring-opening reactions of the heterocyclic ring with nucleophiles, including organometallic reagents [19–24].

The reactivity of aziridines towards ring-opening and ring-expansion relates to their extremely high ring strain (above 110 kJ mol^{-1}), the C—N bond cleavage chemistry dominating the reactivity of these compounds [1,25,26]. The nature of the substituent at the N-atom plays a crucial role in the nucleophilic ring-opening of aziridines through C—N bond cleavage. According to their trend to undergo C—N bond cleavage, aziridines can be classified into two groups, "activated" and "non-activated" [1,2,9,26]. The first group aziridines bear electron-withdrawing substituents at the N-atom such as tosyl or acyl functional groups [15,21], which can stabilize the negative charge of the nitrogen atom and increase the reactivity of the aziridine ring towards nucleophiles. Non-activated aziridines have non-oxygenated substituents at the N-atom, such as the hydrogen atom, alkyl or aryl

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functional groups. In this case, the aziridine ring is more stable, and less reactive towards nucleophiles [13,14,18].

The photochemical cleavage of the aziridine C—N bonds has also been found to be preferred in the gas phase to the alternative ring-opening through cleavage of the C—C bond, particularly for molecules free of substituents at the carbon atoms [27,28]. However, for aziridines bearing electron withdrawing substituents at the ring carbon atoms, the C—C bond cleavage reactions become competitive [27]. The photochemical C—C ring-opening in aziridines is a disrotatory process, yielding azomethine ylides as primary photoproducts (see Scheme 1) [29,30]. The latter can then undergo intramolecular rearrangements via [1,2] hydrogen-atom shift or participate in 1,3-dipolar cycloadditions; less frequently, in addition reactions to nucleophiles [31–36]. The matrix isolation technique was previously applied in the identification and characterization of azomethine ylides resulting from the photo-chemical C—C bond cleavage of phenyl-substituted aziridines in Freon matrices at 77 K [37]. Nevertheless, in what way different substituents in the aziridine ring influence the preference for the carbon-nitrogen or the carboncarbon bond cleavage reactions is not yet well understood [27,38,39].

In the present study, we report on the UV-induced photochemical behavior of a compound that belongs to the class of non-activated aziridines (bearing a hydrogen atom at the ring nitrogen), and have a carboxylate substituent at one of the ring carbon atoms. For this compound one can then expect that both types of photochemistries (C—N and C—C bond cleavages) may operate.

Monomers of methyl aziridine-2-carboxylate (MA2C) were isolated in inert cryogenic matrices and their unimolecular photochemistry was followed by the interpretation of the IR spectra of the starting compound and of the resulting photo-products. In addition to ring-opening photoreactions, UV irradiation using laser light was found to lead to the observation of additional products originating from photofragmentation reactions. A detailed theoretical investigation of the potential energy surfaces of MA2C and of the possible photoproducts resulting from both C—C and C—N bond cleavages of the aziridine ring was also carried out at the DFT(B3LYP)/6-311++G(d,p) level of theory. To the best of our knowledge, no studies on matrix-isolated MA2C and its photochemistry have been reported hitherto.

2. Experimental and computational methods

Methyl aziridine-2-carboxylate (MA2C) (97% purity) was purchased from TCI Europe. Prior to usage, MA2C was additionally purified by the standard freeze-pump-thaw technique. The MA2C vapors were premixed with argon and xenon (N60 and N48, respectively, both supplied by Air Liquide) at a ratio of 1:1000 in a 3 L Pyrex glass reservoir to a pressure of 800 mbar, using the standard manometric procedure. Matrices were prepared by deposition of the mixtures onto a CsI substrate cooled to 15 K (Ar) or 30 K (Xe) assembled inside the cryostat (APD Cryogenics closed-cycle helium refrigeration system, with a DE-202A expander). The temperature of the (MA2C : inert gas) mixture
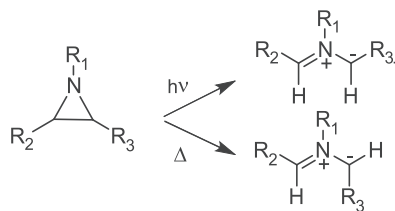
prior to deposition was 298 K, this temperature then defining the conformational composition of MA2C monomers.

The IR spectra, in the 4000–400 cm^{-1} range, were obtained using a Mattson (Infinity 60AR Series) or a Thermo Nicolet 6700 Fourier transform infrared spectrometer, equipped with a deuterated triglycine sulphate (DTGS) detector and a Ge/KBr beam splitter, with 0.5 cm^{-1} spectral resolution. To avoid interference from atmospheric H$_2$O and CO$_2$, a stream of dry air was continuously purging the optical path of the spectrometer.

Matrices were irradiated using two sources. The broadband irradiation was carried out with UV light provided by a 500 W Hg (Xe) lamp (Newport, Oriel Instruments), with output power set to 200 W, through the outer KBr window of the cryostat. A series of longpass optical filters, transmitting UV-light with λ > 397, 367, 328, 313 and 288 nm, was used. No change was observed in the spectra of MA2C upon irradiation under these conditions. Photochemical changes were observed only when irradiation was performed without using any filter, i.e., for λ > 235 nm (this value is defined by the absorbance edge of KBr in UV). Matrices were also irradiated with tunable UV light provided by the frequency doubled signal beam of the Quanta-Ray MOPO-SL pulsed (10 ns) optical parametric oscillator (FWHM ~0.2 cm^{-1}, repetition rate 10 Hz, pulse energy ~1 mJ) pumped with a pulsed Nd:YAG laser.

The quantum chemical calculations were performed using the Gaussian 03 program package [40] at the DFT level of theory, using the split valence triple-ζ 6-311++G(d,p) basis set [41] and the three-parameter B3LYP density functional, which includes Becke's gradient exchange correction [42] and the Lee-Yang-Parr correlation functional [43]. In the case of MA2C, the structures of conformers were optimized at both the DFT and MP2 levels of theory. Relaxed one-dimensional (1-D) potential energy scans and two-dimensional (2-D) potential energy maps were calculated to locate the minima of the possible photoproducts resulting from MA2C ring-opening reactions (for both C—C and C—N bond cleavages). Transition state structures were located using the synchronous transit-guided quasi-Newton (STQN) method [44]. The nature of all described stationary points on the studied potential energy surfaces (PES) was characterized through the analysis of the corresponding Hessian matrices.

Calculated vibrational frequencies and IR intensities were used to assist the analysis of the experimental spectra. The computed harmonic wavenumbers were scaled down by a single factor (0.978) to correct them mainly for the effects of basis set limitations, neglected part of electron correlation and anharmonicity effects. Normal coordinate analysis was undertaken in the internal coordinates space, as described by Schachtschneider and Mortimer [45], using the optimized geometries and harmonic force constants resulting from the DFT(B3LYP)/6-311++G(d,p) calculations. The internal coordinates used in this analysis were defined following the recommendations of Pulay et al. [46].

3. Results and discussion

3.1. Calculated structures and energies for MA2C

The MA2C molecule has one chiral center, carbon atom C3 (see Fig. 1 for atom numbering). The geometric parameters of MA2C reported in this work refer to the S-enantiomer. There are three intramolecular degrees of freedom in MA2C that lead to different conformers: (i) rotation of the ester group around the exocyclic C1—C3 bond; (ii) rotation of the methoxy group around the C1—O10 bond; (iii) inversion at the pyramidal nitrogen atom. The three above listed coordinates can assume two minimum-energy orientations each. They correspond approximately to *cis* and *trans* orientations around the (i) O2=C1—C3—N4, (ii)

Scheme 1. The C—C bond cleavage in aziridine yields azomethine ylide. The ring-opening processes induced by thermolysis (bottom) and photolysis (top) are conrotatory and disrotatory, respectively.