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Evidence for a ketene intermediate in the photochemical transformation of matrix-isolated *o*-nitrobenzaldehyde*

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Abstract

The ketene intermediate generated upon photolysis at 313 or 350 nm of matrix-isolated *o*-nitrobenzaldehyde was stabilized and characterized by UV–vis and IR spectroscopy. Further irradiation resulted in the formation of *o*-nitrosobenzoic acid along with *N*-hydroxybenzisoxazolone. Exclusive formation of the acid was observed when photolysis was carried out at wavelengths greater than 357 nm.

INTRODUCTION

The photochemical transformation of *o*-nitrobenzaldehyde (**1**) to *o*-nitrosobenzoic acid (**2**) was first reported by Ciamician and Silber in 1901 [1]. Later studies were aimed at elucidation of the reaction mechanism [2–4]. It was proposed that this intramolecular rearrangement initially involves aldehyde hydrogen-atom transfer to the nitro group in the excited state, giving a remarkably reactive ketene intermediate (**3**) characterized by a transient absorption spectrum with a maximum at 440 nm.

The application of IR matrix-isolated spectroscopy [5–8], which is characterized by high spectral resolution, allows one to analyze for primary and secondary photochemical reactions and to relate the spectral characteristics of starting materials and photoproducts to specific structural features. This technique has already been successfully applied for characterization

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of intermediates in photochemical transformations of various ortho-substituted phenyl aldehydes [9,10].

Our contribution presents the results of studies on the photochemical transformation of **1** under matrix-isolation conditions. Direct evidence for stabilization of **3** is provided. Spectroscopic characterization of the secondary photoproducts is also given.

EXPERIMENTAL

o-Nitrobenzaldehyde (Fluka, >99%) was used as received. Argon (Aldrich, 99.99%) was passed through low-temperature traps before deposition.

Since the sample pressure was insufficient to prepare a gaseous mixture, argon was passed over a solid substrate placed in the thermostatted tube connected to the deposition line behind the needle valve. The tube was kept at 20–22°C during deposition. Argon was deposited with a flow rate of 50–70 μmol min^{-1} and the total amount deposited varied from 5 to 7 mmol. The sample vapour diluted by the argon carrier stream was condensed onto a caesium iodide window mounted on the expander stage of a Displex DE-202 (ADP Cryogenics) cryostat. During deposition the window support was kept at 18–20 K. The matrix ratio was estimated to be 600–700.

Photochemical reactions were carried out with a high-pressure mercury lamp HBO-200 (Narva). Interference filters UV-KSIF (Zeiss Jena) and glass cut-off filters (Oriel) were used. IR spectra of matrix-isolated species were obtained with an MB 100 (Bomem) FT-IR spectrometer equipped with a wide-band MCT detector working at a resolution of 1 cm^{-1}. UV–vis absorption spectra were measured with a PU 8710 (Philips) spectrophotometer. The irradiation and measurements were performed at 10 K.

RESULTS AND DISCUSSION

In the early stages of the irradiation of matrix-isolated *o*-nitrobenzaldehyde through interference filters 313 or 350 nm, a species possessing the absorption spectrum (λ_{max} 435 nm) shown in Fig. 1 was generated. This absorption is indicative of an extended chromophore and is consistent with the properties expected for **3** [3,4]. Prolonged irradiation bleached the matrix and the spectrum recorded was very close to that observed for matrix-isolated *o*-nitrosobenzoic acid.

The results of parallel observations in the IR region are depicted in Fig. 2. Weak absorptions positioned at 2118 and 2107 cm^{-1} (Fig. 2(b)) clearly represented a ketene stretching vibration of **3**. After prolonged irradiation, these bands were not present in the IR spectrum (Fig. 2(c)). Since **3** was extremely light sensitive, even a careful choice of photolyzing light did not

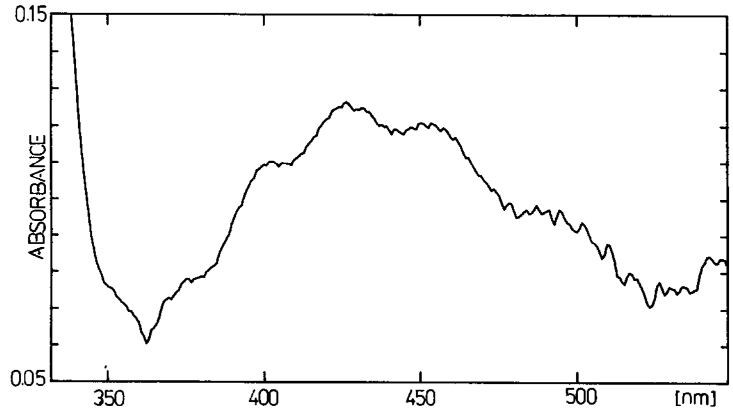


Fig. 1. Difference electronic absorption spectrum of matrix-isolated *o*-nitrobenzaldehyde (1) obtained by subtraction of the spectrum recorded before irradiation from the spectrum recorded after irradiation for 5 min through a 350 nm interference filter.

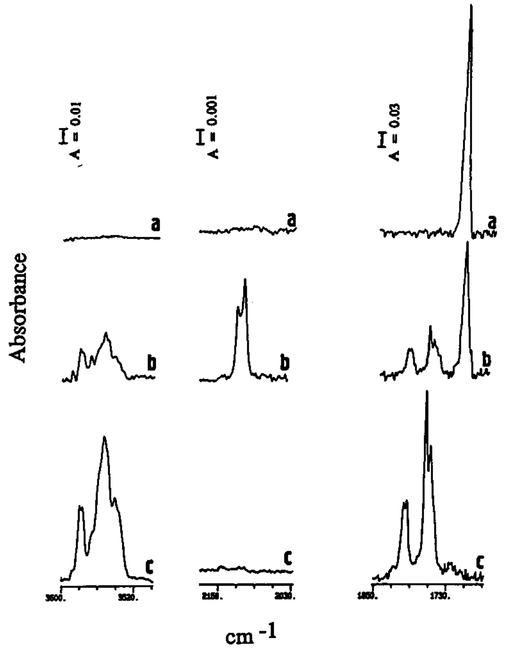


Fig. 2. Expanded hydroxy, ketene and carbonyl stretching regions of the IR spectra of matrix-isolated *o*-nitrobenzaldehyde (1): (a) before irradiation; (b) after irradiation for 5 min; (c) after irradiation for 60 min through a 350 nm interference filter.

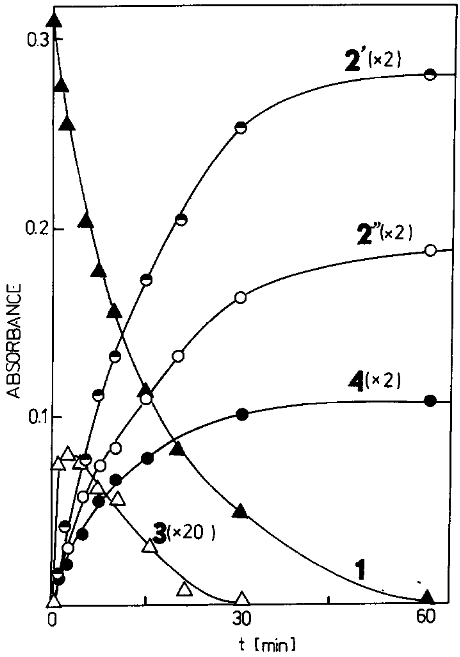


Fig. 3. Changes in the intensities of characteristic bands in the course of the photolysis of matrix-isolated *o*-nitrobenzaldehyde (1) through a 350 nm interference filter: (1) 1711 cm^{-1}; (2′) 1769 cm^{-1}; (2″) 1761 cm^{-1}; (3) 2107 cm^{-1}; (4) 1799 cm^{-1}.

allow us to increase its concentration sufficiently in order to detect any vibrations except the most intense ketene band. The OH stretching vibration of **3** might also be decreased by the strong absorption of secondary photoproducts in this region.

Two secondary photoproducts were evident in the final spectrum. The major one, possessing characteristic absorptions at 1769 and 1761 cm^{-1} in the carbonyl stretching region and at 3553 cm^{-1} in the OH stretching region, is assigned to *o*-nitrosobenzoic acid. All the observed bands of the major photoproduct correlated well with the bands observed in the IR spectrum of matrix-isolated **2**. The minor photoproduct, characterized by a set of two split bands observed in characteristic regions at 3580, 3577 and 1804, 1799 cm^{-1}, is tentatively assigned to *N*-hydroxybenzisoxazolone (**4**).

o-Nitrobenzoic acid was the only product recovered after warming the sample to room temperature. Apparently, a cyclic isomer (**4**) was thermally unstable and rearranged to the acid (**2**). This process might be facilitated by traces of water often present on the window after the matrix experiment.

Changes in intensities of the characteristic bands of the starting material, intermediate and secondary photoproducts in the course of photolysis are shown in Fig. 3. As one would expect, the intensity of the

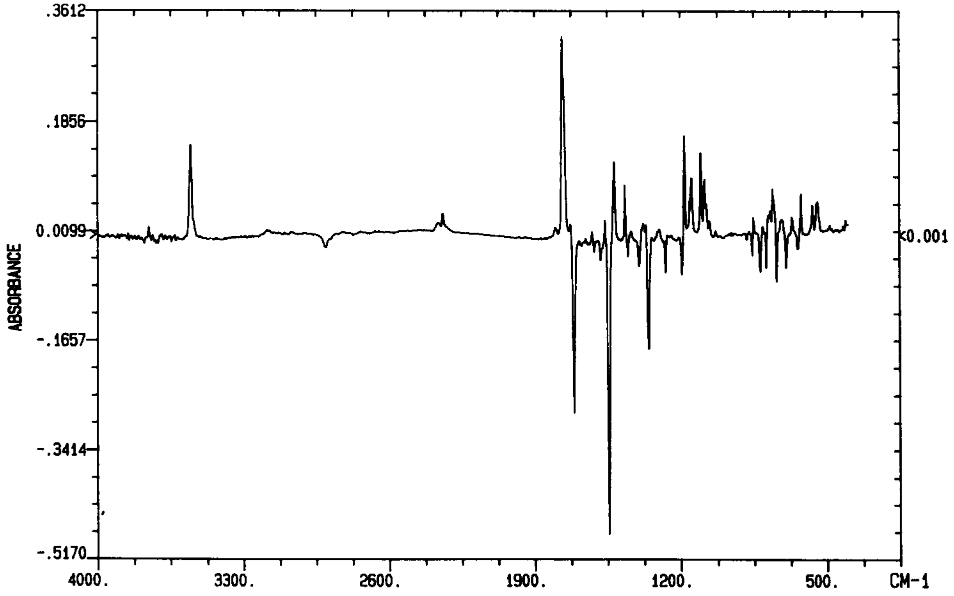
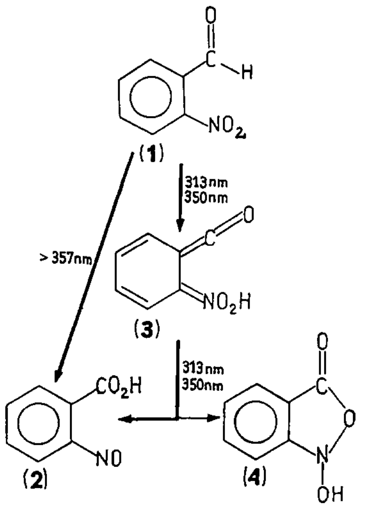


Fig. 4. Difference IR spectrum of matrix-isolated o-nitrobenzaldehyde (1) obtained by subtraction of the spectrum recorded before irradiation from the spectrum recorded after irradiation for 12 min through a 357 nm cut-off filter.

ketene band of **3** (curve 3) was increasing in the early stages, passing over a maximum and later decaying, while the intensities of the bands due to secondary photoproducts were increasing throughout the experiment. Similar results were obtained when photolysis was carried out through a 313 nm interference filter, although the relative distribution between the photoproducts was slightly different compared with experiments with a 350 nm filter.

In experiments in which a 357 nm cut-off filter was used, no ketene intermediate was detected and such reactions resulted in exclusive formation of **2** (Fig. 4). This observation might indicate that irradiation of the sample with light covering the visible transition of the ketene causes its efficient rearrangement to **2**. Irradiation of the final product (**2**) through a 254 nm interference filter gave rise to new intense bands at 3185, 2341, 1525 and 1389 cm^{-1}, which are apparently due to decarboxylation products.

The observed phototransformations of matrix-isolated **1** are summarized in the following reaction scheme.



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