

Calculated Energetics of Rearrangement and Fragmentation on the S_0 Surface of Thioformaldehyde

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Calculations of stationary points on the S_0 surface of thioformaldehyde corresponding to loss of H_2 , isomerisation to thiohydroxycarbene, and to the formation of radical products support the contention that photodissociation is not an important decay process for the $^1A_2(S_1)$ state of H_2CS .

Formaldehyde occupies a central place in fundamental molecular photochemistry and photophysics since it is amenable to both detailed and well-defined spectroscopic¹ and theoretical studies.² Attention has focused on the mechanism of dissociation of $H_2CO(S_1)$ into either molecular ($H_2 + CO$) or radical ($HCO + H$) products. Recent calculation³ of the barrier to H_2 elimination on the $H_2CO(S_0)$ energy surface has yielded a value of $79.6 \text{ kcal mol}^{-1}$,[†] just below the origin of the $S_0 \rightarrow S_1$ transition ($80.6 \text{ kcal mol}^{-1}$). Thus, molecular dissociation of H_2CO is probably kinetically feasible upon excitation to the S_1 state, whilst calculation³ of the barrier for intramolecular isomerisation to hydroxycarbene, $HCOH$ ($81.4 \text{ kcal mol}^{-1}$) on the S_0 surface implies that photochemical rearrangement to $HCOH$ is somewhat less likely to be a competing mechanism than was hitherto believed. Both calculated activation barriers are substantially below the energy required for radical dissociation to $HCO + H$, believed⁴ to be $85\text{--}87 \text{ kcal mol}^{-1}$.

Although the excited states of thioformaldehyde (H_2CS) have been much studied, its photophysics and photochemistry are not properly understood. It has been suggested that photodissociation may not be an important decay process for the $^1A_2(S_1)$ state on account of its lower excitation energy ($46.8 \text{ kcal mol}^{-1}$)⁵ compared to formaldehyde. To provide further insight into the possible decay mechanisms of the S_1 state of H_2CS , we here describe the first accurate *ab initio* calculations of the energetics of H_2 elimination from H_2CS , of isomerisation of H_2CS to thiohydroxycarbene, and of the dissociation of H_2CS to the radical products, $H + HCS$, all reactions being on the S_0 surface.

Minima and saddle points (transition states) on the S_0 surface were located at the Hartree Fock level of approximation using analytic gradient techniques. A triple zeta⁶ valence basis of Gaussian functions [$C(10s6p/5s3p)$, $S(12s9p/6s5p)$,

$H(5s/3s)$] augmented with d polarization functions on the carbon ($\zeta = 0.72$) and sulphur ($\zeta = 0.542$) atoms⁷ was employed. Subsequent to such optimisation of the stationary point geometries, single calculations were conducted at these points to obtain highly correlated wavefunctions using the

Table 1. Optimised geometrical parameters (in Å and degrees) and zero-point vibrational energies for stationary points on the H_2CS potential energy surfaces.

Parameter	Zero-point energy /kcal mol ⁻¹	
	H_2CS	
$r(C-H)$	1.078	16.7
$r(C-S)$	1.600	
$\angle HCS$	122.2	
	<i>trans</i> HCSH (C_s)	
$r(C-H)$	1.091	13.8
$r(C-S)$	1.675	
$r(S-H)$	1.339	
$\angle SCH$	104.4	
$\angle CSH$	100.1	
	Transition structure $H_2CS \rightarrow \textit{trans}$ HCSH	
$r(C-H_1)$	1.086	10.8
$r(C-H_2)$	1.379	
$r(C-S)$	1.694	
$r(S-H_2)$	1.474	
$\angle SCH_1$	116.7	
$\angle SCH_2$	56.2	
	Transition structure $H_2CS \rightarrow H_2 + CS$	
$r(C-H_1)$	1.188	9.8
$r(C-H_2)$	1.406	
$r(C-S)$	1.594	
$\angle SCH_1$	139.5	
$\angle SCH_2$	98.8	

[†] $1 \text{ kcal} = 4.18 \text{ kJ}$.

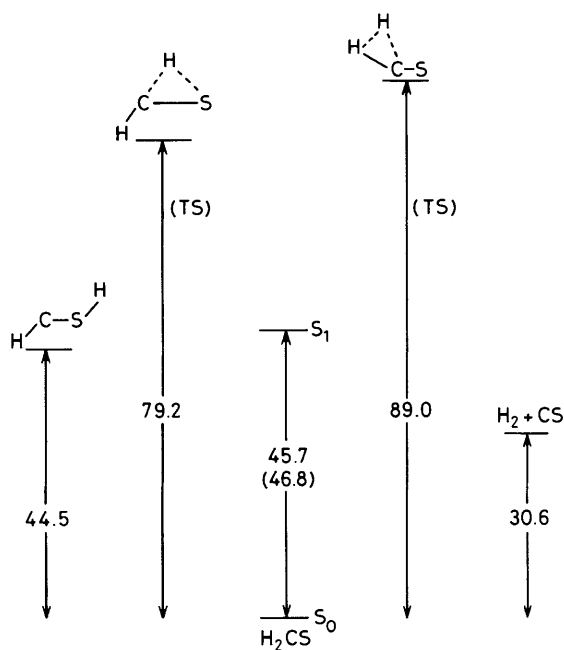


Figure 1. Calculated energies (kcal mol⁻¹) of reaction products and transition states (TS) on the S₀ surface of H₂CS. The value in parenthesis is the experimental S₀ → S₁ transition energy.

configuration interaction (CI) method. In these multireference CI calculations all configurations having coefficients greater than 0.04 were included in the reference set, yielding up to 298 000 configurations. These calculations were carried out using the triple zeta basis augmented by two sets of *d* polarization functions on both carbon and sulphur and a single *p* function on hydrogen.⁸ The energies were then corrected with scaled harmonic zero point vibrational energies calculated at the Hartree Fock level using a 3-21G basis⁹ (see Table 1). The resulting energetics are summarized in Figure 1, and the corresponding optimized geometries are shown in Table 1.

It can be seen that both molecular dissociation and isomerisation are thermodynamically possible from the S₁ state of H₂CS although the energy of *trans-*

thiohydroxycarbene is only slightly lower than the experimental S₀ → S₁ excitation energy. However, the calculated transition states lie considerably above the S₁ energy so that these two processes are kinetically unlikely to occur. In addition the radical dissociation products (HCS + H) are calculated to lie 85.2 kcal mol⁻¹ above the S₀ energy, making them energetically inaccessible from the S₁ state. Thus, although the energetics of these two transition states of H₂CS are similar to those of H₂CO, this finding together with the lower S₀ → S₁ excitation energy in the former molecule supports the contention that photodissociation is not an important decay process for the ¹A₂(S₁) state of H₂CS. This is consistent with the strong emission from highly excited vibrational levels in both laser fluorescence excitation spectra¹⁰ and laser optoacoustic detection spectra,¹¹ in marked contrast to formaldehyde.¹²

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