Photochemical transformations of matrix-isolated cycloalkyl nitrites†

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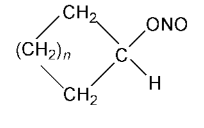
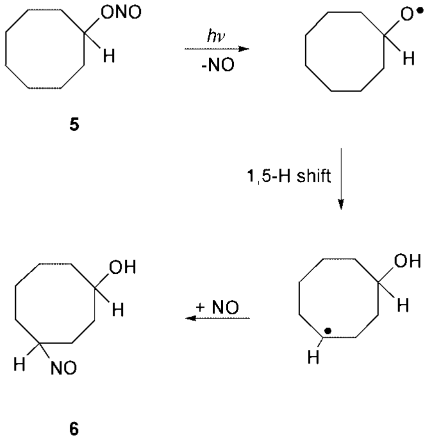
Photochemical transformations of cycloalkyl nitrites isolated in argon matrices have been studied. In the case of cyclohexyl, cycloheptyl and cyclooctyl nitrites complexes of HNO with the corresponding cycloalkyl ketones were formed. Photochemical irradiation of cyclobutyl nitrite resulted in the formation of 4-nitrosobutanal as the major product. Under similar conditions irradiation of cyclopentyl nitrite gave a mixture of 5-nitrosocyclopentanal and the complex of cyclopentanone and HNO.

Introduction

The photochemical transformation of cycloalkyl nitrites (**1**–**5**) have been studied for some time.[1,2] It has been found that only cycloheptyl (**4**) and cyclooctyl (**5**) nitrites undergo the rearrangement known as the Barton reaction.[3,4] As an example, the Barton rearrangement of cyclooctyl nitrite (**5**) results in the formation of 4-hydroxy-1-nitrosooctane (**6**) [reaction (1)], which further undergoes dimerisation. Smaller-ring cycloalkyl nitrites (**1**–**3**) did not undergo the Barton reaction and this was explained in terms of the difficulty of their forming the prerequisite six-membered ring intermediate.



$n = 1$ (**1**)
$n = 2$ (**2**)
$n = 3$ (**3**)
$n = 4$ (**4**)
$n = 5$ (**5**)



(1)

Recent contributions by Grossi[5,6] were aimed at EPR characterisation of the radical intermediates generated upon photolysis of cycloalkyl nitrites. It was assumed that the cycloalkoxy radicals formed upon photolysis of the O–NO bond in **1**–**3** primarily undergo ring fission and only the secondary rearranged and aggregated radical products could be characterised.

Our contribution is aimed at the study of the photochemical transformations of cycloalkyl nitrites under matrix isolation conditions. It is well known that the matrix isolation technique allows the characterisation of singly isolated molecules and the study of their unimolecular reactions induced by light.[7,8] Also, reactive intermediates generated under such conditions can be stabilised and characterised spectroscopically. In addition, some unimolecular reactions studied in matrices can be influenced by the matrix environment, due to the rigid structure of the matrix cages accommodating the studied molecules. In some cases new reaction pathways can be operative, which are not observed in gaseous and liquid phases.[9] Taking the above into consideration, we may expect not only to characterise the primary reactive species generated by light from the cycloalkyl nitrites, but also to correlate the observations made for matrix-isolated molecules with those obtained in solution.

Experimental

All the studied cycloalkyl nitrites were prepared from the corresponding alcohols according to the general method of Hunter and Marriot.[10] All the alcohols, except cyclobutanol, were purchased from Aldrich. Cyclobutanol was synthesised following the known procedure.[11] The cycloalkyl nitrites were vacuum distilled before use and their purity was controlled by GC–mass spectroscopy.

The studied cycloalkyl nitrites were diluted with an excess of argon (usually a mixture 1 : 1000 was used) and deposited onto CsI plate mounted on the expander stage of a Displex DE 202 (APD Cryogenics) cryostat.

Photochemical reactions were carried out with a high-pressure mercury lamp HBO-200 (Narva) and interference filters (Oriel) were used.

IR spectra of matrix-isolated species were obtained with a MB 100 (Bomem) FT-IR spectrometer. UV-VIS absorption spectra were measured with a PU 8710 (Philips) spectrometer. The irradiation and measurement were performed at 10 K. More details about the experimental setup are given elsewhere.[12]

Results and discussion

It has been observed that the strain energy accumulated in cyclobutane and cyclopentane rings can exert a fundamental influence on the behaviour of the cycloalkoxyl radicals primarily

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† A list of the frequencies and intensities of IR spectra recorded for the starting materials and the photoproducts, the calculated (B3LYP/6-31G*) and the observed spectra of generated 4-nitrosobutanal along with a list of the frequencies and intensities are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/b0/b002405h/

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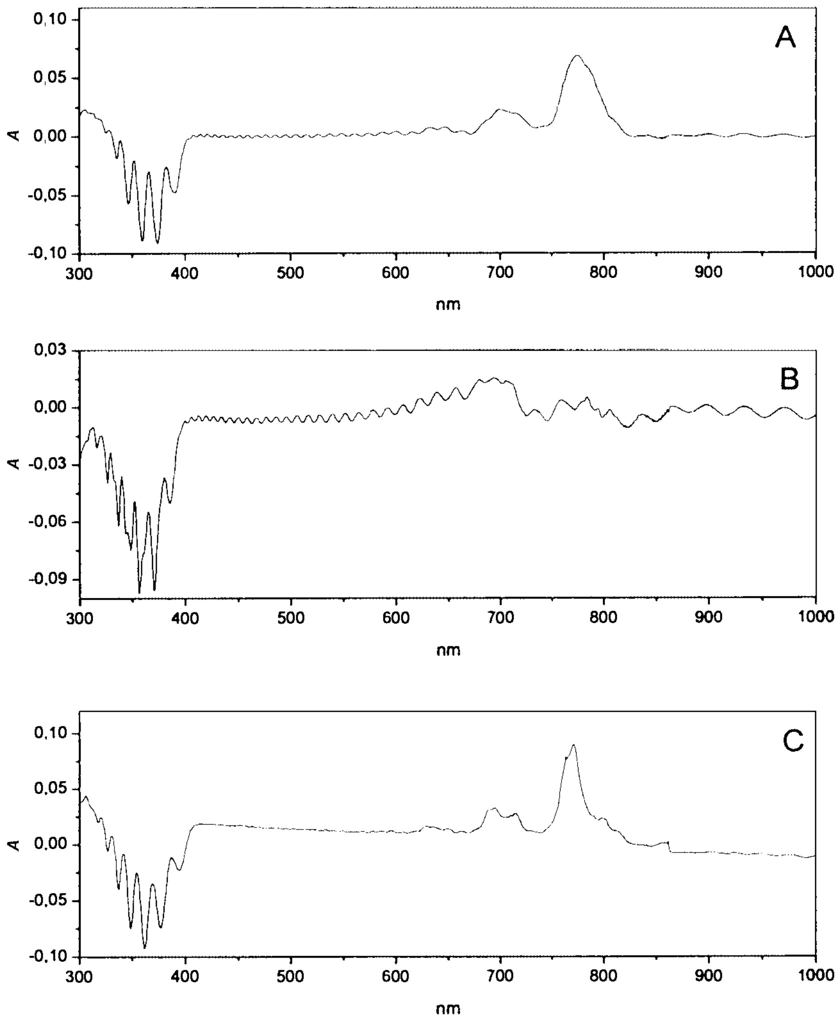
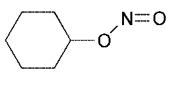


Fig. 1 Difference electronic absorption spectra (spectrum after irradiation minus spectrum before irradiation) for cyclohexyl (A), cyclobutyl (B) and cyclopentyl (C) nitrites isolated in argon matrices at 12 K. The samples were irradiated through the interference filter (λ = 365 nm) for 120 min.

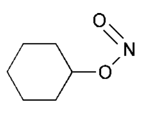
formed, so the observed products of photochemical transformations can depend on the size of the cycloalkane ring. Therefore the results obtained will be discussed separately for each system studied and the conclusions concerning the differences and similarities in photochemical behaviour of the studied systems will be presented at the end of this section.

Cyclohexyl nitrite (3)

The spectra taken for the matrix-isolated **3** before photolysis indicated the presence of two rotamers, s-*trans* (ν_{NO} = 1652.0 cm^{-1}) and s-*cis* (ν_{NO} = 1602.3 cm^{-1}).



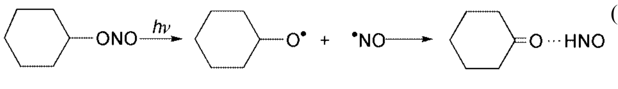
3 (s-*trans*)



3 (s-*cis*)

The relative intensity of the s-*trans*/s-*cis* bands was found to be 3.6. In the course of the photolysis all the characteristic bands of **3** decayed with a similar rate, indicating practically the same photochemical stability for both the s-*trans* and s-*cis* rotamers. The relative intensity of the bands due to the s-*trans*/s-*cis* rotamers remained constant during the photolysis, a fact which indicates a much lower quantum yield of photochemically induced rotamerism compared to O–NO bond cleavage. Similar observations were made for the other cycloalkyl nitrites studied. The presence of rotameric mixtures is well characterised for alkyl nitrites,[13,14] but the photochemical stability of the rotamers is not always similar.[15,16]

The photochemical transformation of matrix-isolated **3** was monitored by electronic absorption as well as by infrared spectroscopy. Careful analysis of the spectra allowed the identification of a bimolecular complex of cyclohexanone and HNO (**7**) as a reaction product. The new absorption bands generated in the region 650–770 nm (Fig. 1A) are characteristic for HNO.[17] Also, new bands in the infrared spectrum (Fig. 2A) observed at 1574.3, 1512.1 and 2728.0 cm^{-1} are due to HNO.[18,19] The observed bands due to HNO complexed with cyclohexanone are, in fact, shifted when compared with monomeric HNO observed in the gas phase (1565.3, 1500.4 and 2684.7 cm^{-1})[20] or in an argon matrix (1563.5 and 2717.0 cm^{-1}).[18] All the characteristic bands for cyclohexanone with a pronounced carbonyl stretch ($\nu_{C=O}$ = 1711.8 cm^{-1}) are seen. This product analysis indicates that the photolysis of cyclohexyl nitrite (**3**) involves O–NO bond cleavage resulting in the formation of a radical pair which disproportionates to give a complex **7** [reaction (2)].



(2)

3 7

A trace of free NO (ν = 1869.6 cm^{-1}) was also seen. A similar conclusion was drawn for the photochemical study of matrix-isolated methyl nitrite, where a complex of formaldehyde and HNO was intercepted.[15]

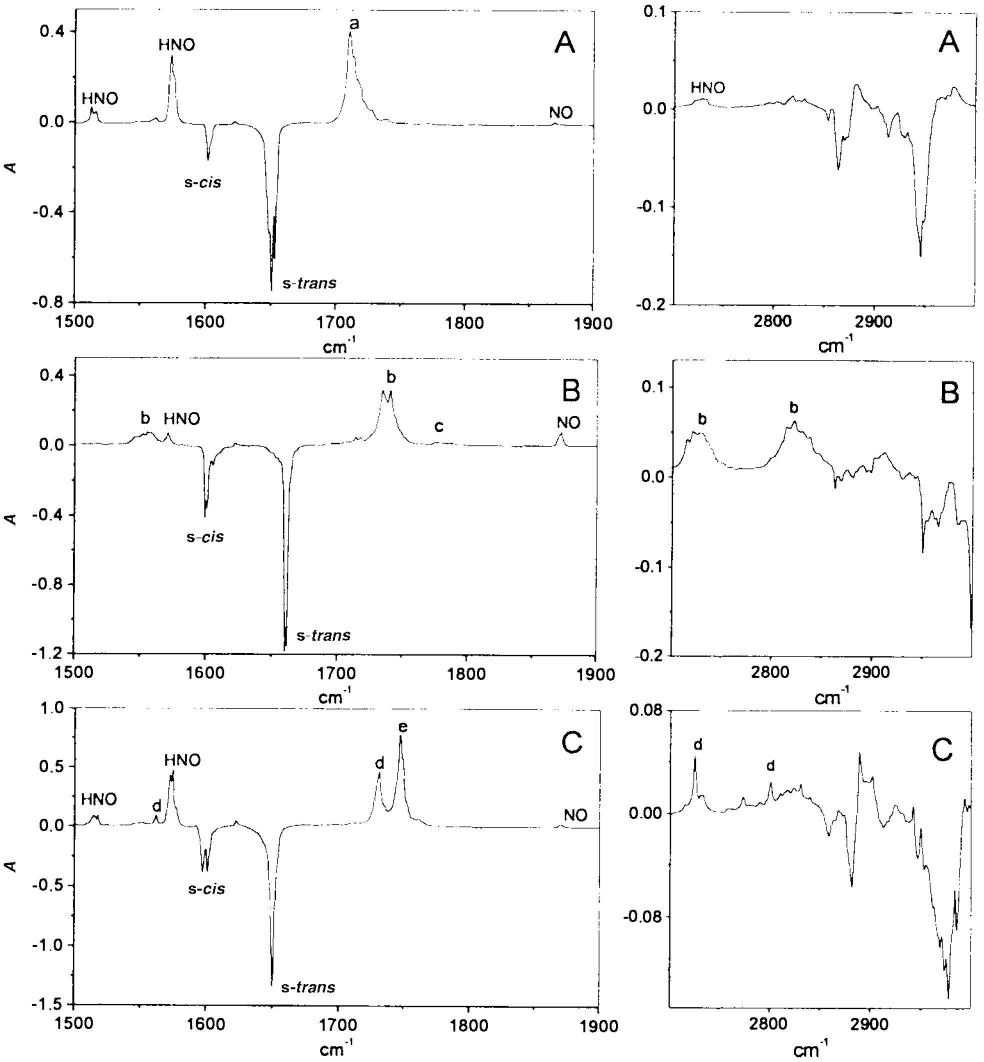
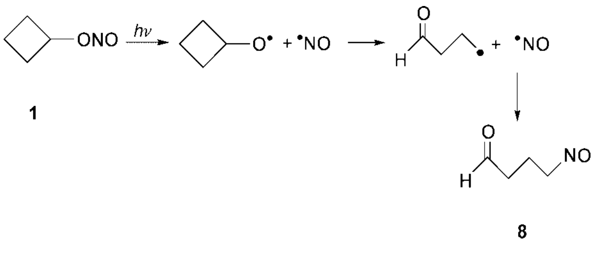


Fig. 2 Difference infrared spectra (spectrum after irradiation minus spectrum before irradiation) for cyclohexyl (A), cyclobutyl (B) and cyclopentyl (C) nitrites isolated in argon matrices at 12 K. The samples were irradiated through the interference filter (λ = 365 nm) for 120 min. The bands generated upon photolysis are labelled and assigned to the following products: (a) cyclohexanone, (b) 4-nitrosobutanal, (c) cyclobutanone, (d) 5-nitrosopentanal, (e) cyclopentanone.

Cyclobutyl nitrite (1)

The photochemical transformations of matrix-isolated **1** are drastically different from those observed for **3**. A major product of the former was identified as 4-nitrosobutanal (**8**). The product assignment was based on a characteristic absorption at $\lambda_{max} \approx 690$ nm (Fig. 1B) typical for nitroso compounds.[21] In the infrared spectrum (Fig. 2B) characteristic bands expected for **8** are seen ($\nu_{C=O}$ = 1736.4, $\nu_{N=O}$ = 1557.4 and ν_{OC-H} = 2727.1, 2822.6 cm^{-1}).[22] Formation of 4-nitrosobutanal (**8**) must therefore involve ring fission as presented in reaction (3).

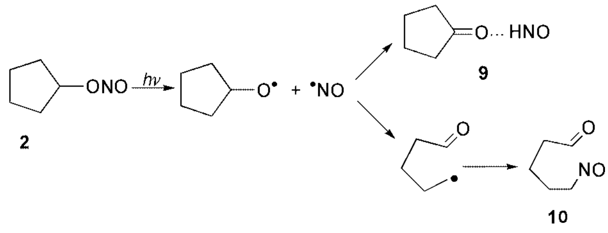


(3)

Careful examination of the spectra also indicated the formation of the complex between cyclobutanone and HNO in only a trace amount. There are very weak bands present in the infrared spectrum that are characteristic for HNO and a weak band at 1780.3 cm^{-1} due to the carbonyl stretch in cyclobutanone. Also a small amount of NO is seen.

Cyclopentyl nitrite (2)

The photochemical observations made for matrix-isolated **2** possess features of the two systems discussed above. In this case, in addition to a complex of cyclopentanone and HNO (**9**), 5-nitrosopentanal (**10**) is seen [reaction (4)]. This assignment is based on the observation of characteristic bands in the electronic absorption spectrum (Fig. 1C) as well as on new bands seen in the IR. 5-Nitrosopentanal can be characterised by the expected bands, typical of the present functionalities, as $\nu_{C=O}$ = 1730.6, $\nu_{N=O}$ = 1563.2 and ν_{OC-H} = 2725.6, 2830.8 cm^{-1}. The observed band at 1746.5 cm^{-1} is as expected for the cyclopentanone carbonyl stretch.



(4)

Cycloheptyl (4) and cyclooctyl (5) nitrites

In a sharp contrast to observations made in solutions,[3,4] where the Barton rearrangement takes place, the phototransformations of matrix-isolated **4** and **5** follow those seen for **3**. The only products identified possess all the features characteristic of the complexes of HNO with cycloheptanone and cyclooctanone, respectively. For example, photolysis of matrix-isolated cycloheptyl nitrite (**4**) [$\nu_{N=O} = 1636.7\ \text{cm}^{-1}$ (s-*trans*) and $\nu_{N=O} = 1599.0\ \text{cm}^{-1}$ (s-*cis*)] resulted in the formation of a complex between cycloheptanone ($\nu_{C=O} = 1697.7\ \text{cm}^{-1}$) and HNO ($\nu_{N=O} = 1574.3\ \text{cm}^{-1}$). Similarly, photolysis of matrix-isolated cyclooctyl nitrite (**5**) [$\nu_{N=O} = 1640.5\ \text{cm}^{-1}$ (s-*trans*) and $\nu_{N=O} = 1599.0\ \text{cm}^{-1}$ (s-*cis*)] gave cyclooctanone ($\nu_{C=O} = 1698.0\ \text{cm}^{-1}$) and HNO ($\nu_{N=O} = 1575.0\ \text{cm}^{-1}$).

Conclusion

The major reaction pathway for the studied matrix-isolated cycloalkyl nitrites involves O–NO bond cleavage, which is followed by disproportionation, resulting in a complex of the corresponding ketone and HNO. However in the case of cyclobutyl nitrite (**1**) and partly in the case of cyclopentyl nitrite (**2**) the cycloalkyl radicals primarily formed undergo ring opening. The follow-up process of NO addition to the ring-opened radical results in the formation of nitrosoaldehydes. On comparing these results with phototransformations in solution, some distinct differences were noticed. First of all, the cyclopentoxyl radical generated in matrices only partially follows the ring fission pathway. Such a process was seen in solution exclusively. Also, cycloheptyl and cyclooctyl nitrites did not give the Barton rearrangement products that are efficiently generated in solution. The observed differences may indicate an influence of the rigid matrix environment on the reaction pathways. One would intuitively expect that for the Barton rearrangement to occur, some rotational freedom is needed to accommodate molecules in the proper geometry for a 1,5-hydrogen shift. Such a process would be seriously restricted in an argon matrix cage. Also, the space-demanding ring-opening process could be inhibited by the rigid matrix environment. On the other hand, the energy of an argon crystal lattice is very small[23] and the excess energy from the excitation process is often sufficient to overcome constraints introduced by the matrix. It seems clear that photochemical transformations of matrix-isolated cycloalkyl nitrites are indeed influenced by the matrix.

Acknowledgements

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