

Thioformaldehyde Radical Anion: a PNO-CEPA *ab-initio* Study¹

By PAVEL ROSMUS and HANS BOCK

(Department of Chemistry, Johann-Wolfgang-Goethe-Universität Niederrurseler Hang,
D-6000 Frankfurt/Main 50, Federal Republic of Germany)

Summary The ground state of thioformaldehyde radical anion (2B_1) is calculated to be bound, near to its quasi-planar equilibrium geometry; the acquisition of an electron: $\text{H}_2\text{C}=\text{S} + e^- \rightarrow \text{H}_2\text{C}=\text{S}^{\cdot-}$ should cause only small changes in the H_2C group but a lengthening of the CS bond.

VARIOUS electronic states of the transient thioformaldehyde and its radical cation have been established already both by theory²⁻⁵ and experiment;^{4,6-8} thus the theoretically predicted low-lying excitation energies of the neutral molecule³ have been confirmed recently by u.v. spectroscopy,⁶⁻⁸ and the electronic states of the thioformaldehyde radical cation observed by photoelectron spectroscopy⁴ have unequivocally been assigned using calculated ionization energies.^{4,5} In contrast, no information is available so far on the parent thioketyl, $\text{H}_2\text{CS}^{\cdot-}$, although thio-carbonyl compounds in general are easily reduced as has been demonstrated: *e.g.* $\text{Bu}^t_2\text{C}=\text{S}$ and $(\text{RS})_2\text{C}=\text{S}$, the radical

anions of which have been characterized by e.s.r. spectroscopy.⁹ The results of *ab initio* calculations for thioformaldehyde radical anion are now reported, which are based on correlated PNO-CEPA (pseudonatural orbital configuration interaction and coupled electron pair approach) wavefunctions.¹⁰

The calculations predict a 2B_1 ground state for the thioformaldehyde radical anion, *i.e.* the additional electron is placed in the $3b_1$ (π) antibonding orbital. On reduction, $\text{H}_2\text{C}=\text{S} + e^- \rightarrow \text{H}_2\text{C}=\text{S}^{\cdot-}$, the geometry changes. Independent calculations for both the neutral and the anionic species by the restricted Hartree-Fock method with a double zeta *s,p* basis set augmented by diffuse *p* functions (Table) yield the following parameters for the radical anion relative to the neutral species: a considerable lengthening of the C=S bond, $\Delta r_{\text{CS}} = +0.15 \text{ \AA}$, an almost negligible change in the C-H bonds, $\Delta r_{\text{CH}} = +0.004 \text{ \AA}$, a slight decrease of the angle $\Delta \angle \text{H}_2\text{C} = -2^\circ$, and an out-of-plane equilibrium angle of *ca.* 8° . However, the potential for this bending co-ordinate is calculated to be extremely flat. In

close analogy, such a quasi-planar structure has also been predicted theoretically³ for the singlet and triplet $1,3A_2$ states of H_2CS arising from the $n \rightarrow \pi^*$ transitions. In contrast to H_2CO ,¹¹ however, no experimental evidence for double potential minima could be detected,⁶ presumably because the inversion barriers are too small.

from CEPA methods, respectively, at the near equilibrium geometry of thioketyl with optimised C-S bond lengths (cf. Table, footnote b). (ii) -0.29 eV (-0.01065 a.u.) from RHF, -0.21 eV (-0.00771 a.u.) from PNO-CI, and -0.25 eV (-0.00918 a.u.) from CEPA methods, respectively, at the experimental geometry of thioformaldehyde.¹³

TABLE. Calculated total energies^a for the ground states of thioformaldehyde and its radical anion along the r_{CS} co-ordinate (in a.u.).

r_{CS}^b	$\tilde{X}^2B_1(H_2CS^-)$ PNO-CI ^c (upper bound)			$\tilde{X}^1A_1(H_2CS)$ PNO-CI ^c (upper bound)		
	RHF	CEPA ^e	RHF	CEPA ^e	RHF	CEPA ^e
3.0	-436.494470	-436.755492	-436.787459	-436.508795	-436.775864	-436.811715
3.15	-436.503989	-436.765563	-436.798977	-436.504278	-436.773636	-436.811891
3.36	-436.504511	-436.773309	-436.810640	-436.485285	-436.757804	-436.800135
3.5	-436.499517	-436.761874	-436.798746	-437.467796	-436.742156	-436.787726

^a The basis set (S. Huzinaga, Technical Report, Approximate Atomic Functions, University of Alberta) of the size $9s, 5p$, for C; $11s, 7p$, for S; and $5s$ for H with additional p set on C ($\xi = 0.05$) and on S ($\xi = 0.06$) has been used for geometry optimisation (cf. text). The energies were obtained with this basis set augmented by further two d sets on C and S ($\xi = 0.65, 1.15$ and $\xi = 0.4, 1.1$, respectively) and a p set on H ($\xi = 0.6$). ^b Calculated for planar geometry with $r_{CH} = 2.069$ a. u. and $\angle H_2C = 116^\circ$. ^c Calculated with configurations selected by an energy threshold of 2×10^{-4} a. u. at $r_{CS} = 3.36$ a.u.

In order to fix the relative positions of the energy surfaces of both the neutral molecule H_2CS and its radical anion, additional calculations with correlated PNO-CEPA wave functions have been performed using the above basis set augmented by d functions on C and S, and by p functions on the hydrogens (Table). We estimate that the calculations accounted for ca. 70–75% of the valence correlation energy in the neutral molecule and for a somewhat smaller fraction in the negative ion, since the extra correlation of the added electron with all others is always more strongly affected by basis set deficiencies.¹² In order to decide whether or not the radical anion ground state is bound, it is sufficient to optimise the bond length r_{CS} using correlated wavefunctions, since the changes in the H_2C group calculated for the acquisition of an electron by $H_2C=S$ are rather small. The CS bond length in $H_2C=S^-$ obtained from the total energies listed in the Table amounts to 1.725 Å (RHF) and 1.773 Å (CEPA), respectively, as compared to the experimental bond length of 1.611 Å for H_2CS .¹³

The calculated energy differences $E(H_2C=S) - E(H_2C=S^-)$ are: (i) 0.30 eV (0.01091 a.u.) from RHF, 0.34 eV (0.01256 a.u.) from PNO-CI, and 0.29 eV (0.01065 a.u.)

Unexpectedly, the correlation contributions to the energy difference between the ion and the neutral molecule have been calculated to be rather small. This is mainly because the extra correlation caused by the added electron is almost matched by the decrease in the correlation energy among other electrons due to the occupancy of the low-lying $3b_1$ orbital. Since errors in the correlation energies are larger for $H_2C=S^-$ than for $H_2C=S$, the calculated electron affinities are too small.

These results strongly suggest that the thioformaldehyde radical anion is bound close to its quasi-planar equilibrium geometry and probably also possesses a small positive adiabatic electron affinity. According to additional preliminary calculations with very diffuse basis sets this is not the case for the first excited (2B_2) state of $H_2C=S^-$ or for the ground state of the dianion $H_2C=S^{2-}$.

The calculations were performed at the Hochschulrechenzentrum in Frankfurt and Darmstadt with the PNO-CEPA program kindly provided by Professor W. Meyer, University of Kaiserslautern.

(Received, 14th August 1978; Com. 883.)

¹ For previous papers on radical ions cf. H. Bock, W. Kaim, M. Kira, H. Osawa, and H. Sakurai, *J. Organometallic Chem.*, 1979, **164**, 295.

² For a comprehensive review see: W. Kutzelnigg, *Pure Appl. Chem.*, 1977, **49**, 981.

³ P. J. Bruna, S. D. Peyerimhoff, R. J. Buenker, and P. Rosmus, *Chem. Phys.*, 1974, **3**, 35.

⁴ B. Solouki, P. Rosmus, and H. Bock, *J. Amer. Chem. Soc.*, 1976, **98**, 6054 and references cited. Cf. also P. Rosmus, B. Solouki, and H. Bock, *Chem. Phys.*, 1977, **22**, 453.

⁵ W. von Niessen, L. S. Cederbaum, W. Domcke, and G. H. F. Dierksen, *J. Chem. Phys.*, 1977, **66**, 4893.

⁶ R. H. Judge and G. W. King, *Canad. J. Phys.*, 1975, **53**, 1927.

⁷ R. N. Dixon and C. R. Webster, *J. Mol. Spectroscopy*, 1978, **70**, 314.

⁸ R. H. Judge, C. R. Drury-Lessard and D. C. Moule, *Chem. Phys. Letters*, 1978, **53**, 82.

⁹ C. P. Klages and J. Voss, *Angew. Chem.*, 1977, **89**, 744; *Angew. Chem. Internat. Edn.*, 1977, **16**, 726; H. Bock, G. Brähler, A. Tabatabai, A. Semkow, and R. Gleiter, *Angew. Chem.*, 1977, **89**, 745; *Angew. Chem. Internat. Edn.*, 1977, **16**, 724; cf. also G. Brähler, Thesis, University of Frankfurt, 1978, and A. Tabatabai, Master Thesis, University of Frankfurt, 1977, for unpublished results in cooperation with M. Cava, R. Gleiter, W. Lakshmikantham, and J. Meinwald.

¹⁰ W. Meyer, *Internat. J. Quantum Chem.*, 1971, **S5**, 59; *J. Chem. Phys.*, 1973, **58**, 1017, and in 'Modern Theoretical Chemistry,' ed. H. F. Schaefer, Plenum, New York, 1977; R. Ahlrichs, H. Lischka, V. Staemmler, and W. Kutzelnigg, *J. Chem. Phys.*, 1975, **62**, 1225 and W. Kutzelnigg in 'Modern Theoretical Chemistry,' ed. H. F. Schaefer, Plenum, New York, 1977.

¹¹ V. T. Jones and J. B. Coon, *J. Mol. Spectroscopy*, 1969, **31**, 131; V. A. Job, V. Sathuraman, and K. K. Innes, *ibid.*, **30**, 365.

¹² F. Sasaki and M. Yoshimine, *Phys. Rev.*, 1974, **A9**, 26. Cf. also P. Rosmus and W. Meyer, *J. Chem. Phys.*, 1978, **69**, 2745, and references therein.

¹³ D. R. Johnson, F. X. Powell, and W. H. Kirchhoff, *J. Mol. Spectroscopy*, 1971, **39**, 136.