

THE UV PHOTOLYSIS OF AZIDOMETHANE AND 3-AZIDOPROPYNE IN NITROGEN MATRICES

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ABSTRACT

IR spectra of azidomethane, 3-azidopropyne and 3-azido-1-d-propyne in nitrogen matrices have been recorded during UV photolysis. In contrast to the simple photolytic reaction of matrix isolated azidomethane (azidomethane \rightarrow methylenimine \rightarrow HCN + HNC), 3-azidopropyne apparently displays more complex reaction paths.

INTRODUCTION

As a part of our spectroscopic investigations of organic azido compounds we have also studied their photolytic reactions in inert gas matrices. From prior analogue studies of azido compounds (refs.1-3) it is known that molecular nitrogen can be eliminated by irradiation of UV light and products deriving from nitrenes are formed. In the present communication we present our preliminary results for the photolytic reactions of azidomethane and 3-azidopropyne.

EXPERIMENTAL

Warning: Organic azido compounds are all explosive and should be handled with the utmost care.

3-azidopropyne was first prepared from 3-bromopropyne using tetramethylguanidiniumazide as an azide-ion source (ref.4). We have found that also iodo-propadiene can be converted to 3-azidopropyne under similar conditions with a yield of 82% (ref.5). However, the most advantageous method to substitute halogen with the azido group is to expose a mixture of the organic halide and an aqueous sodiumazide solution to ultrasonic irradiation (ref.5). Azidomethane was prepared from iodomethane and tetramethylguanidiniumazide in sulfolane (ref.6).

Samples mixed with nitrogen (M/A \sim 750) were deposited on a CsI window in a Displex unit from Air Products and later photolyzed through a quartz window using a medium pressure mercury lamp (Philips 93110E). The IR spectra were recorded with a Bruker IFS 114c fast scan interferometer.

some possible photolytic reactions are shown. As seen, many exotic molecules can - at least in the theory - be formed though not all are equally probable.

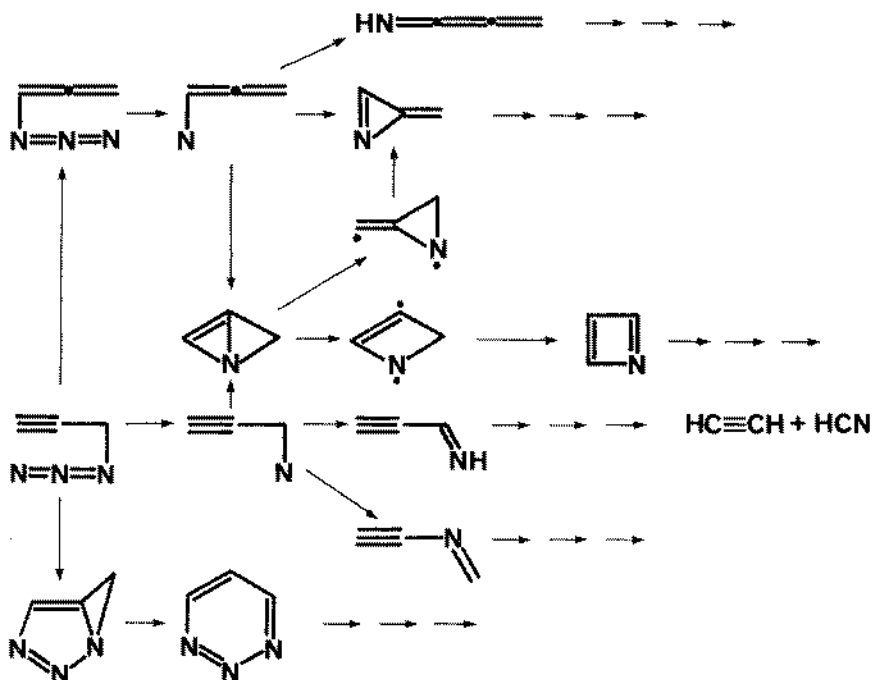


Fig. 2. A priori possible photolysis products of 3-azidopropyne.

We observe at least three "generations" of bands during the photolysis, but we have not yet been able to correlate the new "generations" with the molecules shown in Fig. 2. Further, we are not able to fit the observed absorbances to a reaction of the type: $A \rightarrow B \rightarrow C \rightarrow \dots$. The bands originating from 3-azidopropyne show a perfect (within 5%) exponential decline with the irradiation time, so we are confident that we are in control of the experimental conditions.

In Figs. 3 and 4 are shown examples of the spectral evolution during the photolysis. Most striking is the very strong band at 3450 cm^{-1} - normally the region of amine N-H stretching. However, it is difficult to imagine a reaction route leading from an azide over a nitrene radical to an amine. It may very well be that this "amine-band" in reality originates from the N-H stretching vibration in HNC, appearing ca. 100 cm^{-1} higher in the pure N_2 matrix (refs.2,7). In the present case photolytic production of HNC must be accompanied by the simultaneous formation of ethyne in the same N_2 cage. The perturbation caused by the ethyne molecule would explain this 100 cm^{-1} downward shift. In the frequency

range around 600 cm^{-1} we observe two bands which might be due to the bending modes of HNC, shifted approximately 40 cm^{-1} upwards with reference to the pure N_2 matrix (refs. 2,7). Similar shifts are also observed for the ethyne vibrations.

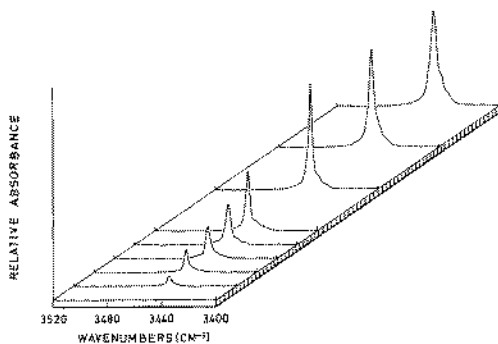


Fig. 3. Evolution of the IR band at 3450 cm^{-1} during UV photolysis. The time intervals are 5 and 15 min.

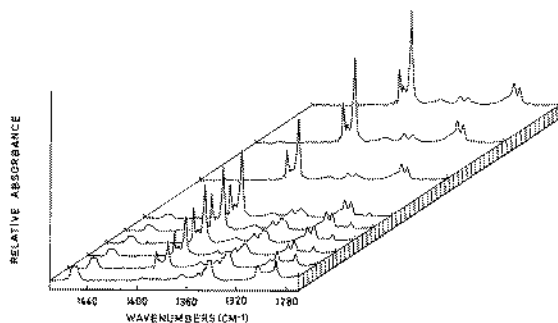


Fig. 4. Evolution of $1470 - 1270\text{ cm}^{-1}$ region during UV photolysis. The time intervals are 5 and 15 min.

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