On the Pyrolysis Mechanism of 2-Pyranones and 2-Pyranthiones: Thermally Induced Ground Electronic State Chemistry of Pyran-2-thione

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This work reports studies of thermochemistry of pyran-2-thione (PT), a sulfur derivative of α-pyrone (AP). Moderate heating of PT results in scrambling of sulfur and oxygen atoms in the molecule and formation of isomeric thiapyran-2-one (TP). The products of pyrolysis of PT were studied experimentally by a combined use low temperature matrix isolation and Fourier transform infrared spectroscopy. The infrared spectrum of the TP monomer isolated in solid argon at 10 K was completely assigned based on comparison with theoretical calculations undertaken at the DFT-(B3LYP)/6-311++G(d,p) level. The upper limit of thermal stability of PT was investigated using the differential scanning calorimetry technique. It was found that pyrolysis of PT is already initiated at temperatures below 130 °C. The mechanism of the observed pyrolytical conversion has been studied theoretically at the MP2/6-311++G(d,p) level, in the ground electronic state. The primary step of the pyrolytical reaction in PT is the α-cleavage of the C=O single bond. It proceeds via an open-ring thio ketene–aldehyde structure, TK1. According to the calculations, the ring-opening reaction from PT to TK1 requires an activation energy less than 80 kJ mol⁻¹, at 130 °C, being the rate-determining step. Further steps of the pyrolytical reaction involve internal rotations around single bonds and [1,5] sigmatropic shift of the aldehydic hydrogen. Pyrolytical ring-opening reactions were studied theoretically also for AP and TP and compared to the pyrolysis of PT. It is suggested that the relative ease of the pyrolytical transformation in PT can be explained in terms of existence of the additional minimum TK1 in the reaction path. No counterparts for this structure could be theoretically located for AP and TP.

Introduction

Chemistry of 2-pyrones has been the subject of numerous studies. It has been shown that nonsubstituted α-pyrone undergoes ring opening upon UV irradiation and affords aldehyde–ketene products (Scheme 1). Experiments with isotopic labeling (¹³C,¹⁸O, D) showed migration of the label within the pyrone ring upon UV irradiation or electron impact (Schemes 2–4, respectively). All mentioned experiments were conducted on pyrones bearing a hydrogen (or deuterium) atom in position 6. If this position was blocked by a methyl group, then the migration of the isotopic label or substituent was not observed. These experiments provided evidence that the electrocyclic ring-opening reaction in pyrone is accompanied by [1,5] sigmatropic shift of the aldehydic

SCHEME 1

SCHEME 2
the same experimental conditions previously,9 and its experimental absorption spectrum is known. The species dominating in the sample can be assigned to TP. The experimental spectrum of TP (bands marked by circles) is in excellent agreement with the theoretical spectrum of the TP monomer, calculated at the B3LYP/6-311++G(d,p) level. Internal coordinates used in the normal modes analysis of TP are given in the Supporting Information Table S1. Assignment of the experimental FTIR spectrum of TP monomer isolated in an argon matrix is given in the Supporting Information Table S2.

All calculations in this work were carried out with the Gaussian 98 program package.12 Different methods and basis sets were used, in conformity with the problem in question. The equilibrium geometries of PT and TP were fully optimized using the B3LYP method (Becke’s three parameter gradient corrected exchange functional13 with the gradient corrected correlation functional of Lee et al.14 and the Vosko et al.15 correlation functional) with the standard 6-311++G(d,p) basis set. Vibration frequencies calculated at the B3LYP/6-311++G(d,p) level of theory provide the best agreement with the experimental infrared spectra, compared to other theoretical methods used in this work.

The characteristic feature of the spectrum of TP is a very strong absorption band (at 1672.5 cm$^{-1}$) due to the stretching vibration of the C=O group. The remaining bands of TP are much weaker. However, almost all theoretically expected bands could be identified in the experimental spectrum of matrix-isolated TP after long accumulation of the spectral signal.

The experimental matrix spectrum contains a vanishingly weak band centered at 2049.6 cm$^{-1}$. This band can result from carbonyl sulfide (OCS).11 The presence of OCS in the matrix can be explained by partial decomposition of pyran-2-thione to carbonyl sulfide and acetylene (C$_2$H$_2$) during pyrolysis. It is, however, difficult to judge whether the decomposition took place and to what extent. Both carbonyl sulfide and acetylene have low boiling points, −50 and −28 °C, respectively. Thus, at room temperature, these products possess sufficient volatility and would easily escape from the cell during manipulations before experiment. No evidence of presence of C$_2$H$_2$ in the matrix was found, indicating that both PT and TP are chemically stable if stored at room temperature.

**Results and Discussion**

**Matrix Isolation Data.** The experimental FTIR spectrum of the products of pyrolysis of PT, deposited into an argon matrix, is presented in Figure 1 (fingerprint region) and in Figure S1 (low-frequency region). It should be noted that there are two main species identifiable in this spectrum. These are pyran-2-thione (reagent) and thiapyran-2-one (expected product). The absorptions due to the reagent, under the used conditions, are very weak, and only the strongest absorption bands could be identified.

The validity of the assignment of the PT signals is doubtless, since we have studied pyran-2-thione under hydrogen, and that both sigmatropic shift and ring-opening reactions are reversible.

One should note that the thermochemistry of 2-pyrones is reported in the literature much less than their photochemistry. Studies of pyrolytic decarboxylation of 5-methyl-6-carboxypyrene showed apparent migration of the methyl group between the 3 and 5 positions.8 Concerning the studies regarding thermal rearrangements of pyran-2-thiones (PT), we are aware of only one work, which reported that, upon heating, pyran-2-thiones quantitatively afforded thiapyran-2-ones (TP) (Scheme 5).5 The product of pyrolysis was identified by Pirkle and Turner using NMR spectroscopy. The reaction was suggested, by analogy with photoinduced process in α-pyrone, to occur via [1,5] sigmatropic shift of the aldehydic hydrogen.

In the present study we also subjected pyran-2-thione to heating to confirm the nature of pyrolytical product(s). As could be expected, heating of pyran-2-thione resulted in formation of thiapyran-2-one, which was unequivocally identified by means of infrared spectroscopy, as will be reported later in this article. Particular emphasis in this work was given to theoretical investigation of the pyrolysis mechanisms, using high level theoretical computations. Comparison of the theoretical results obtained for pyran-2-thione, thiapyran-2-one, and α-pyrene is also given.


**SCHEME 3**

**SCHEME 4**

**SCHEME 5**

The relative amount of PT and TP in the sample was evaluated by comparing the total experimental integral intensity of the corresponding bands in the fingerprint region with the corresponding calculated intensities. This comparison gave a PT/TP ratio in the sample of ca. 1:46. It seems unrealistic to assume that saturated vapor pressures of the two species would differ so much at the experimental conditions. It is much more probable to assume that the ratio 1:46 reflects the relative amount of the two compounds in the mixture after pyrolysis. In other words, conversion of PT into TP after pyrolysis was almost 98%. The theoretical explanation of this fact will be given later in the article.

**DSC Data.** It was previously reported by Pirkle and Turner⁵ that pyran-2-thione rearranges completely to the isomer having sulfur in the ring. They wrote: “30% of PT converted in a single pass through a 370 °C tube. Indeed, this isomerization is so facile that it occurs extensively during attempted gas chromatography at 160 °C (150 °C injector).⁵ In the present work, the lowest limit of thermal stability of PT was estimated by means of differential scanning calorimetry (DSC). A sample of pyran-2-thione was subjected to a series of warming/cooling cycles. During the first warming cycle, the temperature was increased only up to 55 °C, which is only a few degrees above the melting point (Figure 2a, uppermost curve). After one minute, the sample was cooled and crystallization occurred at ca. 24 °C (Figure 2b, uppermost curve).

Subsequently, the compound was subjected to a series of consecutive heating and cooling cycles. In these scans, the upper temperature was increased and the changes in the DSC curves were monitored. All heating curves are collected in Figure 2a, and corresponding cooling curves are collected in Figure 2b, the progress of the experiment being ordered from top to bottom. All the observed transitions in the temperature range studied are presented in Figure 2a,b. Up to 100 °C, no discernible changes were noticed either in the DSC curve profiles or in the peak onset temperature and area, indicating that up to this temperature (bold lines in Figure 2a,b, both belonging to the same cycle) pyran-2-thione does not undergo thermal conversion. Heating the sample up to 130 °C results in changes of both peak positions and line shapes as well as in the shift of the onset temperature of the main melting peak toward a lower temperature (dashed line in Figure 2a). The corresponding cooling curve (dashed line in Figure 2b) exhibits also changes in the profile, with the appearance of new peaks. A decrease in the total crystallization enthalpy is also observed. During the melting of the compound, formation of a new peak, appearing as a shoulder on the higher-temperature side of the main melting peak, can also be observed. After the first manifestation of thermal conversion, the compound was subjected to several cycles of cooling/heating with the same lower (−30 °C) and upper (+130 °C) temperature limits. The isothermal (at +130 °C) hold time of the melt was gradually increased (four lowest curves in Figure 2a,b). This resulted in further thermal conversion of the sample. The complex shapes of the corresponding melting curves as well as the broadening of the pyran-2-thione fusion peaks, together with the shift of their onset temperatures to lower values, are clear evidence of the existence of a mixture of substances.

After prolonged heating (24 h at 130 °C), the DSC cell was inflated but did not show any change in mass. After perforating the cell with a needle, a mass loss of about 15% was observed, indicating that some conversion to gaseous products had occurred. Perforation of the cell was accompanied by appearance of the characteristic smell of a sulfur-containing compound. This observation can explain the appearance of the peak due to carbonyl sulfide in the matrix spectra and evidence a possible decomposition channel of PT.

The main result of the DSC measurements is the demonstration of the fact that the thermal conversion of
PT starts already at moderate heating. The conversion was observed in the temperature range between 100 and 130 °C (the lowest temperature for this process reported to date).

Computational Details. An important part of this study represents theoretical calculations of the pyrolysis mechanisms. As will be shown later, the reaction pathways for pyrolytical interconversions in pyran-2-thione involve bond cleavage and intramolecular proton shift in the electronic ground state. It is known that most variants of density functional theory (DFT) yield a proton transfer barrier that is considerably smaller than the best correlated conventional ab initio results, with a large polarized basis set. It was also reported that an accurate evaluation of ground-state intramolecular proton-transfer pathways requires the inclusion of electron correlation effects. One of the methods being able to provide fairly good geometry and energy parameters for the ground state is MP2. Hence, in this study the potential energy profiles for pyrolytically relevant processes were initially calculated at the MP2/6-31G(d,p) level. In the regions of particular interest, calculations were repeated with basis sets augmented by diffuse functions, using the standard 6-31+G(d,p), 6-311++G(d,p) basis sets. The geometry optimizations of the stationary points at the MP2/6-311++G(d,p) level were followed by frequency calculations at the same theory level, and the obtained frequencies were used to account for the zero-point vibrational energy corrections and to confirm the nature of the stationary points found. The structures corresponding to the true local minima did not have any imaginary frequency. The transition-state geometries were identified by only one imaginary frequency. Visualization of the normal vibration, corresponding to this frequency as well as intrinsic reaction coordinate analyses, was performed on the transition structures to make sure that they led to the desired reactants and products.

To provide qualitative comparison of energies describing excited electronic states of the precursor (PT), several procedures were employed. First, for the geometry corresponding to the closed-ring PT structure, optimized at the RB3LYP/6-311G(d,p) level, calculations of the Franck–Condon vertical excitation energies were performed using the single-excitation CI method. The energies of the lowest 12 excited states were calculated, and it was found that the two lowest excited states of PT are triplets, with excited singlet states being much higher in energy. The energy of the lowest triplet state was equal to 1.9759 eV (191 kJ mol⁻¹). As the next step, the closed-ring PT structure was fully optimized using the single-excitation CI method. The ground state is MP2. Hence, in this study the ground state is MP2.

FIGURE 2. (a) Series of successive DSC melting curves of pyran-2-thione (from top to bottom). Each thermal cycle was initiated and finished at ~30 °C. A scan rate of 10 °C/min was used. Upper temperature turning point and isothermal hold time at this temperature were varied. For each melting curve, upper conditions of the previous thermal cycle are indicated in the figure. For the five first cycles, molten pyran-2-thione was held for 1 min at different temperatures. For the last five cycles, the upper temperature turning point was the same and the hold time was incremented (cumulative time specified in the figure). (b) Series of successive DSC crystallization curves of pyran-2-thione (from top to bottom). Each thermal cycle was initiated and finished at ~30 °C. A scan rate of 10 °C/min was used. Upper temperature turning point and isothermal hold time at this point were varied. For each crystallization curve, upper conditions of the previous melting scan are indicated in the figure. For the five first cycles, molten pyran-2-thione was held for 1 min at different temperatures. For the last five cycles, the upper temperature limit was the same and the hold time was incremented (cumulative time specified in the figure). In both a and b, the bold trace specifies the borderline condition at which no changes in the morphology of the sample and DSC curve were observed. Dashed trace specifies the lowest upper temperature limit at which transformation of pyran-2-thione started to occur.

The lowest excited state of PT is of the order of 200 kJ mol⁻¹. The discrepancies in the energies given by the two methods, it can be assumed that the relative energy of the lowest excited state of PT is of the order of 200 kJ mol⁻¹. On the basis of this estimation, the excited electronic states of PT will be considered in the later discussion as energetically inaccessible.

**Mechanism of Pyrolysis.** Previous experimental studies on pyran-2-thiones bearing a methyl substituent at the 6 position did not show any scrambling of the heteroatoms upon heating. This observation suggests that the pyrolytical transformation of the nonmethylated species includes intramolecular hydrogen atom migration and follows the mechanism depicted in Figure 3. According to this mechanism, at the primary step of the thermal conversion PT undergoes a ring-opening reaction and gives birth to the open-ring thioketene—aldehyde product (TK1). However, TK1 is not spatially prepared for the intramolecular hydrogen migration. Its rotational isomer, TK2, is the one only of eight open thioketene—aldehyde isomers suitable for this process. Upon intramolecular hydrogen transfer, a new species, open-ring thioaldehyde—ketene, is formed. It is named TA2 by analogy with its precursor, TK2. After intramolecular rotation of the thioaldehyde group, the open-ring molecule adopts the geometry TA1, suitable for the subsequent ring closure, and then TP is formed. In the forthcoming section, it will be shown why the described pyrolytical transformation from PT to TP easily occurs already at moderate heating and undergoes almost complete conversion.

**Ring-Opening Reaction.** The energetics of all steps of the transformation depicted in Figure 3 was studied pairwise using theoretical calculations. The first step of the reaction represents the cleavage of the O–C bond in PT. The possibility of existence of a local minimum corresponding to the open form TK1 (see Figure 3) is very important for this study. As was noted in the computational section, the best description of energy and geometry parameters is achieved at the MP2 level of theory. That is why the energy profiles for the ring-open reaction in pyran-2-thione were calculated using the MP2 method. The results are presented in Figure 4.

Initially, all calculations were performed on the planar system. A very characteristic peculiarity of the potential energy curves is the existence of a very flat region around 2.3–2.5 Å, where the calculated gradients along the reaction coordinate approach zero. Inflection on the potential energy surface in this region should correspond to the open-ring thioaldehyde—aldehyde structure TK1. The region between 2.1 and 2.7 Å was studied more carefully, without imposing any restrictions on the geometry of the system (except fixing the OC distance corresponding to the reaction coordinate). The inset in Figure 4 shows that, according to computation at the MP2/6-311++G(d,p) level, a shallow local minimum exists around 2.5 Å. The fully optimized structure corresponding to this minimum is slightly nonplanar (the main nonplanar parameter, the C=C–C=C(=S) dihedral angle, is less than 10°). The energy barrier separating this minimum from the closed-ring PT form is equal to 1.5 kJ mol⁻¹. A calculation carried out on the planar system is also shown for comparison (dashed line in the inset of Figure 4). As seen from the figure, assumption of planarity gives qualitatively the same result for the chosen reaction (ring-opening). The vibrational analysis performed on the optimized nonplanar structure did not reveal any imaginary frequencies. The vibrational levels corresponding to ν₀ → ν₁ single excitations of the four lowest energy vibrational fundamentals of TK1 are situated below the barrier, which from the practical viewpoint means that the open-ring form TK1 might exist. The vibration with the lowest frequency corresponds to the torsion of the C=C–C=C(=S) dihedral angle and connects two mirrorlike minima TK1 and TK1'. The first vibrational level of the nonplanar molecule is higher in energy than the planar...
structure separating two mirror TK1 minima (the minimum on the dashed line in the inset). This fact suggests that the most probable geometry for the TK1 form is effectively planar.

It is also worth commenting on the results obtained with different basis sets. It can be seen that increasing the number of the polarization and diffuse functions used in calculations results in lowering the relative energy of the plateau corresponding to the TK1 form (compare traces A, B, C in Figure 4). Usage of the split valence triple-ζ singly polarized 6-311++G(d,p) basis set (trace C) gives lower relative energies than those obtained with the split valence double-ζ basis sets (traces A, B). Finally, adding a set of f-functions to the basis results in further decrease of the relative energy in the TK1 region. The partial optimization of the open-ring structure, with the O–C distance fixed at 2.5 Å, resulted in its stabilization by more than 4 kJ mol⁻¹ at the MP2/6-311++G(2df,2p) level of theory, compared to the analogous calculation at the MP2/6-311++G(d,p) level. The decrease of the relative energy in the TK1 region with the increase in the number of basis set functions favors the existence of the TK1 form and its involvement in the ring-opening thermal reaction. A remark should be made that the existence of a local minimum corresponding to the open-ring form TK1 was not reproduced in calculations at every theory level used in present study. This fact is in consonance with the theoretical finding reported by Latajka et al.¹⁶ They wrote: “...All types of calculation, DFT or otherwise, have surprisingly similar patterns of dependence upon basis set. The two triple-ζ singly polarized 6-311+G(d,p) and 6-311++G(d,p) sets both yield the highest barriers, which are slightly reduced when more polarization functions are added, as in 6-311++G(2df,2pd) and 6-311+G(3df,3pd).”¹⁶ Now it is clear that the potential energy profiles calculated with the double-ζ basis sets (traces A, B in Figure 4) could be expected to produce a lower barrier. They just failed to produce a minimum in the TK1 region, since this minimum is very shallow as follows from the MP2/6-311+G(d,p) and MP2/6-311++G(d,p) calculations.

Activation Energies. Interconversion between other structures was investigated theoretically as well. There are two types of transformations: intramolecular rotations around single bonds and bond fission (or formation). Unlike the barrier separating TK1 from PT, other barriers were found to be of the order of 30–50 kJ mol⁻¹. Geometries of transition states were optimized using the synchronous transit-guided quasi-Newton (STQN) method with the quadratic synchronous transit (QST) approach.²³ For the internal rotations, the transition states were located with the QST3 option, while for bond fission (or bond formation) the QST2 option was implemented. After optimization, frequency calculations were performed on every stationary point found. The energy parameters and other relevant thermodynamic quantities were calculated at the MP2/6-311++G(d,p) level and are summarized in Table 1 for all stationary points. As can be seen from the table, account for the zero-point vibrational energies results in additional stabilization of all open-ring structures (TK, TA, and TS) with respect to the closed-ring forms (PT and TP). A possible explanation of this fact is that the reaction is not isodemic. The closed-ring forms (PT and TP) have four single bonds and three double bonds, while the open-ring forms (TK and TA) have two single bonds and four double bonds (excluding four C–H bonds present in each case). Simple comparison shows that the ring-opening reaction produces one extra double bond at the expense of two single bonds. And the difference in the zero-point vibrational energies (which are bigger in closed forms) reflects this fact. Further

### Table 1. Thermochemical Data, Theoretically Calculated at the MP2/6-311++G(d,p) Level of Theory, for the Species Relevant to Pyrolysis of Pyran-2-thione

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¹⁶ Latajka et al.¹⁶

The ring-opening reaction in α-pyrone (AP) was also simulated in this study. The energy diagram for the α-pyrone family is presented in Figure 5 along with data for the PT/TP system. The fact to be stressed here is that the activation energy for the ring-opening reaction in AP was calculated to be 126.5 kJ mol\(^{-1}\), which is much higher than that in PT. The geometry of the corresponding transition-state structure is characterized by the aldehyde group rotated by ca. 90° with respect to the plane formed by the remaining heavy atoms. The transition state for the hydrogen shift was also located. Its relative energy with respect to AP was found to be 162.2 kJ mol\(^{-1}\). The geometries of the two transition states in the pyrolysis of α-pyrone are similar to those of the transition states (TS2 and TS3) on the path from PT to TP, but their energies are systematically higher.

The ring-opening reaction represents the rate-determining step for pyrolysis in all three related systems (PT, TP, and AP). Calculated potential energy profiles for this reaction in PT, TP, and AP are shown in Figure 6. Pyran-2-thione is the only one of the three systems that has a flat region on the higher-energy wing of the potential curve. No such peculiarity was found for either TP or AP. In TP, the theoretical search for a minimum with the aldehyde group oriented toward the plane perpendicular to the ring was unsuccessful. During geometry optimization, the aldehyde group was oriented toward the plane formed by the remaining heavy atoms. The reaction in the reverse direction (from TP to PT) would face the barrier of 165 kJ mol\(^{-1}\) at the initial step. This almost 2-fold difference in the activation energies for the forward and reverse processes explains why PT was found to convert almost completely into TP, as evidenced by the matrix-isolation data (Figure 1).

The pyrolytic ring-opening reaction in α-pyrone (AP) was also simulated in this study. The energy diagram for the α-pyrone family is presented in Figure 5 along with data for the PT/TP system. The fact to be stressed here is that the activation energy for the ring-opening reaction in AP was calculated to be 126.5 kJ mol\(^{-1}\), which is much higher than that in PT. The geometry of the corresponding transition-state structure is characterized by the aldehyde group rotated by ca. 90° with respect to the plane formed by the remaining heavy atoms. The transition state for the hydrogen shift was also located. Its relative energy with respect to AP was found to be 162.2 kJ mol\(^{-1}\). The geometries of the two transition states in the pyrolysis of α-pyrone are similar to those of the transition states (TS2 and TS3) on the path from PT to TP, but their energies are systematically higher.

The ring-opening reaction represents the rate-determining step for pyrolysis in all three related systems (PT, TP, and AP). Calculated potential energy profiles for this reaction in PT, TP, and AP are shown in Figure 6. Pyran-2-thione is the only one of the three systems that has a flat region on the higher-energy wing of the potential curve. No such peculiarity was found for either TP or AP. In TP, the theoretical search for a minimum with the aldehyde group oriented toward the ketene moiety, the structure was always converging to the closed-ring TP form at any level of theory. A similar result was reported by Birney,\(^{24}\) who studied α-pyrone in terms of the ring closure (or opening, if seen from the other perspective). He wrote: “Although the flatness of the plateau on the potential energy surface depends on the level of theory, at none of the correlated levels is there a minimum in the vicinity of the [...] structure for zZz1” (by Birney, the zZz1 is the open-ring form obtained from zZz1). The calculations of the ring cleavage reaction in AP, carried out in the present work at the higher theory level, did not result in a minimum on the open-ring side either. These results mean that, to obtain

atures well above 300 °C. On the other hand, for reactions with calculated activation energies in the range 150
-180 kJ mol $^{-1}$ (like in PT), the experimental value of the decomposition temperature was reported to be equal to 200 °C.\textsuperscript{27,28}

Intramolecular Hydrogen Shift. Now let us have a closer look at the intramolecular hydrogen migration. The reaction was investigated in two directions, forward (from TK2 to TA2) and backward (from TA2 to TK2). For the forward reaction, the theoretically calculated energy profiles and related geometry parameters are presented in Figure 7a. The reaction coordinate (abscissa in the lower frame) was chosen as the distance between the migrating hydrogen atom and the carbon atom on the opposite side of the carbon chain. Variation of the reaction coordinate practically did not change the length of the existing aldehydic C−H bond for the most part of the reaction path (Figure 7a, circles in the upper frame). Instead, the curvature of the carbon chain was smoothly increasing, or in other terms, the distance between the terminal carbon atoms of the molecule was smoothly, practically linearly, decreasing (Figure 7a, squares in the upper frame). This change continued until ca. 1.3 Å, when the H⋯C(=O) (Figure 7a, upper frame) and H⋯C(=S) (Figure 7a, lower frame) distances became practically equal, and then the molecule abruptly transformed into its counterpart, with concomitant drastic decrease in energy and change in geometry. The results for the backward reaction are presented in Figure 7b and are very similar. The only important difference is that, upon completion of the reaction, the energy of the system increases.

The transition-state TS3 obtained in the two reactions (forward and reverse) was the same, even though the molecules approached it in a different way. However, in both cases, the molecule left the transition state in a similar abrupt manner. This observation might reflect the fact that the proper reaction coordinate for the intramolecular proton migration should not be the change of the C−H distance, but mainly the change in the curvature of the carbon chain. However, the real reaction coordinate probably involves the simultaneous change of many geometrical parameters and is too difficult to simulate theoretically. Nevertheless, the choice of the reaction coordinate is not that important, since the transition state obtained in the two simulations shown in Figure 7 was the same. Additionally, the same transition state (TS3) was obtained by a direct optimization using the QST2 method, using TK2 and TA2 structures as terminal points.

The optimized geometry of the transition state for the intramolecular proton shift between thiaoaldehyde−ketene and thioketene−aldehyde (TS3) is shown in Figure S3. At first glance, it is clear that the geometry of the carbon backbone of TS3 reminds a closed-ring structure. The optimization at the MP2/6-31G(d,p) level shows that the distance between the terminal C atoms is equal to 2.41 Å in the closed-ring PT molecule. In contrast, in the TA2 and the TK2 forms this distance is equal to 3.15 and 3.23 Å, respectively. The corresponding...
The geometric parameter for the TS3 structure is 2.58 Å, which is much closer to the closed ring.

It is also worth commenting on the symmetry of the transition state. According to Woodward and Hoffmann,29,30 if the observed process is a [1,5] sigmatropic hydrogen shift, the orbital symmetry relationships shall play a determinant role in the course of the transformation. The symmetry-allowed thermal [1,5] hydrogen shift should occur as a suprafacial process, and the saddle-point geometry (in the ground electronic state) should possess a plane of symmetry (and not an axis). This is exactly the case found in this study for the transition state for hydrogen migration in the conjugated aldehyde–ketene (open-ring product of \( R \)-pyrone, see Figure S4).

Figure S4 shows that the migrating hydrogen atom is shifted aside from the plane of carbon atoms (rather than being on the \( C_2 \) axis) and two oxygen atoms are shifted to the opposite side. The overall structure of the transition state is \( C_s \) (and not \( C_2 \)). In the similar process transforming conjugated thioaldehyde–ketene into aldehyde–thioketene, the highest possible molecular symmetry is reduced because of the substitution of one oxygen atom by sulfur. However, the geometry of the transition state in this case is very similar to that one found for the aldehyde–ketene derivative of AP, and the hydrogen migration process can also be described as having the suprafacial character.

Conclusions

This work reports studies of the thermally induced chemistry of pyran-2-thione. The product of pyrolysis of pyran-2-thione was deposited into an argon matrix at 10 K. The product has been unequivocally characterized using infrared spectroscopy as thiapyran-2-one. Matrix isolation data show that the conversion of PT into TP was almost complete after prolonged heating at 200 °C. The limit of thermal stability of pyran-2-thione has been studied by means of DSC. It was found that the thermal conversion of PT starts at temperatures below 130 °C. The reaction pathways for the pyrolysis of PT were calculated at the MP2/6-31G(d,p) level of theory. In addition to pyran-2-thione, pyrolysis pathways were also calculated for the two related systems, thiapyran-2-one and \( \alpha \)-pyrone. It was shown that pyran-2-thione is the only one of the three systems that possesses an additional open-ring conformer TK1. The existence of this conformer reduces the activation energy for the ring-opening reaction in pyran-2-thione to less than 90 kJ mol\(^{-1}\). The bond cleavage represents the rate-determining step of the pyrolytical reactions in all three systems. Further steps include intramolecular rotation along the single C–C


bonds and intramolecular [1,5] sigmatropic proton shift. These steps require smaller activation energies compared to that of the ring-opening reaction. The high directionality of the pyrolytical reaction in PT results from the fact that the final product of the reaction, thiapyran-2-one, lies much lower in energy than the reagent, and the pyrolytical reaction in the opposite direction is inhibited by a very high activation barrier.

**Experimental Section**

The sample of pyran-2-thione was obtained as described in ref 9. A part of the sample, intended for pyrolysis, was placed into a Pyrex glass tube protected against light. The tube with compound was purged by a flux of argon for half an hour and sealed. The sealed tube was then subjected to 2 h of heating at ca. 200 °C in an oven protected from light. After thermal treatment, the glass seal was opened and the forward end of the tube was connected to a needle valve suitable for further deposition of the matrixes. During deposition of the matrix, the rear end of the tube containing the products of pyrolysis was kept at 0 °C. A CsI window was used as optical substrate for matrixes. Argon N60 was used as the matrix gas host. Infrared spectra were registered with a resolution of 0.5 cm⁻¹ in the range 4000–400 cm⁻¹. The Fourier transform infrared spectrometer and low-temperature equipment are described elsewhere.

The thermal stability of pyran-2-thione was studied by DSC using a power compensation instrument. Purge was performed with a helium flux (20 mL/min). Aluminum pans (40 µL) suitable for volatile substances were used. The temperature during cooling/heating runs was scanned at 10 °C/min rate. The instrument was calibrated for temperature with 99.99% indium and 99.9% biphenyl and for enthalpy with indium.

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**Supporting Information Available:** Computed Cartesian coordinates for all structures, experimental and computed vibrational spectra, band assignments, and potential energy distributions for thiapyran-2-one. This material is available free of charge via the Internet at http://pubs.acs.org.