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IR spectroscopic study of thioacrolein and its photoisomerization to methylthioketene

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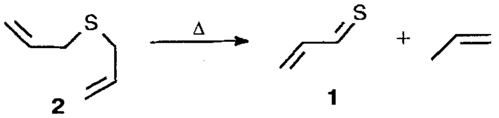
The molecules of thioacrolein (**1**) and metylthioketene (**3**), which are labile under normal conditions, have been studied by the matrix Fourier transform infrared spectroscopy method. Compound **1** was obtained by vacuum pyrolysis (1120 K, 10^{-4} Torr) of diallyl sulfide. The analysis of its IR spectrum shows that **1** exists as a mixture of *s-trans* and *s-cis* conformers. UV irradiation ($\lambda > 248$ nm) of matrix isolated **1** results in a 1,3 hydrogen shift and the formation of **3**, which is characterized by a strong band of antisymmetric stretching vibrations of the thioketene fragment $\nu C{=}C{=}S$ at 1777.2 cm^{-1}. The experimental IR bands of molecules **1** and **3** were assigned to fundamental modes. The relatively low frequencies of the stretching vibrations of the double bonds ($\nu C{=}C$ at 1598.0 cm^{-1} and $\nu C{=}S$ at 1071.8 cm^{-1}) and the heightened frequency of the C—C single bond stretching ($\nu C{-}C$ 1173.7 cm^{-1}) in the spectrum of **1** indicate appreciable delocalization of the electron density in the conjugated π-orbital system.

Key words: thioacrolein, conformers; methylthioketen; pyrolysis; photolysis; matrix isolation; Fourier transform infrared spectroscopy.

By contrast with aldehydes, their sulfur containing analogs, thioaldehydes, are much more labile species inclined to polymerization.[1] For this reason investigating them using common instrumental methods is difficult. This explains the fact that the IR spectra are known for only three members of this class of thioaldehydes (thioformaldehyde,[2] propynethial,[3] and thioformyl cyanide[4]), which were stabilized in inert gas matrices at 10—12 K. One more thioaldehyde, thioacrolein (**1**), has been selectively generated by the pyrolysis of the diallyl sulfide (**2**) (Scheme 1) and studied in the gas phase at low pressure by photoelectron,[5] electron,[6,7] and microwave[7] spectroscopy methods.

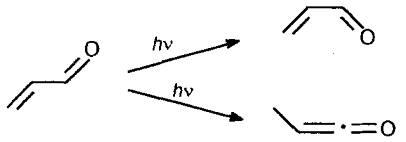
Scheme 1



In addition, the IR spectrum of the products of this reaction, which were frozen at 77 K, have been recorded.[9] However, the frequency values belonging to **1** have not been noted and the vibrational analysis of this molecule has not been done at all.

At the same time, it is known[10,11] that acrolein exists as a mixture of *s-trans* and *s-cis* conformers. Under UV irradiation at various wavelengths (when frozen in an argon matrix) it is either enriched with the thermodynamically less stable *s-cis* form or converted to labile methylketene (Scheme 2). In this case both of the conformers and isomeric ketene have been identified by IR spectroscopy.

Scheme 2



Quantum-chemical calculations show[7,12] that **1** may also exist as *s-cis* and *s-trans* conformers, and the former is more stable by 8.6—11.2 kJ mol^{-1}. The rotational barrier around the single C—C bond in **1** is estimated to be within the range of 26—39 kJ mol^{-1}.

A possible photoisomer of **1**, methylthioketene (**3**), which is also a labile molecule,[13] has been obtained by the pyrolysis of methyl-substituted thiazoles[13] and thiadiazoles[14] (Scheme 3) and studied by microwave spectroscopy.

Since the vibrational spectra of **1** and **3** are not yet known, this work is devoted to the infrared spectroscopic detection of **1**, which is formed according to Scheme 1,

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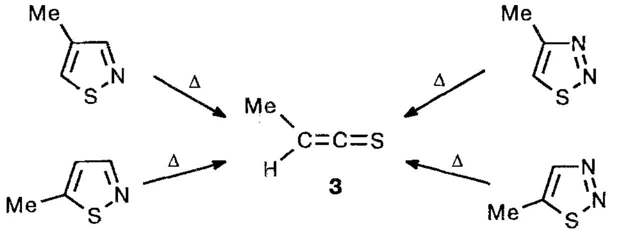
Scheme 3



and the investigation of its behavior in an inert matrix under UV irradiation.

Experimental

The sulfide **2** was obtained by the reaction of allyl mercaptan with allyl chloride in the presence of NaOH in methanol.[15] The IR spectrum of **2** (Ar matrix, 12 K, ν/cm^{-1}) (Fig. 1, *a*): 3090.4 m, 2982.6 m, 2916.6 m, 1833.0 w, 1635.1 m, 1426.6 s, 1398.9 m, 1221.7 m, 1072.2 w, 985.5 s, 925.9 m, 913.4 vs, 892.4 m, 760.8 m, 757.9 m, 705.3 m, 549.1 w. The GC—MS analysis of the product showed the presence of ~3 % of the diallyldisulfide.

The pyrolysis of the starting compound **2** was carried out at 950—1250 K and at a pressure of 10^{-4} Torr in a quartz flow reactor (l = 5 cm, i.d. = 5 mm) which was connected to an optical helium cryostat. The reaction products and the excess of argon (molar ratio Ar : **2** = 500 : 1) were frozen on a polished copper target which was cooled to 12 K with the help of a Displex 208R closed cycle refrigeration system (Air Products & Chemicals).

The IR spectra (4000—400 cm^{-1} range, resolution 1 cm^{-1}) were recorded using an IFS-113v Fourier transform infrared spectrometer (Bruker) supplemented with a reflection unit having an external beam focus.

The photolysis was accomplished using a high pressure UV lamp (1000 W) through a CaF_2 window fitted to the vacuum shroud of the cryostat. To suppress the thermal irradiation the lamp was equipped with a water filter 10 cm long. The wavelengths of the UV light were varied with the help of glass filters 2 mm thick: BS-8 ($\lambda > 360$ nm), BS-5 ($\lambda > 320$ nm) and BS-12 ($\lambda > 250$ nm).

The semiempirical AM1 calculations of the vibrational spectra were performed using the MOPAC program.[16]

Results and Discussion

The pyrolysis of the diallylsulfide. The formation of thioacrolein. The thermodestruction of the precursor **2** at 10^{-4} Torr started at 950 K, and its full conversion was observed at 1120 K. In this case the bands of compound **2** disappeared in the matrix IR spectrum of the pyrolysis products (Fig. 1, *b*). At the same time, the strong bands of propene (3089.9, 3034.7, 2981.4, 2940.0, 2921.4, 2890.1, 2858.0, 1820.0, 1649.8, 1452.9, 1438.9, 1415.3, 1373.8, 1043.3, 997.6, 993.2, 932.4, 916.3, 908.8, 578.3 cm^{-1}) and very weak bands of allene (1955.2 and 837.2 cm^{-1}), CS_2 (1527.8 cm^{-1}), and the allyl radical (801.0 cm^{-1})[17,18] were observed in the spectrum. (The allyl radical appeared as a result of the thermolysis of the concomitant diallyldisulfide.[18]) A set of new bands at 3108.5 w, 2989.9 m, 2723.0 v.w, 1959.1 v.w, 1909.9 v.w, 1886.8 m, 1598.0 m, 1424.2 v.s, 1396.5 m, 1355.0 m, 1305.8 m, 1297.6 w, 1279.1 m, 1173.7 m, 1136.8 m, 1071.8 s, 1001.9 s, 954.9 m, 943.0 s, 890.0 m, 871.0 w and 553.5 w cm^{-1} also appeared in the spectrum. When the matrix was warmed up to 35—40 K in order to cause the diffusion of molecules, only the band of the allyl radical at 801.0 cm^{-1} vanished from the spectrum. At the same time the bands of propene, allene, CS_2, and the above-mentioned set remained in the spectrum. However, further warming of the matrix and evacuation of the evaporated argon led to the disappearance of the bands that did not belong to propene.* In this case the disappearance of the bands of allene and CS_2 can be attributed to their initial low intensity and broadening of all bands due to the intermolecular interactions as the result of the removal of argon from the matrix. After warming the target up to 20 °C a thin layer of a polymer that was insoluble in organic solvents and possessed high adhesion to the metal, was formed. The infrared spectrum of this polymer in a KBr pellet matched the spectrum of a thioacrolein polymer.[9] After collection of the pyrolysis products in a separate ampule and their redeposition in a matrix, only the bands of stable molecules were observed in the spectrum. These compounds were propene, as the main component of the mixture, and minor amounts of allene and CS_2. There were also traces of hexa-1,5-diene, the product of the recombination of the allyl radicals, present in the mixture.

In our opinion, all of the bands that irreversibly disappeared after annealing of the matrix belong to a labile molecule less reactive than the allyl radical. We assigned these signals to molecule **1** on the basis of the following analysis.

First, it is known[5—9] that the gas phase thermolysis of compound **2** leads to the selective formation of molecule **1**.

Second, the positions and relative intensities of a number of the bands in the spectrum of the intermediate that we observed are close to the positions and intensities of the bands in the spectrum of acrolein (see Table 1). This fact allows us to consider these structures to be similar.

Finally, the matrix IR spectrum of the products of the thermolysis of **2** at 1120 K, which ensured full conversion of the starting compound, and the spectrum of the products obtained at a higher temperature (1250 K), were practically identical. The exception was a small increase in the intensity of the band at 1527.8 cm^{-1}, belonging to the vibration of the CS_2

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* Three bands near 1600, 1170 and 1060 cm^{-1} were presented in the spectrum of the pyrolysis products of **2** frozen at 77 K[9] and disappeared after the reaction mixture was warmed up to ~100 K.

molecule. This indicates that the intermediate formed has high thermodynamic stability. In fact, the quantum-chemical calculations predict[5] that among the thirteen possible normal valence isomers of C_3H_4S, the thioacrolein is the most thermodynamically preferable structure.

We can exclude the formation of molecules **3**—**14**. Compounds **5**, **7**, and **8** are stable under ambient condi-

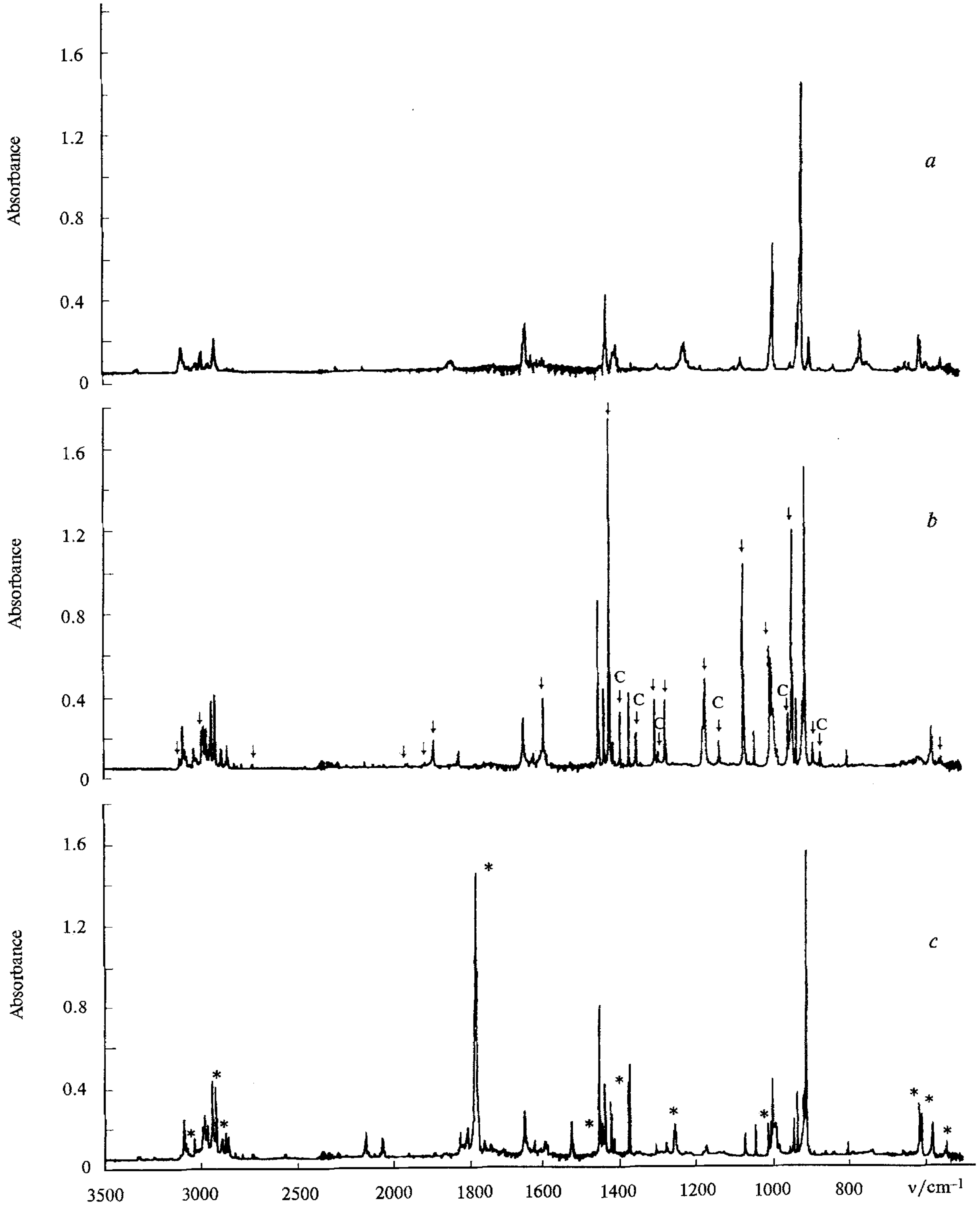

Fig. 1. The IR spectra in the argon matrix at 12 K: *a*, the compound **2**; *b*, the products of the pyrolysis (1120 K, 10^{-4} Torr) of compound **2**; *c*, the products of pyrolysis after irradiation of the matrix by UV light at $\lambda > 248$ nm. The arrows mark the bands of molecule **1**, C is *s-cis*-**1**; asterisks mark the bands of molecule **3**.

Table 1. The assignment of the vibrational frequencies in the IR spectra of *s-trans*-thioacrolein, *s-trans*-acrolein, propynethial, and thioformyl cyanide

Vibration number	Symmetry	Assignment	Vibrational frequency, ν/cm^{-1}				
			$H_2C{=}CHCH{=}S$[a]		$H_2C{=}CHCH{=}O$[b]	$HC{\equiv}CCH{=}S$[c]	$N{\equiv}CCH{=}S$[d]
			exptl	calcd			
1	A'	ν^{as} CH_2	3108.5	3205	3101		
2	A'	ν CH	2989.3	3173	2988		
3	A'	ν^{s} CH_2	2989.3	3143	2988		
4	A'	ν (S)CH, (O)CH	2723.0	3072	2800		
		$\nu_{10}+\nu_{11}$	1959.1				
		$2\times\nu_{15}$	1886.8				
5	A'	ν C=C	1598.0	1826	1621		
6	A'	δ CH_2	1424.2	1443	1418[e]		
7	A'	δ SCH, OCH	1305.8	1362	1362[e]	1320	1318
8	A'	δ CCH	1279.1	1290	1275		
9	A'	ν C—C	1173.7	1274	1153		
10	A'	ν C=S, C=O	1071.8	1083	1709	1107	1102
14	A"	ρ_t CH_2	1001.9	1072	993		
15	A"	ρ_w CH_2	943.0	997	959		
11	A'	δ_r CH_2	890.0	920	877	895	824
16	A"	ρ SCH, OCH	—	914	846		
17	A"	ρ CCH	553.5	592	556		
12	A'	δ CCS, CCO	—	463	600[e]	492	
13	A'	δ CCC	—	282	327		
18	A"	Torsion	—	101	151		

[a] This work. [b] See Ref. 20. [c] See Ref. 2. [d] See Ref. 3. [e] See Ref. 10.

tions and should remain in the reaction mixture. The unstable thiirene **13** was identified in an argon matrix by IR spectroscopy[19] and its bands do not coincide with those we observed. The isomers **3**, **4**, **6**, **11**, and **12** should have strong bands of stretching vibrations of either an S—H bond (2600—2500 cm^{-1}), cumulenic C=C=C (1970—1940 cm^{-1}) and C=C=S (1800—1750 cm^{-1}) bonds, or a triple C≡C bond (2150—2100 cm^{-1}). However, we did not find any visible signals within the mentioned ranges. Although the other cyclic isomers **9**, **10**, and **14** should not have strongly marked characteristic bands, in our opinion, their formation in this reaction is not very probable from the thermodynamic point of view.


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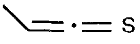
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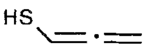
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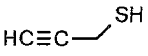
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$\mathrm{Me{-}C{\equiv}C{-}SH}$
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$\mathrm{HC{\equiv}C{-}SMe}$
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8


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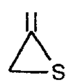
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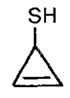
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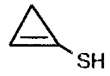
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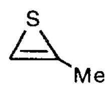
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14

Thus, all of the aforesaid gives us every reason to believe it is the infrared spectrum of molecule **1** that we have recorded.

In the IR spectrum of the molecule **1** we found many more bands than necessary for the description of the fundamental vibrations of this structure in the bending region 1400—850 cm^{-1}. As has been noted, acrolein[10,11] and divinyl[20] in the gas phase exist as a mixture of *s-trans-* and *s-cis*-conformers. After freezing in a matrix their bands are exactly identified, and the difference between the frequency values of the same types of vibrations of the conformers may reach 40 cm^{-1}. In addition, both forms of molecule **1** have also been predicted.[7,12] In connection with this, we propose that the increase in the number of the bands in the matrix spectrum of **1** is the result of the presence of both conformers in the mixture, viz., *s-trans* and the energetically less preferable *s-cis*. Unfortunately, because of the high reactivity of thioacrolein we were not able to study the conformational equilibrium at various temperatures as was done in the cases of stable acrolein[10] and divinyl.[20] Nevertheless, we observed the different behavior of the bands assigned to molecule **1** under UV light. Thus, the bands at 1909.9, 1396.5, 1355.0, 1297.6, 1136.8, 954.9, and 871.0 cm^{-1} completely disappeared after irradiation of matrix by light with $\lambda > 248$ nm. At the same time, the rest of the bands of **1** proportionally decreased. Hence, we assign the mentioned bands to the vibrations of *s-cis*-**1**. In an earlier work[10] some bands of *s-cis*-acrolein appeared to be doublets with splitting up to 5 cm^{-1}. In that case the ratio of the band intensities in these doublets significantly varied depending on whether thermal or photochemical methods were used to generate the *s-cis* conformer. Moreover, the mixture of the conformers of acrolein was thermally enriched with the *s-cis* form up to ~30% and after the irradiation by UV light with $300 < \lambda < 600$ nm (filter BG-23, thickness 2 mm) — up to ~40%. In our case the bands that we assign to *s-cis*-**1** are practically not split in the spectrum of the pyrolysis products of **2** (Fig. 2, *a*). However, after irradiation of the matrix by light with $\lambda > 360$ nm (filter BS-8, thickness 2 mm) for 1 h these bands decreased slightly and split (Fig. 2, *b*). Simultaneously some lowering of the band intensities of the *s-trans* conformer took place. As was observed in Ref. 10, the relative intensities of the new satellite bands at 1910.6, 1398.4, 1356.9, 1301.2, 1138.0, 955.6, and 877.9 cm^{-1} were higher than the intensities of the parent bands. The observed band splitting was probably caused by the conditions of the formation and stabilization of *s-cis*-**1**: either from a gas phase or immediately in a rigid matrix. It should also be noted that the ratio of the total intensity of the doublet bands of *s-cis*-**1** to the band intensities of *s-trans*-**1** after irradiation increased by a factor of ~1.25—1.3 (Fig. 2, *b*). This fact proves that the mixture is enriched with the *s-cis* conformer (see Ref. 10). The further successive irradiation of the matrix by the light with $\lambda > 320$ nm and $\lambda > 250$ nm led at first to a synchronous decrease in the intensities of these doublets (the relative intensities of the bands of *s-trans* conformer were retained) (Fig. 2, *c*) and then to their disappearance (Fig. 2, *d*).

Thus, the investigation results in the first registration of the matrix IR spectrum of the labile thioacrolein molecule, which exists in the gas phase as a mixture of two conformers. Comparing the spectrum of molecule **1** with the well-known spectra of acrolein[21] and the thioaldehydes, propynethial[3] and thioformyl cyanide[4], and using the results of semiempirical AM1 calculations, we assigned the observed IR bands of the energetically more preferable *s-trans* form to the fundamental modes (Table 1).

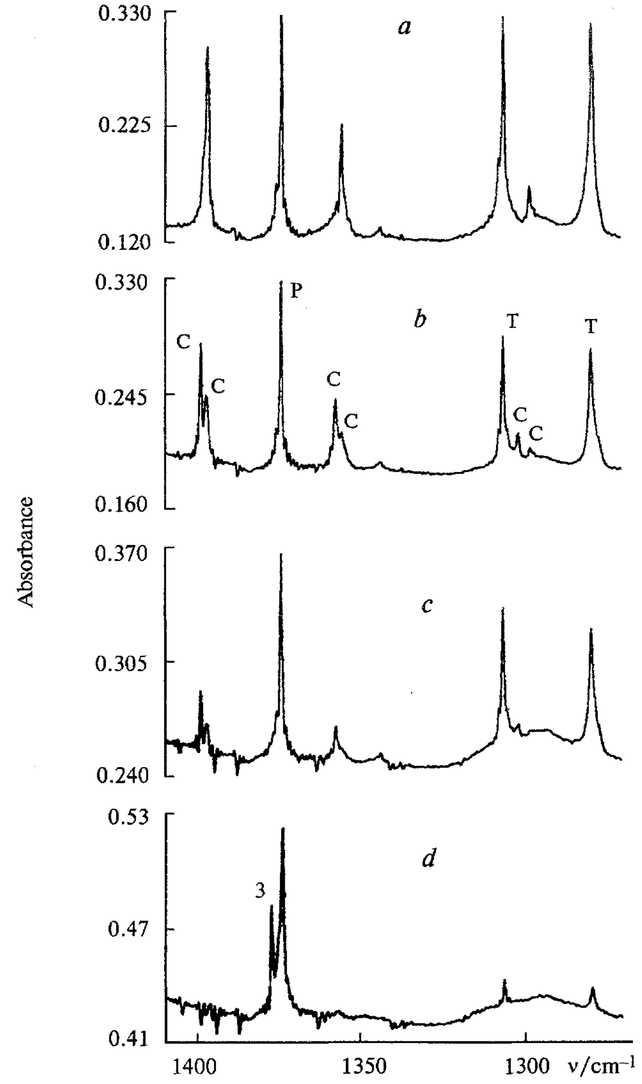


Fig. 2. The IR spectra of the pyrolysis products (1120 K, 10^{-4} Torr) of compound **2** in an argon matrix at 12 K in the region 1410—1270 cm^{-1} (*a*); after successive irradiation of the matrix by light at λ/nm: 360 (*b*), 320 (*c*) и 250 (*d*). C is *s-cis*-**1**, T is *s-trans*-**1**, P is propene.

The molecule of *s-trans*-**1** has C_s symmetry and must have 18 (13A'+5A") active fundamental vibrations in the IR spectrum, ten of which belong to the vinyl group. Of the two bands in the region of stretching vibrations of C—H bonds, we assigned the band at 3108.5 cm^{-1} to the antisymmetric vibration of the CH$_2$ group ($\nu^{as}CH_2$). The second band at 2989.3 cm^{-1} may belong with equal probability to either the vibration of the C—H bond in the methyne group or the symmetric vibration of the methylene fragment. The band at 1598.0 cm^{-1} is responsible for the stretching vibration of the double C=C bond (νC=C). The in-plane deformations, scissoring (δCH_2) and rocking ($\delta_r CH_2$), appear as the strong band at 1424.2 cm^{-1} and the band of medium intensity at 890.0 cm^{-1}, respectively. At the same time, the strong bands at 1001.9 and 943.0 cm^{-1} belong to the out-of-plane torsion ($\rho_t CH_2$) and wagging ($\rho_w CH_2$) vibrations. Finally, the medium band at 1279.1 cm^{-1} and the weak band at 553.5 cm^{-1} correspond to in-plane δCCH and out-of-plane ρCCH deformations of the C—H bond in the methyne group.

Four fundamental vibrations are possible for the thioformyl group in molecule **1**, and three of them were identified by us. Thus, the very weak band at 2723.0 cm^{-1} probably belongs to stretching vibrations of the C—H bond (νSCH). The absorbtion at 1305.9 cm^{-1} corresponds to in-plane bending vibrations of this bond (δSCH). The stretching vibrations of double the C=S bond in the various thiocarbonyl compounds lie in the region 1020—1250 cm^{-1} (see Ref. 22). At the same time, the bands near 1100 cm^{-1} in the IR spectra of propynethial[3] and thioformylcyanide,[4] which were studied recently, belong to the νC=S vibration. For this reason, of the two bands of *s-trans*-**1** lying in the mentioned region, the strong line with the lower wavenumber at 1071.8 cm^{-1} belongs, in our opinion, to the νC=S vibration. The second band at 1173.7 cm^{-1} is similar in value and structure to the band near 1150 cm^{-1} assigned to the stretching vibration of the single C—C bond in the spectrum of matrix isolated acrolein.[10] The AM1 calculation predicts the same assignment of these bands.

The out-of-plane deformation ρSCH (A") band was not found in the spectrum, probably due to its low intensity. The bands belonging to the frame deformations of molecule **1** δCCC (A'), δCCS (A') and torsion vibration (A") around the single C—C bond either lie outside the measurement limits (below 400 cm^{-1}) or are low intensive and were not observed in our case either.

It should be noted that the frequency 1598.0 cm^{-1} of the stretching vibration of the double C=C bond in the spectrum of molecule **1** is ~30 cm^{-1} lower than that of the analogous vibration in the spectrum of acrolein (1627 cm^{-1}). On the other hand, the frequency of the stretching vibration of the single C—C bond (νC—C 1173.7 cm^{-1}) is ~20 cm^{-1} higher than that of acrolein (1153 cm^{-1}). At the same time, the value of νC=S, 1071.8 cm^{-1}, of molecule **1** is ~30 cm^{-1} lower than this value in the spectra of propynethial (1107 cm^{-1}) and thioformyl cyanide (1102 cm^{-1}). Hence, we may assume that as a result of the delocalization of electron density the weakening of the terminal double bonds and the strengthening of the central single C—C bond in the thioacrolein are more significant than in the other molecules being compared. In other words, the delocalizing action of the thioformyl group on the vinyl group is stronger than the action of the formyl group. And, *vice versa*, the action of the vinyl group on the thioformyl group is stronger than the action of the ethynyl or cyano groups.

The photolysis of thioacrolein and the formation of metylthioketene. The products of the pyrolysis of diallylsulfide **2** isolated in an argon matrix were irradiated with unfiltered UV light with $\lambda > 248$ nm for 1 h. Under these conditions propene does not photolyze and its bands remain intact. At the same time, as was mentioned above, the bands of the *s-trans* conformer of molecule **1** synchronously diminished and the bands belonging to the *s-cis* conformer vanished completely. Simultaneously, the very strong band at 1777.2 cm^{-1} with satellites at 1800.5 and 1756.1 cm^{-1} as well as a number of bands of various intensities at 3057.8 w, 2938.8 s, 2896.1 w, 2872.2 m, 2734.3 w, 2559.6 w, 1446.6 m, 1377.2 s, 1256.9 m, 1010.0 m, 952.2 w, 859.4 w, 612.8 s, 607.0 s, and 541.7 m cm^{-1} appeared in the spectrum. These bands also disappeared after annealing of the matrix, the collection of the products, and their subsequent redeposition in a new matrix.

As has been noted above, acrolein frozen in an argon matrix was converted into methylketene by UV irradiation.[11] An analysis of the literature shows that strong bands in the 1750—1800 cm^{-1} region in the spectra of sulfur-containing molecules are characteristic of the thioketene, C=C=S, group. For example, the strong bands at 1755 and 1793 cm^{-1} in the matrix spectra of thioketene[23] and trimetylenethioketene[24] belong to the antisymmetric stretching vibration of C=C=S fragment. In this connection, we believe that in our case a molecule with a thioketene group, methylthioketene **3**, which is characterized by the strong band at 1777.2 cm^{-1}, has been formed. Among the other bands that appeared after the photolysis of the thioacrolein, the absorptions at 3057.8, 2938.8, 2872.2, 1446.6, 1377.2, 1256.9, 1010.0, 612.8, and 541.7 cm^{-1} belong to the vibrations of the MeCH group of thione **3** (Table 2). Thus, the band at 3057.8 cm^{-1} can be assigned to the stretching vibration of the C—H bond in the methyne fragment. The strong band at 2938.8 cm^{-1} and the medium band at 2872.2 cm^{-1} correspond, probably, to the stretching vibrations of protons in the methyl group. The deformations in the methyl groups of propene and methylallene[21] are described by the bands lying in the regions 1440—1455 cm^{-1}, 1370—1380 cm^{-1}, 1040—1110 cm^{-1}, and 960—1080 cm^{-1}. In this connection, we believe that the absorptions at 1446.6, 1377.2, and 1010.0 cm^{-1} belong to the methyl deformations, ν_5, ν_6, and ν_{15}, respectively.

Table 2. The interpretation of the vibrational spectrum of metylthioketene

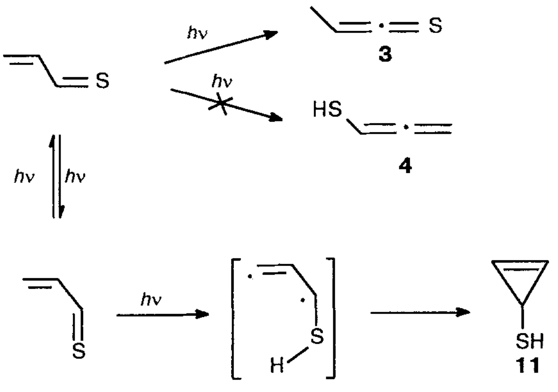
Vibration number	Symmetry	Assignment	ν/cm^{-1} $H_3CCH=C=S$	
			exptl.	calcd.
1	A'	ν CH	3057.8	3155
2	A'	ν^{as} CH_3	2993.0	3141
13	A"	ν^{as} CH_3	2938.8	3054
3	A'	ν^{s} CH_3	2872.2	3040
4	A'	ν^{as} C=C=S	1777.3	1958
5	A'	δ^{as} CH_3	1446.6	1440
14	A"	δ^{as} CH_3	—	1384
6	A'	δ^{s} CH_3	1377.2	1379
7	A'	δ CH	1256.9	1337
8	A'	δ^{s} CH_3	—	1235
15	A"	δ^{as} CH_3	1010.0	1073
9	A'	ν C—C	952.2*	1071
10	A'	ν^{s} C=C=S	859.4*	824
16	A"	ρ CH	612.8	786
11	A'	δ CCC	541.7	628
12	A'	δ CCS, CCO	—	419
17	A"	ρ CCS, CCO	—	219
18	A"	Torsion	—	135

* See text.

Out-of-plane vibrations of the methyne protons in various olefins absorb in a wide range from 500 to 800 cm^{-1} (see Ref. 21) and, as a rule, their signals are strong. Therefore, we ascribed the strong band at 612.8 cm^{-1} to the ρCH vibration. The medium band at 1256.9 cm^{-1} has been assigned to the in-plane vibration of the C—H bond in the methyne fragment, δCH. The absorption at 541.7 cm^{-1} corresponds, probably, to the bending vibration δCCC of the carbon part of molecule **3**. The appearance of the absorption at 607.0 cm^{-1} near the band at 612.8 cm^{-1} can probably be explained by the influence of the «site effect» in the irregular matrix.

Some weaker bands at 2896.1, 2734.3, 2559.6, 952.2, and 859.4 cm^{-1} have been observed in the spectrum of the photolysis products, and the band at 2559.6 cm^{-1} belongs to a molecule having an SH group. In this case, the more probable structures, which could be formed in this process as thioacrolein isomers, are the thiols **4** and **11** (Scheme 4 is similar to the scheme proposed in a recent work[11] concerning the photolysis of crotonaldehyde).

Scheme 4



However, the absence of a band near 1950 cm^{-1}, which is characteristic of the allene group, in the spectrum of the photolysis products excludes the formation of molecule **4**. Thus, one can assume that under our conditions compound **1** under UV irradiation is also transformed into molecule **11**. In this connection, the weak bands at 952.2 and 859.4 cm^{-1}, which could be assigned to the stretching vibrations νC—C and ν^{as}C=C=S in molecule **3**, could be ascribed to the vibrations of this minor product, as well.

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