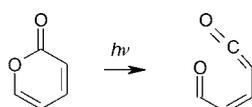


Photochemical α -Cleavage in Pyran-2-thione: Generation of Aldehyde–Thioketene and Thioaldehyde–Ketene Photoproducts

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The photochemical ring-opening reaction leading to cleavage of the C–O α -bond in α -pyrones, and other similar photoreactions observed in closely related unstrained cyclic carbonyl compounds such as 2,4-cyclohexadienones^[1] and pyrimidones,^[2] are well documented. In the case of α -pyrones (Scheme 1), because of the high reactivity of the ketene



Scheme 1. Conventional presentation of the ring-opening process leading to formation of conjugated aldehyde–ketene species from closed-ring α -pyrone molecules.

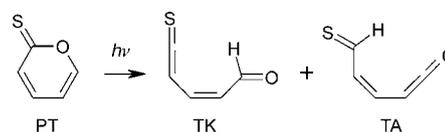
moiety, the open-ring conjugated ketene photoproducts can be stabilized only in solid, low-temperature inert matrices.^[3,4] The intense, characteristic infrared band due to the antisymmetric stretching vibration of the —C=C=O group, appearing in the 2140–2130 cm^{-1} spectral region, facilitates the identification of ketene photoproducts.

Open-ring conjugated ketenes are usually presented as structures shown in Scheme 1. However, it is improbable that such isomers of conjugated ketenes could be stabilized under any conditions. It was recently demonstrated^[3] that these forms revert barrierlessly to stable, closed-ring structures. The detailed structural analysis carried out for the conjugated aldehyde–ketene generated upon UV irradiation of α -pyrone strongly suggests^[3] that the isomers, which are stabilized in a matrix, must adopt a conformation with at least one of the groups rotated around a single or double bond of the open-chain structure.

Contrarily to the carbonyl compounds, the photochemical cleavage of an α -bond is believed not to occur for thiocarbonyl compounds,^[5] though Pirkle et al. reported^[6] pyranthiones that underwent thermal rearrangements (similar to that depict-

ed on Scheme 1) during pyrolysis at elevated temperatures. The known exceptional cases of photochemical α -cleavage concern only the species with C=S groups directly attached to small (three- or four-membered), strained rings.^[7]

Herein, we report the experimental observation of the photochemical ring opening, by cleavage of the C–O α -bond in pyran-2-thione (Scheme 2). In this compound the thiocarbonyl group is attached to a relaxed, six-membered ring.



Scheme 2. Photochemical transformation of pyran-2-thione (PT) to aldehyde–thioketene (TK) and, subsequently, to thioaldehyde–ketene (TA), experimentally observed herein.

The unimolecular photochemistry of pyran-2-thione was studied by a combined usage of the matrix isolation technique and FTIR spectroscopy. The infrared spectral signatures of the primary photogenerated aldehyde–thioketene (TK) isomeric forms, as well as those of the secondary products, thioaldehyde–ketene (TA) isomers, were assigned on the basis of theoretical calculations carried out at the B3LYP/6-311++G(d,p) level.

In the matrix isolation experiments, a sample of pyran-2-thione^[8] (PT) was placed into a glass tube protected against light and connected to the chamber of the cryostat with a needle valve. The vapor of the compound was introduced into the cryostat chamber through the needle valve together with large excess of the host matrix gas (argon N60, Air Liquide) coming from a separate line. A cold (10 K) CsI window mounted on the tip of an APD Cryogenics DE-202 A closed-cycle helium refrigerator was used as optical substrate. Care was taken to keep the guest-to-host ratio in the matrixes low enough to avoid association. The matrixes were irradiated through the outer KBr window of the cryostat, with UV light ($\lambda > 337$ nm) provided by a 150 W xenon short-arc lamp (Osram XBO 150W/CR OFR). The infrared spectra were recorded with 0.5 cm^{-1} resolution using a Mattson (60 AR Infinity Series) FTIR spectrometer equipped with a KBr beamsplitter and a deuterated triglycine sulphate (DTGS) detector. The Gaussian 98 program package^[9] was used for the DFT calculations, which were carried out at the B3LYP/6-311++G(d,p) level of theory.

The fingerprint region of the infrared spectrum of PT monomers isolated in an Ar matrix, at 10 K, is presented in Figure 1. This spectrum is compared with the results of the theoretical calculations, and good agreement is observed, enabling full assignment of the observed bands (the complete list of assignments is provided in Table S01 of the Supporting Information together with calculated data). It is obvious from Figure 1, that after the matrix deposition, and before the irradiation, experimental sample consists exclusively of isolated PT molecules and does not contain any other species.

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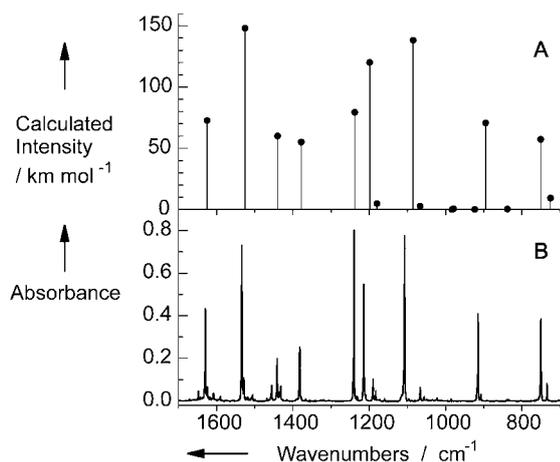


Figure 1. The fingerprint region of the infrared spectrum of pyran-2-thione: A) theoretical spectrum calculated at the B3LYP/6-311++G(d,p) level; B) experimental spectrum of monomers of the compound isolated in an argon matrix at 10 K. Theoretical frequencies were scaled using a factor equal to 0.978.

In situ UV irradiation ($\lambda > 337$ nm) of the matrix-isolated compound led to the opening of the pyran-2-thione ring. The photoreaction manifested itself by the decrease of the initial IR spectrum and by the appearance, in the 1800–1650 cm^{-1} region, of new, characteristic bands (Figure 2). These bands

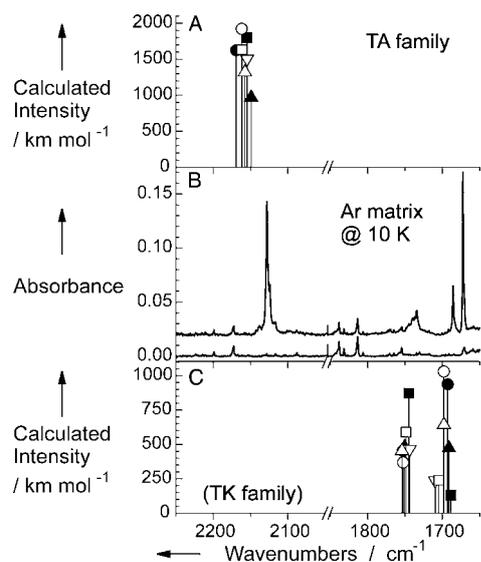


Figure 2. Infrared spectra (2300–1600 cm^{-1} region) showing the formation of open-ring conjugated isomers of pyran-2-thione isolated in argon matrix upon in situ irradiation. Frame B: lower trace: spectrum recorded immediately upon deposition of the sample; upper trace: spectrum recorded after 320 minutes of irradiation with a 337 nm cut-off filter. Frames A and C show the calculated spectra for the possible thioaldehyde-ketene (TA; A) and aldehyde-thioketene (TK; C) isomers. Theoretical frequencies were scaled with the factor 0.978.

were assigned to the stretching vibrations of the thioketene ($-\text{C}=\text{S}$)^[10] and the aldehyde ($-\text{C}(=\text{O})\text{H}$) groups. The theoretically predicted spectra for the seven different open-ring conjugated aldehyde-thioketene (TK) forms, in the $\nu\text{C}=\text{S}$ thioketene antisymmetric stretching and $\nu\text{C}=\text{O}$ aldehyde stretching

regions, are also shown in Figure 2, unequivocally demonstrating the photoproduction of the conjugated aldehyde-thioketene. Note that under the present experimental conditions (10 K) thermal processes leading to open-ring products cannot occur, though conformational interconversion between the different forms of the aldehyde-thioketene may take place. However, the identification of the photoproduced individual opening isomeric forms is difficult, because all seven possible isomers give rise to characteristic absorptions predicted to lie close to each other and are easily accessible energetically under the present photochemical excitation (see Table S02 and Figure S01 in the Supporting Information).

As shown in Figures 2 and 3, along with the absorptions appearing in the 1800–1650 cm^{-1} region, new absorptions grew in the 2150–2100 cm^{-1} region. These absorptions must be due to other photoproducts, since none of the aldehyde-thioketene isomeric forms should exhibit bands in this region. The strong absorption around 2130 cm^{-1} is characteristic of the $\nu\text{C}=\text{C}=\text{O}$ ketene antisymmetric stretching vibration^[3,4] and evidences formation of the open-ring thioaldehyde-ketene (TA) isomers (see Figure S02 in the Supporting Information for structures). The theoretically predicted spectra for all possible TA forms, in the 2300–1600 cm^{-1} region, are also shown in Figure 2. Also in this case, the identification of the particular TA conformers is complicated by the fact that they are predicted to give rise to $\nu\text{C}=\text{C}=\text{O}$ bands at nearly the same frequency (see Table S03 in the Supporting Information).

Formation of the thioaldehyde-ketene species can be possible by an intramolecular hydrogen-transfer reaction analogous to that occurring in the conjugated aldehyde-ketene generated from α -pyrone.^[11] Only one of the TK conformers (that depicted in Scheme 2 and TK4 in Figure S01 in the Supporting Information) is well aligned for intramolecular H-atom abstraction. The thioaldehyde-ketene is then initially produced in the conformation depicted in Scheme 2 (conformer TA4 in Figure S02), which subsequently isomerizes to other TA conformational states.

The sequence of processes leading to formation of the TK and TA species is easily demonstrated by following the evolution of the respective characteristic bands with time of irradiation (see Figure 3). The bands due to TK (in the 1660–1750 cm^{-1} region) clearly emerge since the very beginning of the irradiation, while those originated from TA (at 2110–2140 cm^{-1}) after five minutes of irradiation are still not discernible and start to grow considerably later. Based on this observation, we attribute the TK family of compounds to primary and TA to secondary photoproducts.

A final remark shall be done regarding the possibility of photoproduction of the Dewar isomer of pyran-2-thione as a competitive reaction with the above-described open-ring photoprocess. Photoproduction of the Dewar isomer of α -pyrone is a well-known process and has been used to generate cyclobutadiene (together with CO_2).^[3,11–13] Indeed, the relative efficiency of the Dewar isomerization and open-ring reaction leading to the conjugated aldehyde-ketene was found to depend strongly on the presence of substituents in the pyrone ring. For example, in the unsubstituted α -pyrone the kinetically pre-

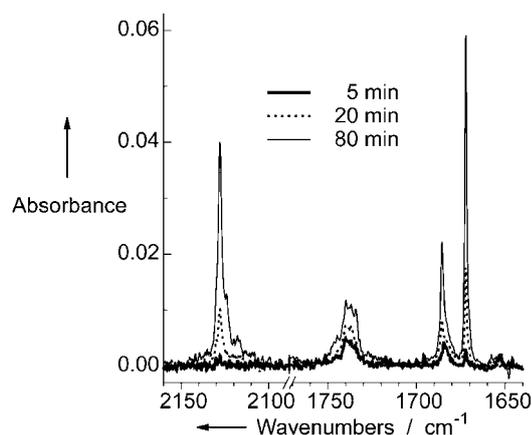


Figure 3. Selected experimental infrared spectra ($2150\text{--}1650\text{ cm}^{-1}$) showing progress and sequence of generation of different photoproducts during irradiation of pyran-2-thione isolated in an argon matrix at 10 K. The sample was irradiated with a high-pressure Xenon arc lamp fitted with a filter transmitting light with $\lambda > 337\text{ nm}$. The spectrum of the nonirradiated sample is subtracted. Cumulative irradiation times are specified in the main frame.

ferred reaction is the ring-opening process, while in 4,6-dimethyl- α -pyrone, 4-hydroxy-6-methyl- α -pyrone and 4-methoxy-6-methyl- α -pyrone the Dewar isomerization strongly dominates.^[3,4,11–15] Herein, the possibility of occurrence of a similar process in pyran-2-thione, leading to photoproduction of cyclobutadiene and COS, was also considered. However, no signs of absorptions due to either cyclobutadiene and COS or the Dewar isomer could be found in the spectra of the pyran-2-thione irradiated matrices, clearly indicating that under the present conditions this process does not take place.

In conclusion, the ring-opening photochemical reaction leading to the cleavage of the α -bond in a thiocarbonyl compound with an unstrained six-membered ring was observed for the first time. UV irradiation of the matrix-isolated pyran-2-thione was shown to efficiently promote this photoreaction, yielding the aldehyde-thioketene species, which after subsequent rearrangement can be transformed in its isomeric thioaldehyde-ketene.

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Keywords: IR spectroscopy • isomers • matrix isolation • photochemistry • vibrational spectroscopy

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