Detection of Rotational Isomers by Variable Temperature Photoelectron Spectroscopy. A New Technique in the Realm of Molecular Conformational Analysis[1]

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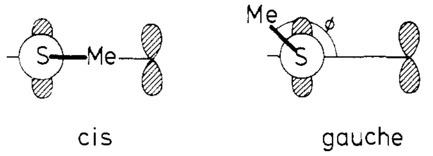
Abstract: The photoelectron spectra of methyl vinyl sulfide have been recorded over the range of temperature 20–600 °C. The observed spectral changes are quantitatively explained in terms of a temperature dependent equilibrium between cis and gauche rotamers of this molecule. The energy difference between both forms is measured to be 2.3 ± 0.2 kcal/mol with the cis form being the more stable one.



Rotational isomerism in methyl vinyl sulfide has been regarded by microwave spectroscopy,[2] electron diffraction,[3-5] infrared spectroscopy,[6] and conventional photoelectron spectroscopy.[7] The results are contradictory. Only the cis form has been found by microwave and photoelectron spectroscopy at room temperature while the electron diffraction pattern at 190–200 °C points to a mixture of both cis (33%) and gauche (66%) isomers.[3] These proportions have recently been slightly corrected (i.e., to 38% cis and 62% gauche).[4] The presence of the conformers in proportions expected of their statistical or near statistical weights (notice that there are two identical gauche forms) suggested zero (or near zero) energy difference between them. The reported results only admit the following alternative: either the sizable proportion of the gauche isomer was overlooked by two of the spectroscopic methods,[2,7] or the conformational energy difference cannot be zero. Below we can show by means of variable temperature photoelectron spectroscopy[8] (VTPES) that the latter choice is the correct one. More in harmony with our results are findings from infrared spectroscopy[6] and an independent electron diffraction study.[5] Our proof constitutes the first application of the new technique[8,9] to molecular conformational problems.[10]

Experimental Section

The methyl vinyl sulfide was obtained commercially and purified by fractional distillation: bp 68 °C (lit.[6] 68 °C); $n^{22}\mathrm{D}$ 1.4834 (lit.[6] $n^{20}\mathrm{D}$ 1.4845); GLC analysis showed it to be >99.5% pure. The photoelectron spectra were recorded on a Perkin-Elmer PS-16 spectrometer equipped with a heated target chamber.[8] Heating is accomplished by a bifilar stainless steel electric heater and the sample temperature is measured by a thermocouple inserted in the gas stream. To exclude decomposition products an analogous series of spectra were taken with the same heated target chamber mounted externally and connected with Perkin-Elmer's usual gas target chamber through a sufficiently long tube to allow cooling of the sample vapor to room temperature. The spectra were analyzed in the region ranging from 9.5 to 13 eV using a curve-fitting program. The program applies a point-by-point correction of the digitized spectra (by hand at standard intervals of 0.1 eV) for the change in spectrometer transmission with energy.[11] In the present case, four symmetric Gaussians are placed at the respective four peak positions without constraining line widths and peak heights. The nonlinear least-squares fit was carried out using the subroutine FAUSGL of the Telefunken TR 440 computer system.

Results and Discussion

Figure 1 shows the calculated lowest Koopmans' ionization potentials[12-16] (identical with the orbital energies of the highest occupied orbitals) of methyl vinyl sulfide as a function of the CCSC dihedral angle ϕ ($\phi = 0$ relates to the cis form). The sequence of corresponding ion states is independent of ϕ. Their ordering with increasing energy is n_π, $\pi_{C=C}$, n_σ, and C–S. The states are labeled according to the designation of orbitals from which they arise. n_π and n_σ are the sulfur lone pair orbitals extending perpendicular to or in the CSC plane, respectively. C–S refers to the C–SMe bonding orbital and $\pi_{C=C}$ denotes the ethylene π orbital. The changes in predicted state energies are most easily interpreted in terms of the well known n/π ($n = n_\pi$ and $\pi = \pi_{C=C}$) conjugative and the C–S/π hyperconjugative interaction models. At $\phi = 0$ (cis conformation) C–S/π hyperconjugation is not allowed, but the n/π interaction is fully developed. In consequence, the n_π state is raised in energy and the $\pi_{C=C}$ state is stabilized. At $\phi = 90°$, n/π interaction is excluded and C–S/π hyperconjugation is predominant thereby lowering the C–S state and raising the $\pi_{C=C}$ state. *Accordingly, the* $\pi_{C=C}$ *ionic state energy is expected to be the most sensitive probe for rotational isomerism.*

Figure 2 displays the photoelectron spectra of methyl vinyl sulfide at four selected temperatures (70, 225, 500, and 594 °C). The most prominent feature of the spectra is the occurence of a new band (2a) in the $\pi_{C=C}$ ionization region at higher temperatures, just in advance of band ②. The maximum of band (2a) is located at about 10.5 eV (cf. the spectrum at 594 °C). The spectra with the externally mounted heated target chamber (see Experimental Section) are, over the whole range of temperature studied (room temperature to 600 °C), identical to the room temperature spectrum. This result shows that band (2a) (i.e., the shoulder in the spectrum at 594 °C and the broadening of the π band region at lower temperatures) is not caused by decomposition products. Other sources for the observed changes are unlikely.[17] Thus we assign band (2a) as the $\pi_{C=C}$ ionization of the gauche form and the experimental results are most consistently interpreted in terms of a *temperature dependent equilibrium between the more stable cis and the somewhat less stable gauche rotamers* in agreement with the aforementioned calculated results.

This qualitative interpretation is in full accordance with a quantitative analysis of the relevant spectra region between 9.5 and 13 eV (for the methods used see the Experimental Section, and for some examples at 70, 225, 500, and 594 °C see Figure 3). The intensity ratios $I_{(3)}/I_{(2)}$, $I_{(3)}/I_{(2a)}$, and $I_{(2)}/I_{(2a)}$ derived therefrom (i.e., the area ratios as computed from the respective Gaussians) at various temperatures applied

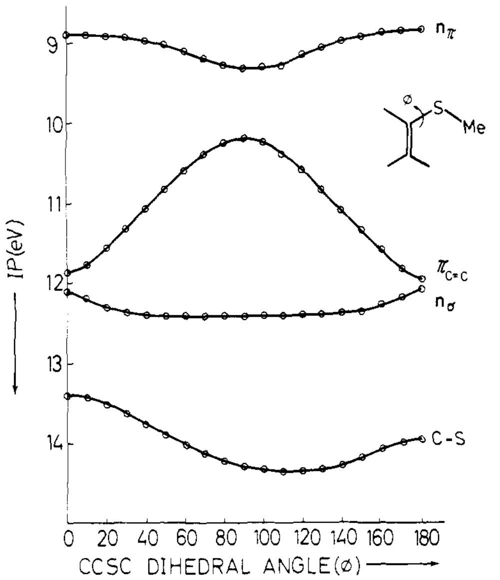


Figure 1. Calculated (using the CNDO/S method in conjunction with a spd basis) Koopmans' ionization potentials[12-16] for the four lowest ionizations of methyl vinyl sulfide vs. the CCSC dihedral angle ϕ ($\phi = 0$ pertains to the cis form). The ionic states are labeled according to the designation of orbitals from which they arise.

Table I. Measured Relative Band Intensities $I_{③}/I_{②}$, $I_{③}/I_{(2a)}$, and $I_{②}/I_{(2a)}$ and Equilibrium Constants K_c as a function of Temperature for Methyl Vinyl Sulfide

Temp, °C	Rel band intensities			$K_c = n_{cis}/n_{gauche}$[a]
	$I_{③}/I_{②}$	$I_{③}/I_{(2a)}$	$I_{②}/I_{(2a)}$	
28	1/0.93	1/0.06	1/0.07	15.2
70	1/0.84	1/0.09	1/0.11	9.0
118	1/1.02	1/0.12	1/0.12	9
171	1/0.63	1/0.18	1/0.28	4
225	1/0.83	1/0.19	1/0.23	4.4
305	1/0.62	1/0.30	1/0.49	2.1
392	1/0.69	1/0.30	1/0.43	2.3
500	1/0.64	1/0.38	1/0.59	1.7
548	1/0.66	1/0.47	1/0.71	1.41
594	1/0.65	1/0.54	1/0.82	1.2

[a] Calculated on the base of eq 3.

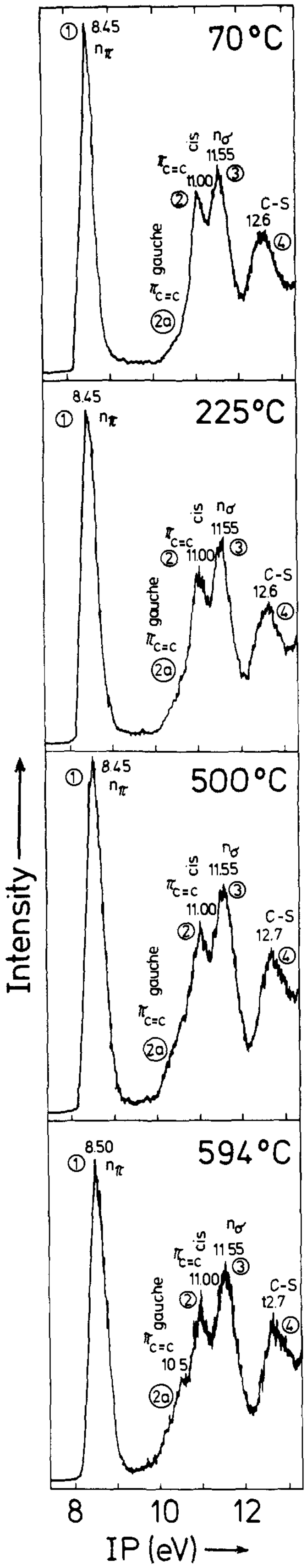


Figure 2. Photoelectron spectra of methyl vinyl sulfide at four selected temperatures (70, 225, 500, and 594 °C) with assignments. The numbers associated with each band are vertical ionization potentials in eV.

are listed in Table I. We see that $I_{③}/I_{②}$ is a slowly varying function of temperature while $I_{③}/I_{(2a)}$ and $I_{②}/I_{(2a)}$ depend heavily on temperature. These ratios can be simply expressed in terms of the equilibrium constant $K_c = n_{cis}/n_{gauche}$ (n denotes the concentration) and respective relative differential photoionization cross sections (σ denotes the cross section) as follows:

$$\frac{I_{③}}{I_{②}} = \frac{1}{K_c}\frac{\sigma_{n_\sigma,\mathrm{gauche}}}{\sigma_{\pi,\mathrm{cis}}} + \frac{\sigma_{n_\sigma,\mathrm{cis}}}{\sigma_{\pi,\mathrm{cis}}} \qquad (1)$$

$$\frac{I_{③}}{I_{(2a)}} = K_c\frac{\sigma_{n_\sigma,\mathrm{cis}}}{\sigma_{\pi,\mathrm{gauche}}} + \frac{\sigma_{n_\sigma,\mathrm{gauche}}}{\sigma_{\pi,\mathrm{gauche}}} \qquad (2)$$

$$\frac{I_{②}}{I_{(2a)}} = K_c\frac{\sigma_{\pi,\mathrm{cis}}}{\sigma_{\pi,\mathrm{gauche}}} \qquad (3)$$

Assuming that all relevant relative cross sections are equal to one, eq 1 to 3 at once explain the differing strength of dependence of the measured intensity ratios upon temperature and, moreover, make K_c accessible as a function of temperature. The K_c values derived from eq 3 are also listed in Table I.[18] From a plot of ln K_c vs. $1/T$ (Figure 4) the difference $\Delta E_0{}^0$ in the total bonding and vibrational energy between both conformers was found to be −2.3 ± 0.2 kcal/mol and for the ratio of partition functions $Q^0{}_{cis}/Q^0{}_{gauche} = 0.4 \pm 0.1$.[18] From infrared spectroscopy[6] (in the range of temperature 30 to 125

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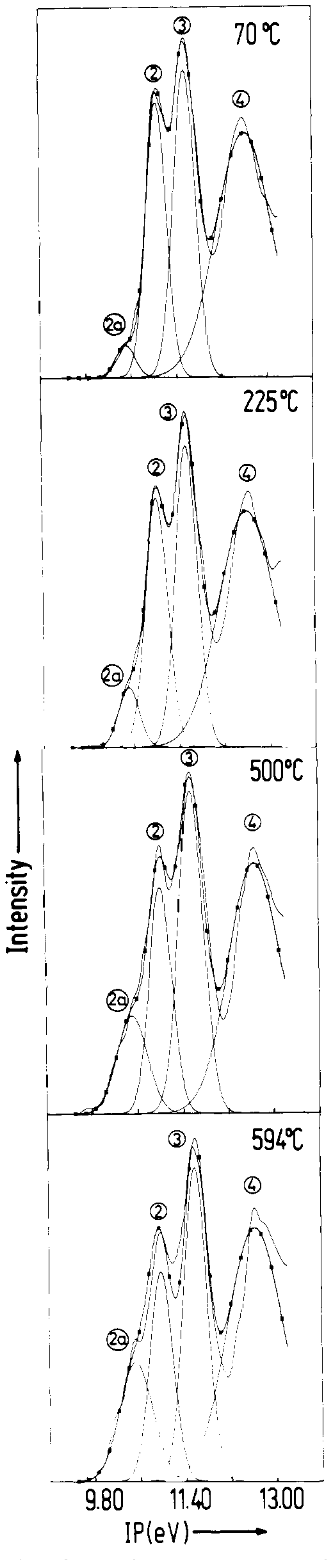

Figure 3. Curve fitting of photoelectron spectra of methyl vinyl sulfide at four selected temperatures (70, 225, 500, and 594 °C). Traces without marks refer either to the spectral part studied as redrawn from the respective digitized and corrected (for the energy dependence of the analyzer transmission[11]) spectrum or to one of the four Gaussians used to generate the spectrum. The trace marked by crosses is the generated spectrum (i.e., the sum of the Gaussian components). For further details, consult the Experimental Section.

°C) $\Delta E_0{}^0 = -1.4$ kcal/mol was estimated (standard error and experimental details are not specified in ref 6).

To summarize, there is a temperature dependent equilibrium between the cis and gauche conformers in the gas phase. The energy difference between both forms is measured to be 2.3 ± 0.2 kcal/mol with the cis form to be the most stable one. According to our results, there are about 94% of the molecules in the cis form at room temperature just as at 40 °C, and about 81% at 200 °C. These values are in concordance with the microwave and previous photoelectron spectral results at room temperature and also with the proportion of cis form derived from an electron diffraction study by Derissen and Bijen,[5] namely 79 to 89% at 40 °C, and also with the infrared results.[6] However, in sharp contrast with all these results are the 33–38% of the cis (!) form at 200 °C derived from electron diffraction studies by Samdal and Seip.[3,4] These results must be questioned as the present photoelectron spectra at varying temperatures most directly indicate.

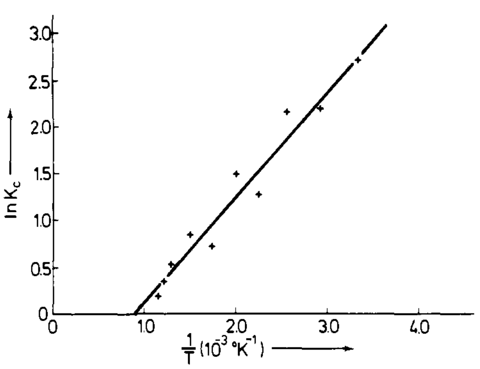

Figure 4. Plot of $\ln K_c = n_{cis}/n_{gauche}$ vs. $1/T$ for methyl vinyl sulfide over the range of temperature 20–600 °C.

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(10) After the present paper was submitted a paper (see ref 9a) appeared also pointing, with qualitative results, to the possibility of studying conformational equilibria with the VTPES technique and a quantitative study of rotational isomerism in thioanisole by two of the present authors has gone to press: A. Schweig and N. Thon, *Chem. Phys. Lett.*, **38**, 482 (1976).

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(12) Ion states calculated on the base of Koopmans' theorem[13] and the CNDO/S method (spd basis and PSS1 parametrization scheme).[14] In order to check the Koopmans' state predictions we also calculated improved ion states using a recently developed CI approach.[15,16] The latter results fully corroborate the validity of Koopmans' theorem in the present case.

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(17) Vibrational broadening of band ② or the occurrence of features akin to "hot bands" might constitute such sources (at least at lower temperatures where a distinct shoulder (2a) is not discernible). To get some estimation of the magnitude of such effects ethylene was studied by VTPES. It was found that the half-width of the relevant π ionization band grew only from

320 to 480 meV when raising the temperature from room temperature to 550 °C. The change is of the same order as the observed increase in the width of band ① in the spectrum of methyl vinyl sulfide and is thus much smaller than the found change connected with the occurrence of the new band (2a) in the same spectrum.

(18) It is interesting to note that the values $\Delta E_0{}^0 r = -2.4 \pm 0.2$ kcal/mol and $Q^0{}_{cis}/Q^0{}_{gauche} = 0.3 \pm 0.1$ as derived from eq 2 agree, within the limits of error, with those derived from eq 3. Equation 1 cannot be used because the changes in the *I*③/*I*② values (see Table I) are insignificant when compared to the experimental errors involved.

Isotopically Selective Spectroscopy and Photochemistry of *s*-Tetrazine in Crystals and Mixed Crystals at Low Temperature[1]

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Contribution from the Department of Chemistry and Laboratory for Research on the Structure of Matter, The University of Pennsylvania, Philadelphia, Pennsylvania 19174. *Received February 9, 1976*

Abstract: The high resolution ${}^1B_{3u}(n\pi^*)$-${}^1A_g$ absorption, single isotopic fluorescence, and single isotopic fluorescence excitation spectra of normal *s*-tetrazine and the ${}^{15}N$, ${}^{13}C$, and D monosubstituted *s*-tetrazines in natural abundance in benzene at 1.6 K; the photophysics and photochemistry of *s*-tetrazine in solution (300 K) and solid (4.2 to 1.6 K); and the laser isotope enrichment of *s*-tetrazine in mixed crystals (1.6 K) are reported and discussed. All spectra were dominated by the single promoting mode $\nu_{6a}(a_g)$. The zero-point state energy of the ${}^1B_{3u}(n\pi^*)$ transition of normal, ${}^{15}N_1$, ${}^{13}C_1$, and D_1 tetrazine is 17 233.9, 17 236.9, 17 237.5, and 17 241.7 cm^{-1}; $\nu_{6a''}$ is 727.3, 723.2, 720.2, and 717.9 cm^{-1}; and $\nu_{6a'}$ is 702.5, 695.3, 683.9, and 677.2 cm^{-1}, respectively. The fluorescence lifetime in benzene (300 K) is 450 ± 55 ps corresponding to a quantum yield of 1.1×10^{-3}. In solution (300 K) and solid (1.6 K) the fluorescence quantum yield is constant throughout the region of appreciable absorption strength. There is *no* observable intersystem crossing. The triplet $[({}^3B_{3u}(n\pi^*)]$ pumped phosphorescence quantum yield is ca. 0.5×10^{-3}. The predominant depopulating mechanism of both the ${}^1B_{3u}$ and ${}^3B_{3u}$ states of *s*-tetrazine is a photoenhanced decomposition. This reaction shows marked spin selectivity $[k({}^1B_{3u})/k({}^3B_{3u}) = 2.1 \times 10^5]$ and proceeds, even in mixed crystals at 1.6 K, to produce directly the stable products $N_2 + 2HCN$ quantitatively. Samples of ${}^{15}N$ and ${}^{13}C$ monosubstituted *s*-tetrazine (in benzene) were purified from natural abundance by a laser isotope separation and purification scheme in the solid at 1.6 with enrichment factors of 10^4. Mixtures of enriched photoproducts were also produced.

I. Introduction

Recently there have been exposed some unique photochemical properties of the molecule *s*-tetrazine.[2] Following excitation with visible light the stable molecules HCN and N_2 are produced with high quantum yield. This reaction is the reverse of the structurally analogous classic acetylene condensation to produce benzene. A main objective of our study was to try to understand the reaction mechanism and the extent to which it can be related to the electronic structure and nonradiative properties of the photoexcited states. Another aspect of our study concerns laser-induced separation of isotopes, since in cases such as *s*-tetrazine many of the features required for efficient separation are present. These include low energy absorption spectra that are readily accessible by visible lasers; stable photoproducts that do not undergo efficient isotopic exchange reactions; a high photochemical quantum yield; and finally, the existence of substantial isotope shifts for C, N, and H atoms. These isotope shifts arise because the electronic excitation involves changes in the electronic distribution around all the atoms in the molecule.

We have shown in our earlier work that the photochemical decomposition of *s*-tetrazine can also be brought about in molecular mixed crystals at 1.6 K, thereby introducing the reality of studying single vibronic level photochemistry in low-temperature solids. In the present paper a detailed assessment of this general approach will be given.

The photophysical properties of azines have been extensively studied both in the condensed and gaseous phases. They all have $n\pi^*$ states, singlets and triplets, that are frequently intermeshed with the $\pi\pi^*$ states of benzene parentage. The radiationless processes that occur after excitation follow no general course: they often appear to be medium induced, and in the condensed phase intersystem crossing is frequently an efficient process. Knight and Parmenter[3] have recently summarized the data available for dilute gases of the azines. Until recently it was thought that the azines were relatively stable to light absorption into their lowest energy states. *s*-Tetrazine is clearly not stable in visible light,[2,4,5] and gaseous pyridazine was recently shown to produce N_2 with a quantum yield of 0.12 following excitation to its lowest $n\pi^*$ singlet state.[6] Thus it is clear that even after considerable experimental and theoretical effort beginning in the early 50's,[7,8] the azines continue to pose interesting and unanswered questions regarding both their physical and chemical behavior.

Two excited electronic states of *s*-tetrazine in the 4000–8000-Å region have been characterized: these are the ${}^1B_{3u} \leftarrow {}^1A_g$ and ${}^3B_{3u} \leftarrow {}^1A_g$ transitions both of which consist mainly of a progression of a 700 cm^{-1} vibrational mode, 6a. A further absorption occurs in the region of 3000 Å and this has been assumed to correspond to an $n \rightarrow \pi^*$ transition. Following the synthesis of *s*-tetrazine in 1906 by Curtius[9] and the observation of sharp line spectra in the gas by Koenigsberger and Vogt[10] the spectroscopy of tetrazine was extensively studied in the vapor,[10-13] solutions,[14,15] and in crystalline and mixed crystalline systems at low temperatures.[4,5,15,16] Recently attention was focused on the kinetics of the radiative[4,5,17,18] and nonradiative[2] processes that tetrazine undergoes in various media.

II. Experimental Methods

(1) Materials and Sample Preparation. *s*-Tetrazinedicarboxylic acid was synthesized by the method of Spencer, Cross, and Wiberg.[11] For the neat and mixed crystal work a stockpile of *s*-tetrazine was prepared