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Investigation of Potential Energy Surface of Thioformaldehyde-S-S-dioxide by MNDO Method
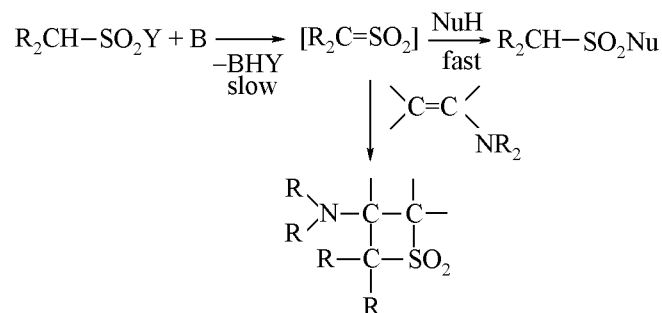
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Abstract—Potential energy surface of thioformaldehyde-S-S-dioxide (sulfene) was of complicated multi-extremal character with minima corresponding to several isomers; the structure and interconversion thereof was studied by MNDO method. The structural dynamics of sulfene is the main reason of its abnormally high reactivity.

Thiocarbonyl-S-S-dioxides (sulfenes) are among compounds with poorly studied molecular structure first of all due to their extreme instability even at low temperature, Sulfenes are intermediates of sulfonyl transport with participation of derivatives (mainly halides) of aliphatic sulfonic acids, of cycloaddition processes, of a number of rearrangements interesting for syntheses. Although the sulfenes were first mentioned at the beginning of the past century [1, 2], their existence was proved only later by kinetic and synthetic methods [3–6].

Sulfenes are obtained *in situ* commonly by treating with bases (alkali, amines) the derivatives of aliphatic sulfonic acids [3–6]. The definite conditions of reaction depend to a considerable extent on the base strength, polarity of the environment, and on acidity of the α-hydrogen in the alkanesulfonic derivative [7–9]. The sulfenes thus arising are capable to add with high velocity molecules with labile hydrogen atoms or the other binding agents, e.g. ethylenes activated with donor substituents. In the absence of compounds trapping sulfenes occurs fast oligomerization into a complicated mixture of compounds [10].
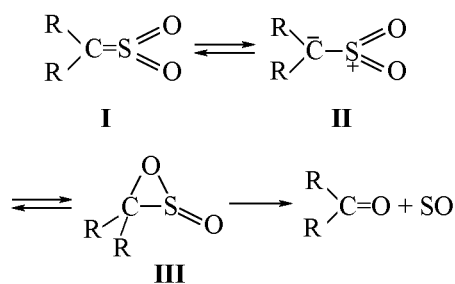
The role of sulfenes in organic reactions is fairly versatile [4, 6]. However the numerous attempts to stabilize and preparatively isolate them failed as a rule, and the data on their reactivity originates from reactions carried out *in situ* [6–9].

Proceeding from the formal analogy to sulfines (thiocarbonyl-S-monoxides) whose structure was studied by microwave spectroscopy, gas phase electronography, and X-ray diffraction analysis the structure of sulfenes was assumed in the literature to be planar [4, 6, 11, 12]. However this assumption does not explain the great difference in reactivity of these seemingly alike classes of sulfur-containing compounds.

Regretfully, the problem of the abnormally high reactivity of S,S-dioxides of thiocarbonyl compounds as compared to the corresponding S-monoxides was not yet studied in detail theoretically, much less experimentally. Sulfenes (**I**) are presumed to be easily transformed in gas phase into ylides (**II**) and sultines (**III**) followed by decomposition of the latter into ketone and sulfur monoxide [12].

$$R_2CH-SO_2Y + B \xrightarrow[\substack{-BHY \\ slow}]{} [R_2C=SO_2] \xrightarrow[fast]{NuH} R_2CH-SO_2Nu$$

Y = Hlg, OR; B = N(Alk)₃, Py, OH⁻; Nu = RO, R₂N, RNH, RS; R = Alk, Ar.

The target of this study is theoretical investigation of the potential energy surface (PES) of the simplest sulfene representative, thioformaldehyde-S-S-dioxide,
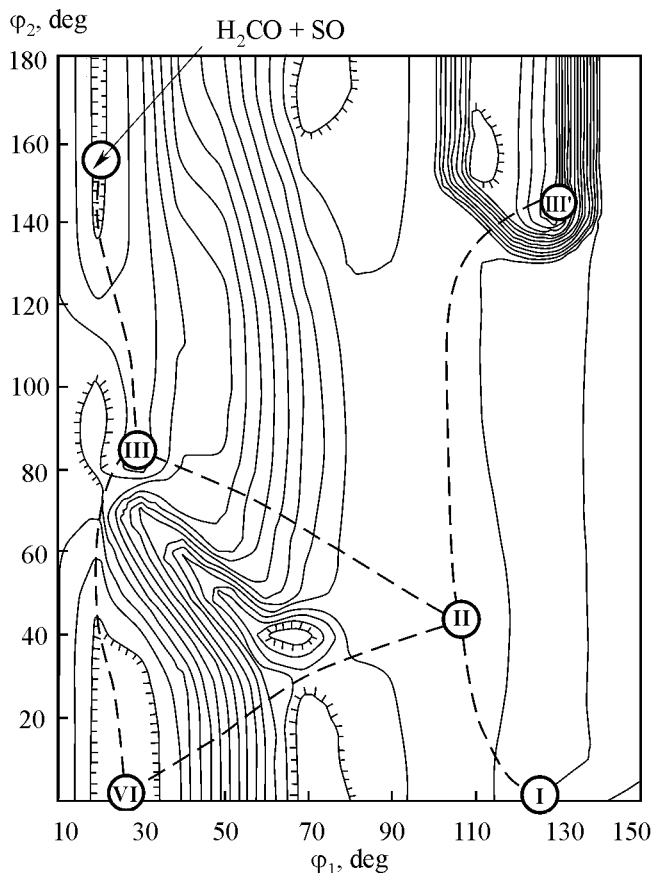
Fig. 1. Potential energy surface of sulfene. Dependence of ΔH_f^0 (kcal mol^{-1}) on the values of Φ_1 and Φ_2 angles. Isenergic contours are drawn through each 10 kcal mol^{-1}. The isomer numbering as in text.

by semiempirical MNDO method [13] that provides sufficient accuracy in calculating compounds with SO$_2$ groups. The calculations were carried out on IBM PC/AT 386/387 with the use of software MOPAC (3.1) [14]. Alongside the isomers **I–III** shown on the scheme the following were also taken into consideration:
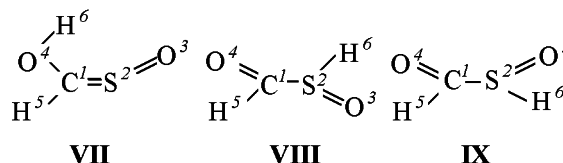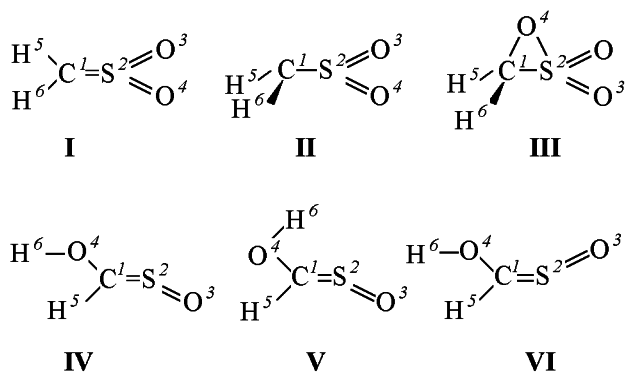
The scanning process for PES was started from structure **I** by variation of the bond angle $\Gamma C^1 S^2 O^3$ (η_1) in the range 10–150 deg with 10 deg step, and of the dihedral angle $\Gamma H^5 C^1 S^2 O^3$ (η_2) in 0–180 deg interval with the same step. All the other geometrical parameters were fully optimized. The dependencies of formation enthalpy for CH$_2$SO$_2$ system on the values of the above angles are presented on Fig. 1, and in the table are given the calculated characteristics of sulfene isomers resulting from complete geometry optimization.

On the PES of sulfene the regions of isomers **I–IV** existence are clearly seen, and also the region where dissociation of sulfene into sulfur monoxide and formaldehyde occurs. It is remarkable that only isomers **III** and **IV** are relatively stable, whereas isomers **I** and **II** are extremely unstable and prone to rearrange into **III**. This is demonstrated on Fig. 2 where is presented the variation in formation enthalpy along the isomerization path **I**→**II**→**III**→H$_2$CO+ SO. The minimum on PES corresponding to isomer **I** is so small that the change by 0.5 deg in the dihedral angle η_2 already results in isomerization. The latter process affords ylide **II** that may be regarded as stereochemically nonrigid molecule (the energy in these systems suffers small changes at large alterations in some geometrical parameters, in the case in question in the dihedral angle η_2 in the 2–70 deg range).

Thus even small perturbation (e.g., temperature change or solvation) produces a situation where the "planar" sulfene **I** cannot exist. On the other hand, the life time of the "ylide" sulfene **II** is also very short: it can rapidly add to trapping agents present in the system (e.g., activated ethylenes), undergo oligomerization, or rearrange into sultine **III** virtually with no energy consumption. Note that isomerization **II** → **IV** already requires additionally about 15 kcal mol^{-1} and thus the process is less probable. Yet this process may be regarded as a link between sulfenes and functionally-substituted sulfines (oxy-sulfines) and may be of special interest as promising for application of thiocarbonic acids S-oxides to preparative syntheses [15].

In the series of isomeric hydroxysulfines **IV–VII** the most energetically feasible (ΔH_f^0 –13.67 kcal mol^{-1})

Sulfene isomers characteristics

Isomer	Formation enthalpy, kcal mol^{-1}	Ionizing energy, eV	Dipole moment, D	Atomic charges[a-d], a.u.			
				C	S	O^x	H^x
I	130.27	10.34	4.40	−0.247	0.983	−0.484	0.116
II	117.27	10.23	7.78	0.141	0.980	−0.632	0.071
III	28.70	10.23	4.11	0.047	0.692	−0.562[a]	0.058[c]
						−0.310[b]	0.075[d]
IV	−10.49	8.90	5.24	−0.076	0.583	−0.609[a]	0.099[c]
						−0.209[b]	0.213[d]
V	−9.79	8.97	4.96	−0.035	0.483	−0.595[a]	0.131[c]
						−0.200[b]	0.216[d]
VI	−9.90	8.79	6.26	−0.090	0.562	−0.585[a]	0.082[c]
						−0.176[b]	0.206[d]

Isomer	Geometrical parameters (bond length, Å, and angles, deg)[a-e]				
	r(C–S)	r(S–O^x)	r(C–H^x)	ГCSO^x	ГH^{x}YZ
I	1.601	1.529	1.082	118.8	119.6[e]
II	1.814	1.507	1.086	105.4	120.7[e]
III	1.864	1.484[a]	1.103[c]	108.9[a]	115.2[c,e]
		1.732[b]	1.102[d]	43.8[b]	117.8[d,e]
IV	1.628	1.505[a]	1.097[c]	106.2[a]	123.0[c,e]
		1.332[b]	0.950[d]	117.7[b]	113.3[d,f]
V	1.634	1.508[a]	1.099[c]	107.0[a]	123.1[c,e]
		1.329[b]	0.951[d]	123.9[b]	115.0[d,f]
VI	1.623	1.502[a]	1.098[c]	111.3[a]	116.6[c,e]
		1.328[b]	0.951[d]	123.7[b]	113.4[d,f]

Notes: x = [a] 3, [b] 4, [c] 5, [d] 6; [e] Y = C^1, Z = S^2; [f] Y = O^4, Z = C^1.

is compound **VII** apparently due to formation of an intramolecular hydrogen bond between atoms H^6 and O^3 that stabilizes the molecule. The interconversion of hydroxysulfines was not specifically treated here. We can yet mention that according to published data [15] the sulfines isomerization occurs not by rotation around C=S bond but due to inversion with respect to sulfur atom.

As regards isomers **VIII** and **IX** there are no published indications to intermediate formation thereof in sulfenes rearrangements. It is however highly probable that the range of compounds **VIII** and **IX** existence should correspond to narrow limits of experimental conditions at high-temperature gas phase processes, for instance, at flash-thermolysis of sulfonyl derivatives [5, 12], where arising sulfenes participate in fast rearrangements. One route leading to sulfenes under such extremal conditions is the interaction between singlet carbenes and sulfur dioxide [12].

$$\begin{matrix} H \\ H \end{matrix} > C: \;+\; SO_2 \;\rightleftarrows\; \begin{matrix} H \\ H \end{matrix} > C = SO_2$$
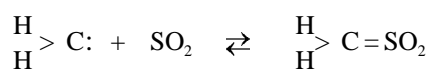
Although the mechanism of this reaction is hardly investigated we assume two routes as the most probable: carbene nucleophilic attack on sulfur atom in SO$_2$ to furnish isomers **I** and **II**, and also insertion into the S=O double bond yielding sultine **III**; in the latter case occurs a significant gain in energy. Further transformations of sultine are energy-consuming and contain both thermodynamically favorable reactions (formation of isomers **IV–VII**, decomposition of the molecule into sulfur dioxide and formaldehyde) and unfavorable ones that are difficult to realize (formation of isomers **VIII, IX**, ΔH_f^0 46.15 and 50.04 kcal mol^{-1}, respectively).

Our studies permit a construction of the most probable scheme for rearrangement mechanism with the isomers under consideration.

The reaction between a singlet carbene and sulfur dioxide may take two competing routes: either insertion into a double bond or nucleophilic attack on the sulfur atom. The second path leads to "planar" sulfene **I** that under usual conditions rearranges into isomers **II** and **III**.

The part played by isomer **II** in the specific features of sulfene reactivity was widely discussed in the literature. Its existence in the highly polar liquid phases is regarded as more probable than that of isomer **I**. Therewith the solvation interaction with the environment results in weakening of the C=S bond and distortion of the planar structure of sulfene. Regretfully the lack of experimental data on sulfene structure permits only presumptions on the sulfenes behavior in liquid media. It is possible that abnormal reactivity of these molecules is due to existence in the media of high dielectric permittivity of the solvation-stabilized isomers, ylides **II**. In the gas phase where the presence of the highly polar ylide compounds is thermodynamically unfavorable "planar" isomer **I** seems less probable.
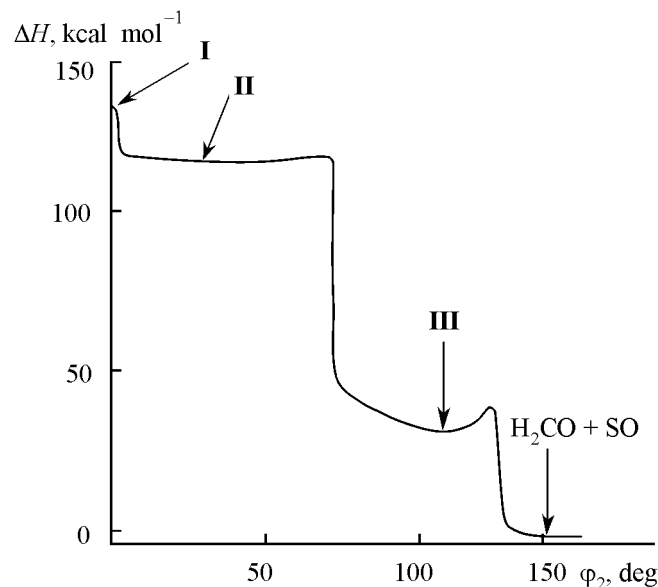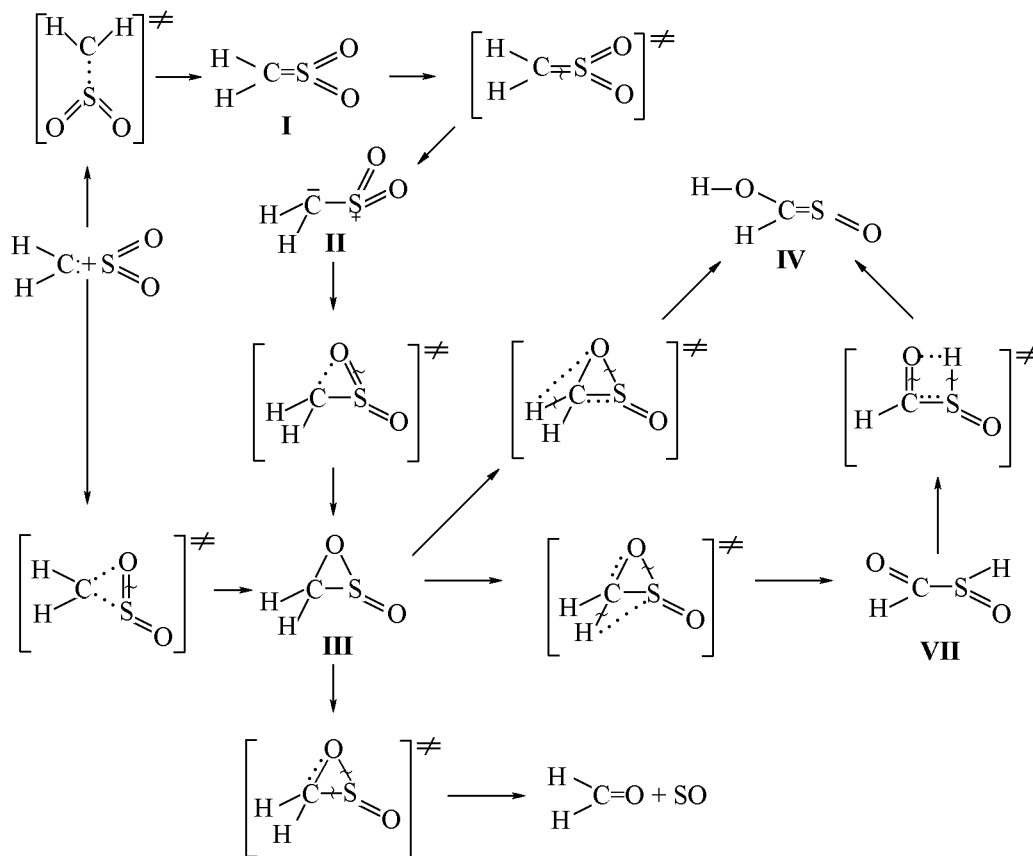

Fig. 2. Energy profile of the process **I** → **II** → **III** → H_2CO + SO along the minimum energy consumption path-route (dashed line on Fig. 1).

Thus sulfene as compared to sulfine is considerably more mobile molecule easily undergoing rearrangements and therefore opening the opportunity to versatile chemical reactions.

We like to mention in conclusion that further study of the role of different sulfene isomers in the processes where they take part should obviously include both the investigations with the use of unique equipment, unusual reaction conditions, and also calculations along sophisticated procedures enabling to reveal the fine specific features of reaction mechanism.

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