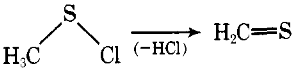
Unstable Intermediates. 4.[1] Thioformaldehyde

Sir:

We wish to report the gas-phase synthesis of pure monomeric thioformaldehyde, its He(I) photoelectron spectrum, and ab initio calculations for the $H_2C{=}S$ molecular ground state as well as for the individual $H_2C{=}S^+$ radical cation states.

Methylsulfenyl chloride decomposes in the gas phase at $p = 13$ Pa above 860 K quantitatively[2]



(1)

The hydrogen chloride split off can be removed by stoichiometric ammonia injection forming an ammonium chloride deposit on the walls of the reaction chamber (Figure 1). According to the recorded He(I) photoelectron spectrum (Figure 2), pure[3] monomeric thioformaldehyde is obtained.

Methylsulfenyl chloride, prepared by chlorination of dimethyl disulfide,[4] evaporates at room temperature and passes a Teflon valve into a 40 cm long quartz spiral ($\phi = 1$ cm) heated by an electric oven to 860 K as measured by the oven thermoelement. Pure ammonia evaporates at ~195 K ($p \sim 7700$ Pa) and passes the 7 cm long capillary ($\phi = 0.5$ mm) of the flow meter filled with Silicone oil as well as a Teflon valve. Both gases mix in the reaction chamber of ~0.5 l. volume kept at room temperature. The stoichiometric ratio of the pyrolysis mixture to ammonia is controlled by vanishing excess ammonia or excess hydrogen chloride ionization bands continuously recorded by the attached photoelectron spectrometer at 10.85 and 12.75 eV, respectively. Careful optimization of the reaction conditions yields pure monomeric thioformaldehyde (Figure 2).

The He(I) photoelectron spectrum of the 12 valence electron molecule $H_2C{=}S$ exhibits five of the six valence ionization energies[5] (Table I), which—within the framework of qualitative orbital notation:[6] $n_S < \pi_{CS} < \sigma_{CS}{}^p < \sigma_{CH_2}{}^- < (\sigma_{CH_2}{}^+ - 3s_S) < \sigma_{CS}{}^s$—can be compared to the increased PE values[7] for its isovalence electronic analogue $H_2C{=}O$.

Table I summarizes the experimental results, ab initio SCF orbital energies, and vertical ionization energies as calculated by restricted Hartree-Fock (RHF), pseudonatural orbital configuration interaction (PNO-CI),[8] coupled electron pair

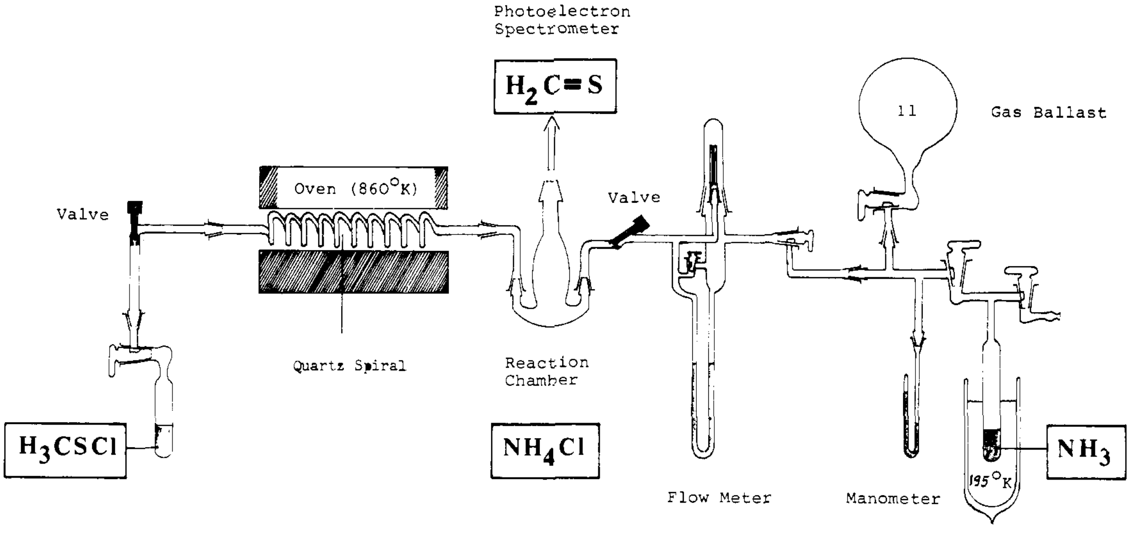


Figure 1. Vacuum-line apparatus for gas-phase synthesis of pure monomeric thioformaldehyde.

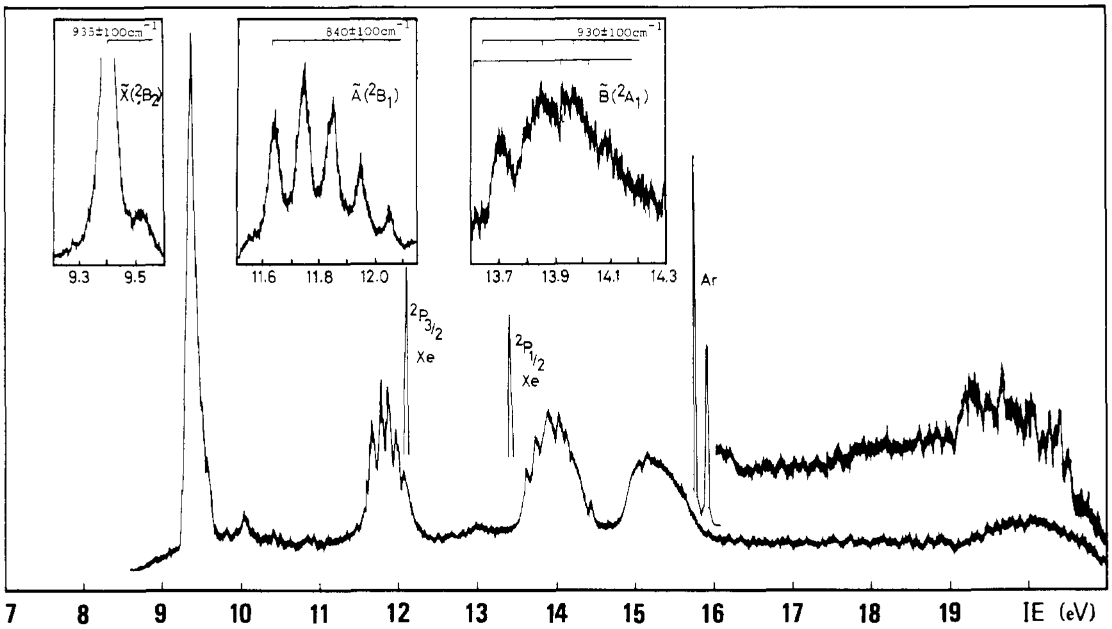


Figure 2. He(I) photoelectron spectrum of thioformaldehyde with expanded records for the $\tilde{X}(^2B_2)$, $\tilde{A}(^2B_1)$, and $\tilde{B}(^2A_1)$ radical cation states.

Table I. Observed Ionization Energies IE_n of $H_2C{=}S$, Their Assignment by Different Calculations ($-\epsilon_J^{SCF}$, ab Initio SCF; GF, Greens' Function Approximation; RHF, Restricted Hartree Fock Open Shell Method; CI, Configuration Interaction), and the Total Energies for the Neutral Ground State

State	IE_n[a]	$-\epsilon_J^{SCF}$		GF	RHF	CI
$\tilde{X}\ ^2B_2$	9.38	$3b_2$(n)	9.44	9.12	8.25	9.08[b]
$\tilde{A}\ ^2B_1$	11.76	$2b_1(\pi)$	11.25	11.63	10.31	11.49[b]
$\tilde{B}\ ^2A_1$	13.85	$7a_1(\sigma)$	14.62	13.82	13.46	13.75[b]
$\tilde{C}\ ^2B_2$	15.20	$2b_2$	17.40	15.80	15.81	15.78[c]
$\tilde{D}\ ^2A_1$	19.9	$6a_1$	21.97	19.45	21.12	20.22[c]
$\tilde{E}\ ^2A_1$		$5a_1$	28.87		27.42	26.00[c]
$\tilde{S}$ 1s hole			2502.3		2471.3	
2s hole			243.6		233.6	
2p hole			180.5		169.7	
C 1s hole			307.9		296.0	
E_{total} (eV)[d] RHF	11 878.067 97					
CI[c]	11 885.336 84 (upper bound)					
CI[b]	11 886.276 37					

[a] Maximum of band or most intense subband. [b] CEPA. [c] PNO-CI. [d] 1 au = 27.21167 eV.

Table II. Changes in RHF Gross Atomic Populations upon Ionizations $H_2C{=}S \rightarrow H_2C{=}S^{\cdot +}$

Atom	$\tilde{X}(^2B_1)$	$\tilde{A}(^2B_1)$	$\tilde{B}(^2A_1)$	$\tilde{C}(^2B_2)$	$\tilde{D}(^2A_1)$	$\tilde{E}(^2A_1)$
H	−0.126	−0.116	−0.136	−0.217	−0.171	−0.142
C	−0.114	−0.225	−0.237	−0.070	−0.133	−0.156
S	−0.635	−0.542	−0.489	−0.497	−0.525	−0.561

approach (CEPA),[8] and many-body Greens' function[9] (GF) methods for the ground state geometry.[3a] The three lowest ionization energies of $H_2C{=}S$ are already well reproduced by the ab initio SCF orbital eigenvalues: a comparison with the RHF and CI values demonstrates that correlation and rearrangement energy contributions are of opposite sign and nearly cancel each other (Table I). Obviously, about 75% of the correlation contribution to the ionization energies in these states are accounted for by the CEPA calculations, and—considering the imposed limitations[10] in the size of the basis set and in the configuration expansion—deviations of only 0.1 to 0.3 eV from the experimental values are rather satisfactory. On the contrary, anomalous behavior of correlation energy contributions is found for the higher excited states of H_2CS^+ because some doubly excited (shake-up) configurations become nearly degenerate with the singly-ionized parent configurations.[8]

The RHF open-shell calculations also demonstrate (Table II) that simple orbital pictures[6] no longer adequately represent the electron distribution in the individual radical cation states. Although the $\tilde{X}(^2B_2)$ state expectedly shows the highest sulfur contribution and the $\tilde{C}(^2B_2)$ state exhibits a nearly constant carbon population, altogether a rather delocalized cation charge is calculated for all valence ionizations.

In conclusion, it might be noted that thioformaldehyde has been established in 1971 as a constituent of the interstellar medium.[11]

References and Notes

(1) Preceding (so far unspecified) publications of this series: (a) (1) SSO, H. Bock, B. Solouki, P. Rosmus, and R. Steudel, *Angew. Chem., Int. Ed., Engl.*, **12,** 933 (1973), (b) (2) H_2CSO, E. Block, H. Bock, S. Mohmand, P. Rosmus, and B. Solouki, *ibid.*, **15,** 383 (1976); (c) (3) HNSO, B. Solouki, P. Rosmus, and H. Bock, *ibid.*, **15,** 384 (1976).

(2) Master Thesis S. Mohmand, University of Frankfurt 1976.

(3) Thioformaldehyde has been repeatedly identified in pyrolysis mixtures, cf., e.g., (a) D. R. Johnson, F. X. Powell, and W. H. Kirchhoff, *J. Mol. Spectrosc.*, **39,** 136 (1971); (b) J. W. C. Johns and W. B. Olson, *ibid.*, **3.9,** 479 (1971); (c) H. W. Kroto and R. J. Suffolk, *Chem. Phys. Lett.*, **15,** 545 (1972); (d) M. E. Jacox and D. E. Milligan, *J. Mol. Spectrosc.*, **58,** 142 (1975); (e) ref 1b.

(4) Cf., e.g., I. B. Douglass in "Organic Sulfur Compounds", N. Kharasch, Ed., Vol. 1, Pergamon Press, Oxford, 1961, p 350.

(5) Values IE_1 and IE_2 previously reported by Kroto and Suffolk[3c] and ref 1b are fully confirmed.

(6) Cf., e.g., W. L. Jorgensen and L. Salem "The Organic Chemist's Book of Orbitals", Academic Press, New York, N.Y., 1973, p 84.

(7) Cf., e.g., W. Domcke and L. S. Cederbaum, *J. Chem. Phys.*, **64,** 612 (1976), and literature quoted.

(8) W. Meyer, *Int. J. Quantum Chem.*, **55,** 341 (1971), and *J. Chem. Phys.*, **58,** 1017 (1973). We thank Professor Meyer for providing his program. Further details of the calculations including also shake-up states will be published elsewhere.

(9) Cf. ref 7; the results for $H_2C{=}S$ are a private communication by W. v. Niessen, L. S. Cederbaum, W. Domcke, and H. Diercksen.

(10) The Gaussian type orbital basis sets are of the size: 9s, 5p, 2d for C, 11s, 7p, 2d for S, 5s, 1p for H. All valence electrons have been correlated and threshold of 2×10^{-4} hartree has been used for selecting configurations. Atomic calculations with these parameters suggest that also for the ground state of $H_2C{=}S$ about 75% of the valence correlation energy has been covered (Table I). For another CI treatment of $H_2C{=}S$ cf. P. J. Bruna, S. D. Peyerimhoff, R. J. Buenker, and P. Rosmus, *Chem. Phys.*, **3,** 35 (1974).

(11) M. W. Sinclair, J. C. Ribes, N. Fourikis, R. D. Brown, and P. D. Godfrey, *Int. Astron. Union Circ.*, No. 2362 (Nov 1971).

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Quenching of Olefin Metathesis. Evidence for the Generation of Metal–Carbene Intermediates from Noncarbenoid Precursors[1a]

Sir:

Recently, we reported[1b] the conversion of the nonconjugated diene system **1** into the cyclobutane derivative **2** through interaction with the well-established metathesis catalyst[2] derived from phenyltungsten trichloride and aluminum chloride. This same catalyst system was found to be very effective in the