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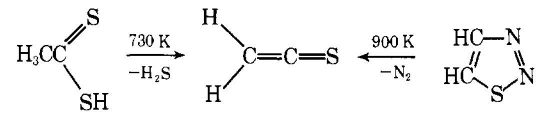
Unstable Intermediates. 5.[1] Thioketene

Sir:

The capability of photoelectron spectrometers to record "molecular finger-prints" provides an efficient analytical tool to screen thermal decompositions in the gas phase for specific low-temperature reaction channels.[1,2]

Thus the PE spectra[3] of Figure 1 prove that thioketene[4,6-8] is the only thermolysis product of both the H_2S abstraction from dithioacetic acid at 730 K and the N_2 elimination from 1,2,3-thiadiazole above 900 K:[3]

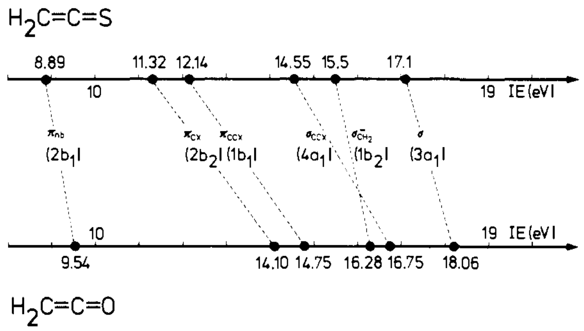

(1)

The identity of $H_2C{=}C{=}S$—and at the same time the exclusion of other possible valence isomers like ethynyl mercaptan,[8] $HC{\equiv}CSH$, or thiirene[8] under the reaction conditions[3]—can be established beyond doubt in many ways.[9] The rather reliable results of PNO-CEPA calculations[9,11] for individual radical cation states do reproduce the spectroscopic ionization patterns with an accuracy of better than 0.3 eV (Figure 1 and Table I). Orientating SCF calculations carried out in addition suggest that thioketene is the preferred species among its possible tautomers: According to the total energies resulting with identical basis sets for idealized geometries, thioketene is more stable by ~74 kJ/mol than ethynyl mercaptan and by ~552 kJ/mol than thiirene. The assignment of the first two PE bands to π-type ionizations is supported by radical cation stretching frequencies $\tilde{\nu}^+$ (Table I) which correspond to the reduced thioketene stretching vibration $\tilde{\nu}_{CS}$ 1760 cm^{-1} in the molecular ground state. Furthermore, comparison with the PE spectra of iso(valence)electronic molecules like ketene $H_2C{=}C{=}O$[10,13] shows the expected close resemblance. Obviously, all vertical ionization energies are reduced due to the smaller effective nuclear charge of sulfur. The electron distribution in the molecular ground state as well as the changes in the individual radical cation states are summarized in Table II.

Table II. Charge Distribution in the Ground State of $H_2C{=}C{=}S$ and Changes in RHF Gross Atomic Populations upon Ionization to the Individual Radical Cation States $H_2C{=}C{=}S^{\cdot +}$

Atom	H	C_1	C_2	S
$^1A_1$[a]	0.868	6.233	6.054	15.974
$\tilde{X}(^2B_1)$	−0.09	−0.27	−0.04	−0.51
$\tilde{A}(^2B_2)$	−0.10	−0.11	−0.23	−0.47
$\tilde{B}(^2B_1)$	−0.10	−0.19	−0.19	−0.43
$\tilde{C}(^2A_1)$	−0.09	−0.19	−0.20	−0.42
$\tilde{D}(^2B_2)$	−0.19	−0.13	−0.13	−0.36
$\tilde{E}(^2A_1)$	−0.16	−0.13	−0.19	−0.36
$\tilde{F}(^2A_1)$	−0.12	−0.21	−0.12	−0.42
$\tilde{G}(^2A_1)$	−0.11	−0.18	−0.17	−0.43

[a] Ground state.



According to the restricted-Hartree-Fock calculations (Table II), in the ground state the H_2C carbon bears a considerable negative charge. The largest change in the sulfur atom population occurs upon ionization to the radical cation ground state $\tilde{X}(^2B_1)$; the hydrogens are most strongly influenced in the $\tilde{D}(^2B_2)$ and $\tilde{E}(^2A_1)$ states.

Both decompositions (eq 1) yield thioketene exclusively; neither starting materials nor traces of other by-products are visible in the PE spectra (cf. Figure 1). Nevertheless, as con-

Table I. Vertical Valence Ionization Energies of CH_2CS IE_n (eV) and Radical Cation Vibrational Frequencies

State	$-\epsilon^{SCF}$	RHF	CEPA	IE_n[a]	ν^+,[b] cm^{-1}
$\tilde{X}(^2B_1)$	8.98 $3b_1$ (π)	8.19	8.85	8.89	1450; 700
$\tilde{A}(^2B_2)$	11.44 $3b_2$	10.31	11.28	11.32	1660; 680
$\tilde{B}(^2B_1)$	13.65 $2b_1$ (π)	12.60	12.44	12.14	710
$\tilde{C}(^2A_1)$	15.92 $9a_1$	14.39	14.75	14.55	950
$\tilde{D}(^2B_2)$	17.03 $2b_2$	15.51	15.31	(15.5)	
$\tilde{E}(^2A_1)$	19.49 $8a_1$	18.46	17.65	(17.2)	
$\tilde{F}(^2A_1)$	27.00 $7a_1$	25.77			
$\tilde{G}(^2A_1)$	30.32 $6a_1$	28.79			
Total energies $\tilde{X}(^1A_1)$ state (eV)[c]:					
SCF	−12 907.944 84				
PNO-CI (upper bound)	−12 914.810 53				
CEPA	−12 915.711 02				

[a] Values of most intense subbands without vibrational corrections. [b] Error bounds are about ±80 cm^{-1}. [c] 1 au = 27.21167 eV.

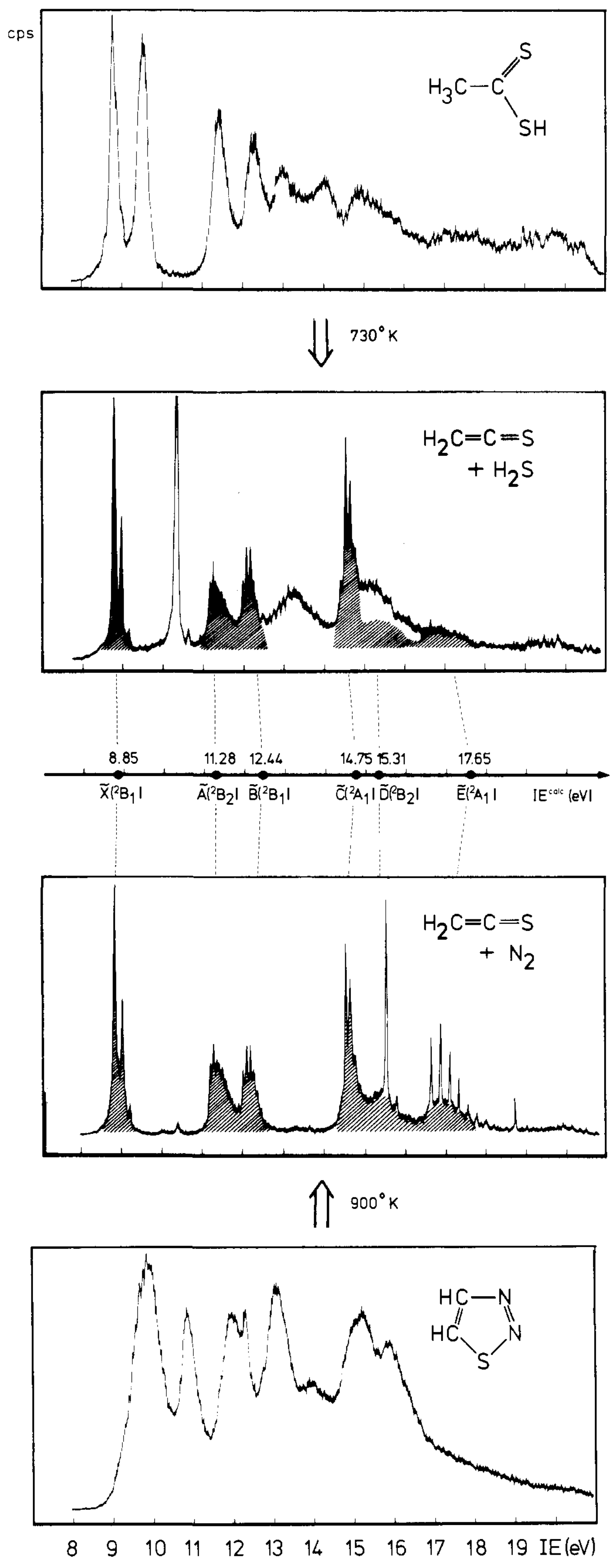


Figure 1. PE spectra of dithioacetic acid, of 1,2,3-thiadiazole, and of their decomposition products at 730 and 900 K, respectively (hatched: $H_2C=C=S$; reference PE spectra of H_2S and N_2; cf., e.g., ref 10), and correlation with calculated ionization energies[11] for $H_2C=C=S$.

cerns their probably uniform mechanisms, only more general rationalizations are readily at hand: according to bond enthalpy parameters, in dithioacetic acid the -C—S- bond should be the weakest ($\Delta H_b \sim 270$ kJ/mol), and, therefore, the radical chain presumably starts via the •SH radical.[14] In the 1,2,3-thiadiazole thermolysis no evidence is found for ethynyl mercaptan;[8,15] on the other hand an analogous hydrogen shift accompanies the formation of a C=X double bond, e.g., in the thermal HCl expulsion from ethylene chlorhydrin yielding exclusively acetaldehyde.[16]

References and Notes

(1) Part 4: $H_2C=S$, B. Solouki, P. Rosmus, and H. Bock, *J. Am. Chem. Soc.*, **98**, 6054 (1976).

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(3) Cf. the Master Thesis of G. Bert, University of Frankfurt, 1977. The liquid educts evaporate at room temperature ($p \sim 10$ Pa) and pass a quarz tube 30 cm long and of ~1 cm diameter, heated by an oven of the specified temperature. The distance between oven and spectrometer target chamber amounts to ~25 cm, suggesting for thioketene a half-life time of more than 1 s.

(4) The parent molecule thioketene—considerably less stable than its alkyl derivatives—has been reported to be generated by heating *tert*-butyl ethynyl sulfide $R_3CSC{\equiv}CH$[6] or hexamethyltrithiane $(R_2CS)_3$[7] or photolyzing 1,2,3-thiadiazole,[8] and to be identified in matrix[8] or in the gas phase[7] by infrared[6,8] or microwave spectra.[7]

(5) Cf. the recent review by R. Mayer and H. Kröber, *Z. Chem.*, **15**, 91 (1975), and in addition G. Seybold and C. Heibl, *Angew. Chem., Int. Ed. Engl.*, **14**, 248 (1975).

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(11) The PNO-CEPA (Pseudonatural Orbital—Coupled Electron Pair Approach) calculations[9] started from an ab initio SCF wave function obtained from a GTO basis set (C: 9s/5p/1d, S: 11s/7p/1d, H: 5s/1p) at a geometry adopted from stable thioketenes[12] or from standard structural parameters. An energy threshold 2×10^{-3} eV has been used for selecting configurations; for further details see ref 9.

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(14) The 730 K pyrolysis of dialkyl sulfides

$$R_3CSSCR_3 \xrightarrow{\Delta T} H_2S + \tfrac{1}{8}S_8 + R_2C{=}CH_2$$

($R = H, CH_3$) is most probably initiated by R_3CS• radicals; cf. Master Thesis of S. Mohmand[2], University of Frankfurt, 1976.

(15) The methyl derivative $HC{\equiv}CSCH_3$ exhibits in the lower energy region PE bands at 8.81, 10.34, 11.62, and 12.59 eV; cf. the Master Thesis of U. Stein,[2] University of Frankfurt, 1975.

(16) Master Thesis of H. Zacharias,[2] University of Frankfurt, 1976.

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Synthesis, Trapping, and Dimerization of 9,10-Benzotricyclo[3.3.2.$0^{3,7}$]deca-3(7),9(10)-diene. X-Ray Crystal Structure of the Dimer

Sir:

The preparation of bridgehead olefins with torsionally strained double bonds has been an area of intense synthetic activity in recent years.[1] A much less studied class of bridgehead olefins consists of those in which the carbons forming the double bonds are pyramidalized,[2] as they are in dehydrobenzene and small cycloalkynes.[3] Several years ago we developed transannular reductive ring closure as a key step in the preparation of a series of such olefins.[4,5] In this communication we