J. Am. Chem. Soc. 1989, 111, 2782-2785

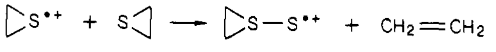
The Hemibonded Dimer Radical Cation of Thiirane

Peter M. W. Gill, Peter Weatherall, and Leo Radom*

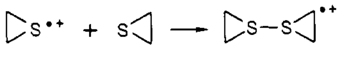
Contribution from the Research School of Chemistry, Australian National University, Canberra, A.C.T. 2601, Australia. *Received June 24, 1988*

Abstract: Ab initio molecular orbital theory has been used to study the formation and reactions of the sulfur–sulfur hemibonded dimer radical cation of thiirane. Two fragmentation pathways, hemibond cleavage and ethylene extrusion, leading to the fragmentation of this species have been examined. The barriers to these processes are found to be similar and moderately large (127 and 160 kJ mol^{-1}, respectively). The results obtained have been used to rationalize the findings of recent gas-phase and Freon-matrix studies of the ion–molecule reactions of thiirane.

A recent series of investigations has revealed an intriguing class of ion–molecule reactions involving thiirane (**1**). In a gas-phase kinetic study,[1] Baykut, Wanczek, and Hartmann (BWH) examined the rates at which **1** and its radical cation (**2**) react to form, in the first instance, a sulfonated thiirane radical cation (**3**) and a molecule of ethylene (**4**) in what they term a "sulfur-transfer reaction". They find that reaction 1 takes place rapidly and that, in subsequent steps, further sulfur atoms may be successively transfered to **3** from additional neutral thiirane molecules. Indeed, the kinetic schemes of BWH included species in which concatenations of up to four sulfur atoms are present. The concept of sulfur-transfer reactions was generalized in the gas-phase work of Freiser,[2] who showed that even transition-metal atoms like cobalt can act as the initiator in analogous sulfur-transfer propagation reactions (reaction 2). In a very recent paper,[3] Qin, Meng, and Williams (QMW) have further explored the ion–molecule chemistry of thiirane through elegant ESR studies of **1** and **2** using the low-temperature solid-state Freon radiolysis technique.[4] They observe the formation of ethylene and infer that, as in the BWH experiments, the extrusion takes place via sulfur-transfer reaction 1. They also report compelling ESR evidence that, in the Freon matrices, **1** and **2** initially dimerize to form the thiirane dimer radical cation **5**. They therefore propose that **5** is an intermediate on the potential surface for sulfur transfer between thiirane cation **2** and a neutral thiirane molecule **1**.


2 1 3 4 (1)


1 4 (2)


2 1 5 (3)

Our interest in thiirane dimer cation **5** arises in part because the two thiirane moieties in **5** are linked by a three-electron ($\sigma^2\sigma^*$) sulfur–sulfur bond. We have recently carried out extensive calculations on systems containing bonds of this type[5,6] and have referred to such bonds as *three-electron hemibonds*[5] because they have a formal bond order of $^1/_2$. Hemibonded systems have also been the subject of other theoretical[7] and experimental[8] studies.

In this paper, we present the results of a detailed examination of the thiirane dimer radical cation (**5**) with particular emphasis on its binding with respect to thiirane (**1**) + thiirane radical cation (**2**) and on its possible decomposition involving extrusion of ethylene. We have also conducted parallel calculations on two closely related systems, namely the dimer radical cation **6** of hydrogen sulfide and the mixed dimer radical cation **7** of thiirane and hydrogen sulfide. Although our results refer strictly only to isolated molecules in the gas phase, they nonetheless provide information that may be useful in the interpretation of processes which occur in other, more condensed, phases.

Method and Results

Standard ab initio molecular orbital calculations[9] of the equilibrium geometries and energies of the hemibonded dimers (**5–7**) of H_2S and thiirane and some of their various possible fragmentation products (**1–4** and **8–11**) were performed with use of a modified version[10] of the GAUSSIAN 86 system of programs.[11] Complete geometry optimizations were conducted at the Hartree–Fock (HF) level employing, successively, the minimal STO-3G, the split-valence 3-21G, and the split-valence plus d-polarization 6-31G(d) basis sets. The structures obtained by using the 6-31G(d) basis set are shown in Figure 1. The spin-restricted (RHF) and spin-unrestricted (UHF) formalisms were used in calculations on singlet and doublet species, respectively, and the expectation value $\langle S^2 \rangle$ of the spinsquared operator was found, in each of the UHF calculations, to be very close to the value (0.75) appropriate to a pure doublet state. Subsequently, MP2 (second-order Møller–Plesset perturbation theory) single-point energies were calculated at the HF/6-31G(d) geometries by using the 6-31G(d) basis set in order to provide more reliable estimates of relative energies. In the case of thiirane dimer cation **5**, the UMP2/6-31G(d) single-point energy calculation involved 114 basis functions and required more than 2 h of CPU time on a Fujitsu FACOM VP-100 supercomputer. Harmonic vibrational frequencies were calculated[12] and the resulting zero-point vibrational energies, after scaling by 0.9 to account for their overestimation at the Hartree–Fock level of theory, were used to provide

---

(1) Baykut, G.; Wanczek, K.-P.; Hartmann, H. *Adv. Mass. Spectrom.* **1980**, *8A*, 186.

(2) Freiser, B., unpublished: footnote 52 in ref 3a.

(3) (a) Qin, X.-Z.; Meng, Q.-C.; Williams, F. *J. Am. Chem. Soc.* **1987**, *109*, 6778. (b) Qin, X.-Z.; Williams, F. *J. Chem. Soc., Chem. Commun.* **1987**, 257.

(4) (a) Shida, T.; Haselbach, E.; Bally, T. *Acc. Chem. Res.* **1984**, *17*, 180. (b) Symons, M. C. R. *Chem. Soc. Rev.* **1984**, *13*, 393.

(5) Gill, P. M. W.; Radom, L. *J. Am. Chem. Soc.* **1988**, *110*, 4931.

(6) Gill, P. M. W.; Radom, L. *J. Am. Chem. Soc.*, in press.

(7) See, for example: Clark, T. *J. Am. Chem. Soc.* **1988**, *110*, 1672 and references therein.

(8) See, for example: (a) Musker, W. K.; Wolford, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3055. (b) Alder, R. W. *Acc. Chem. Res.* **1983**, *16*, 321. (c) Bonifacic, M.; Asmus, K.-D. *J. Org. Chem.* **1986**, *51*, 1216. (d) Ganghi, N.; Wyatt, J. L.; Symons, M. C. R. *J. Chem. Soc., Chem. Commun.* **1986**, 1424.

(9) Hehre, W. J. Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(10) (a) Nobes, R. H.; Riggs, N. V.; Smith, B. J.; Wong, M. W. Unpublished. (b) Baker, J. *J. Comput. Chem.* **1986**, *7*, 385.

(11) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; DeFrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Pople, J. A. GAUSSIAN 86, Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh PA.

(12) The frequencies were calculated at the 6-31G(d)//6-31G(d) level for all systems except the large dimers **5** (3-21G//3-21G) and **7** (3-21G*//3-21G*).

0002-7863/89/1511-2782$01.50/0

Table I. Calculated Total Energies (hartrees) and Zero-Point Vibrational Energies (kJ mol^{-1}) of Species Related to the Dimer Cations of H_2S and Thiirane[a,b]

		HF/STO-3G[c]	HF/3-21G[d]	HF/6-31G(d)	MP2/6-31G(d)	ZPVE[e]
Thi	**1**	−470.276 76	−473.157 12	−475.546 81	−475.928 82	140.4
Thi$^{\bullet+}$ ($^2B_1$)	**2**	−470.075 09	−472.865 12	−475.260 08	−475.612 39	139.0
Thi–S$^{\bullet+}$ ($^2A''$)	**3**	−863.262 51	−868.424 07	−872.769 36	−873.242 38	145.1
C_2H_4	**4**	−77.073 95	−77.600 99	−78.031 72	−78.284 35	129.4
Thi–Thi$^{\bullet+}$ (^2B_u)	**5**	−940.384 32	−946.056 49	−950.833 34	−951.589 52	279.7[f]
H_2S–$SH_2^{\bullet+}$ (^2B_u)	**6**	−788.421 43	−793.094 02	−797.026 11	−797.260 96	90.1
Thi–$H_2S^{\bullet+}$ ($^2A'$)	**7**	−864.407 24	−869.587 64	−873.939 44	−874.420 61	183.9[g]
SH_2	**8**	−394.311 63	−396.704 67	−398.667 32	−398.788 20	38.9
$H_2S^{\bullet+}$ ($^2B_1$)	**9**	−394.062 80	−396.351 37	−398.326 99	−398.425 31	38.3
H_2	**10**	−1.117 51	−1.122 96	−1.126 83	−1.144 10	25.0
H_2S–$S^{\bullet+}$ ($^2A'$)	**11**	−787.270 58	−791.923 34	−795.847 96	−796.061 58	50.8

[a] HF/6-31G(d) optimized structures, unless otherwise noted. [b] "Thi" represents the thiirane unit. [c] HF/STO-3G optimized structures. [d] HF/3-21G optimized structures. [e] HF/6-31G(d)/HF/6-31G(d) values scaled by 0.9, unless otherwise noted. [f] HF/3-21G//HF/3-21G value scaled by 0.9. [g] HF/3-21G*//HF/3-21G* value scaled by 0.9.

Table II. Calculated Relative Energies (kJ mol^{-1}) of Possible Fragmentation Products of the Dimer Cations of H_2S and Thiirane[a,b]

	HF/ STO-3G[c]	HF/ 3-21G[d]	HF/ 6-31G(d)	MP2/ 6-31G(d)	MP2/ 6-31G(d)[e]
Thi–Thi$^{\bullet+}$ (**5**)	0	0	0	0	0
Thi$^{\bullet+}$ + Thi	85	90	69	127	127
Thi–S$^{\bullet+}$ + C_2H_4	126	83	85	165	160
H_2S–$SH_2^{\bullet+}$ (**6**)	0	0	0	0	0
$H_2S^{\bullet+}$ + SH_2	123	100	83	125	112
H_2S–$S^{\bullet+}$ + H_2	88	125	135	145	131
Thi–$H_2S^{\bullet+}$ (**7**)	0	0	0	0	0
Thi$^{\bullet+}$ + SH_2	54	47	32	53	47
Thi–S$^{\bullet+}$ + H_2	71	107	114	90	76
$H_2S^{\bullet+}$ + Thi	178	208	172	175	169
H_2S–$S^{\bullet+}$ + C_2H_4	165	166	157	196	192

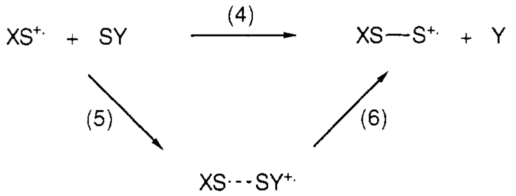
[a] HF/6-31G(d) optimized structures, unless otherwise noted. [b] "Thi" represents the thiirane unit. [c] HF/STO-3G optimized structures. [d] HF/3-21G optimized structures. [e] Including zero-point vibrational correction.

zero-point vibrational corrections to the calculated relative energies. The calculated total and relative energies are summarized in Tables I and II, respectively. We note that, as we found in our earlier study[5] of **6**, electron correlation has a marked effect on the energies of hemibonded species relative to their fragmentation products. Our best relative energies correspond to MP2/6-31G(d)//HF/6-31G(d) values together with zero-point vibrational corrections and, unless otherwise noted, these are the values referred to within the text.

Discussion

An initial task before embarking on the examination of the thiirane ion dimer (**5**) was to characterize both neutral thiirane (**1**) and its radical cation (**2**). The RHF/6-31G(d) geometry of the neutral thiirane molecule (**1**) is in satisfactory agreement with the accurate microwave structure of Okiye et al.[13] The calculated C–C bond length (1.473 Å) is slightly shorter than the experimental value (1.484 ± 0.003 Å) while the theoretical and experimental C–S bond lengths are almost identical (1.811 and 1.815 Å, respectively). Although the thiirane radical cation (**2**) has been the subject of some experimental and theoretical inquiry,[1,3,14-16] no ab initio study of it has previously been reported. Our calculations indicate, in contradistinction to the case of the analogous oxirane molecule[17,18] (however, see ref 19), that the thiirane skeleton does not easily ring-open upon ionization and that the ring-closed structure (**2**) lies lower in energy than the ring-opened form.[20] Indeed, we find that ionization has a relatively small effect on the structure of thiirane (compare **1** and **2** in Figure 1) and QMW have noted[3a] that **2** is the first example of a ring-closed heterocyclopropane radical cation. Finally, we note that the adiabatic ionization energy of thiirane, calculated at the MP2/6-31G(d) level of theory (Table I), is 8.6 eV, which is somewhat smaller than the photoionization measurement[14] (9.05 eV) of Butler and Baer.

Scheme I



a: X = H_2, Y = H_2

b: X = H_2, Y = C_2H_4

c: X = C_2H_4, Y = H_2

d: X = C_2H_4, Y = C_2H_4

In the light of the relationship between the BWH[1] and QMW[3] experiments, it is convenient to formulate the relevant reactions in general terms as shown in Scheme I. Thus, for example, reaction 4d is the sulfur-transfer reaction in the thiirane system studied by BWH,[1] while reactions 5d and 6d are respectively the dimerization and ethylene extrusion processes observed for thiirane by QMW.[3]

We have previously calculated[5,6] the three-electron hemibond energy in **6** to be 111 kJ mol^{-1} at the MP4/6-311G(MC)(d,p)//MP2/6-31G(d) level of theory.[21] Because of the much larger

---

(13) Okiye, K.; Hirose, C.; Lister, D. G.; Sheridan, J. *Chem. Phys. Lett.* **1974**, *24*, 111.

(14) Butler, J. J.; Baer, T. *Org. Mass. Spectrom.* **1983**, *18*, 248.

(15) Glidewell, C. *J. Chem. Soc., Perkin Trans. 2* **1984**, 407.

(16) Rao, D. N. R.; Symons, M. C. R.; Wren, B. W. *J. Chem. Soc. Perkin Trans. 2* **1984**, 1681.

(17) (a) Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Am. Chem. Soc.* **1979**, *101*, 5540. (b) Cimiraglia, R.; Miertus, S.; Tomasi, J. *J. Mol. Struct.* **1980**, *62*, 249. (c) Clark, T. *J. Chem. Soc., Chem. Commun.* **1984**, 666. (d) Nobes, R. H.; Bouma, W. J.; MacLeod, J. K.; Radom, L. *Chem. Phys. Lett.* **1987**, *135*, 78.

(18) (a) Corderman, R. R.; Le Breton, P. R.; Buttrill, S. E.; Williamson, A. D.; Beauchamp, J. L. *J. Chem. Phys.* **1976**, *65*, 4929. (b) Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Chem. Soc., Chem. Commun.* **1978**, 724. (c) Snow, L. D.; Wang, J. T.; Williams, F. *Chem. Phys. Lett.* **1983**, *100*, 193. (d) Bally, T.; Nitsche, S.; Haselbach, E. *Helv. Chim. Acta* **1984**, *67*, 86. (e) Williams, F.; Dai, S.; Snow, L. D.; Qin, X.-Z.; Bally, T.; Nitsche, S.; Haselbach, E.; Nelsen, S. F.; Teasley, M. F. *J. Am. Chem. Soc.* **1987**, *109*, 7526. (f) Snow, L. D.; Williams, F. *Chem. Phys. Lett.* **1988**, *143*, 521.

(19) (a) Symons, M. C. R.; Wren, B. W. *Tetrahedron Lett.* **1983**, *24*, 2315. (b) Symons, M. C. R.; Wren, B. W. *J. Chem. Soc., Perkin Trans. 2* **1984**, 511. (c) Rhodes, C. J.; Symons, M. C. R. *Chem. Phys. Lett.* **1987**, *140*, 611.

(20) The ground state of the ring-opened isomer of thiirane radical cation is planar (point group C_{2v}; state symmetry $^2A_2$) with a C–S bond length of 1.667 Å and a C–C separation of 2.683 Å. It lies 77 kJ mol^{-1} (MP2/6-31G(d)//HF/6-31G(d) with zero-point vibrational correction) higher in energy than the ring-closed form.

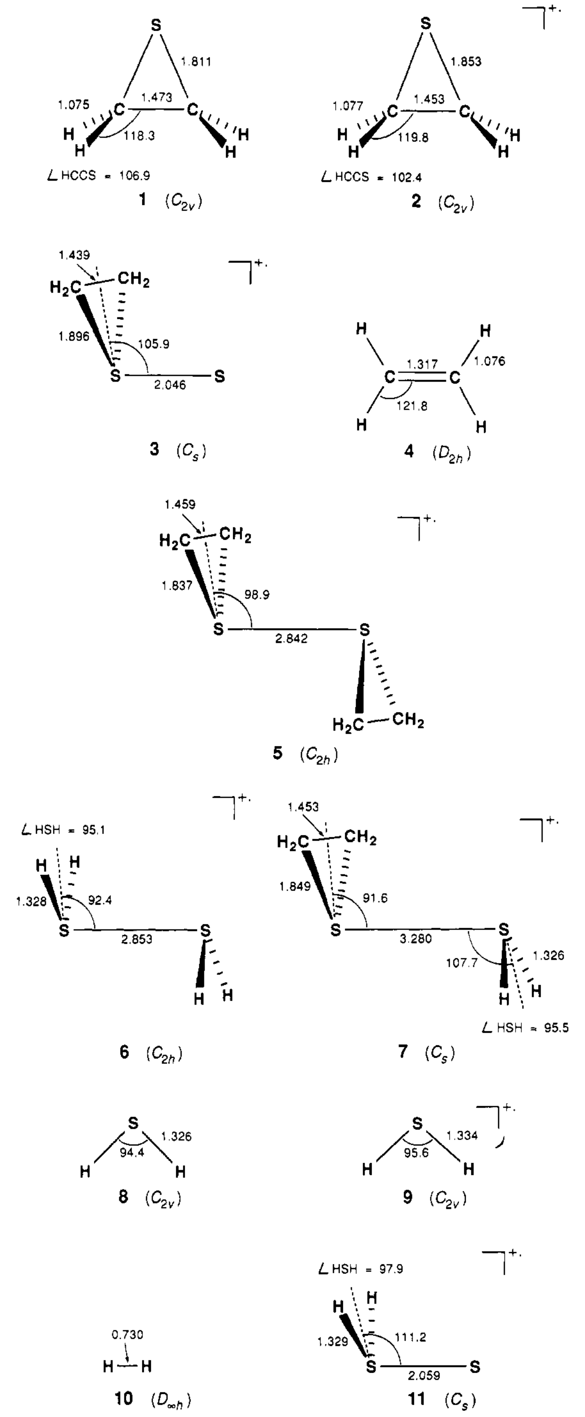


Figure 1. Optimized structures (HF/6-31G(d), bond lengths in Å, bond angles in deg) of the dimer radical cations of H_2S and thiirane and of some of their fragmentation products.

size of some of the systems (e.g. **5**) considered in the present study, calculations at such a level would have been prohibitively expensive. Nevertheless, it is pleasing to note from Table II that the highest level of theory which we are using in this paper, MP2/6-31G(d)//HF/6-31G(d), leads to a hemibond energy (112 kJ mol^{-1}) in **6** that is in very satisfactory agreement with the previous, higher-level, estimate. The previous calculations[5,6] also established a trans conformation for $H_2S{\cdots}SH_2^{\bullet+}$, as shown in **6**. We have assumed similar trans conformations for **5** and **7** in the present study. However, it should be noted that because the S$\cdots$S bond is rather long, internal rotation in these hemibonded dimer cations can take place quite readily.

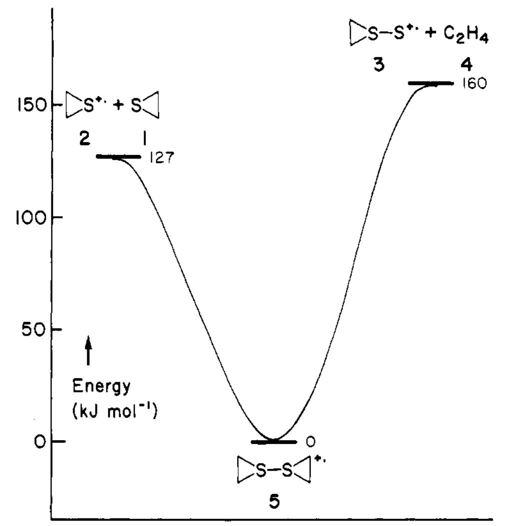


Figure 2. Schematic potential energy surface for the formation of the thiirane dimer radical cation (**5**) from thiirane (**1**) and thiirane radical cation (**2**) and its ethylene-extrusion fragmentation.

In previous papers, we argued[5,6] that the S–S three-electron hemibond in $XS{-}SY^{\bullet+}$ should be comparatively weak when the first ionization energies of XS and SY are significantly different. Consequently, we might expect that the hemibond strength in **5** will be comparable to that in **6** (i.e. ~111 kJ mol^{-1}), while that in mixed dimer cation **7** should be substantially less. The results in Table II support this qualitative prediction. Of the three dimer cations, **5** and **6** possess the strongest three-electron hemibonds (D_0 = 127 and 112 kJ mol^{-1}, respectively), while that in **7** is much weaker (D_0 = 47 kJ mol^{-1} relative to **2** + **8**). This is reflected also in the comparison of the S–S bond lengths in **5** and **6** with that in **7** (2.842 and 2.853 versus 3.280 Å, Figure 1).

Our calculations indicate that the dimerization reaction which produces the thiirane dimer cation (**5**) has a very substantial driving force (127 kJ mol^{-1}) and is barrier-free (Figure 2). It thus seems entirely reasonable that, as QMW have observed in Freon matrices,[3] the neutral and ionized thiirane molecules should rapidly combine with one another, even at the very low temperatures that were used, and that the ESR signal due to the resulting hemibonded dimer cation **5** should be stable.

Because the extrusion reactions of $XS{-}{-}SX^{\bullet+}$ can lead in principle to two possible pairs of dissociation fragments, namely $XSS^{\bullet+}$ + X and XSS + $X^{\bullet+}$, we have determined, in each case, which of the pairs of fragments has the lower energy. We find (as shown in Scheme I) that it is the XSS rather than the X moiety that bears the positive charge. Thus, for example, we have confirmed the experimental finding[1,3a] that it is neutral ethylene (+ $C_2H_4S_2^{\bullet+}$ radical cation (**3**)), rather than ethylene radical cation (+ neutral $C_2H_4S_2$), that is the preferred extrusion product of **5**.

The extrusion fragmentations are predicted (Table II) to be somewhat less thermodynamically favourable than the cleavage of the sulfur–sulfur hemibond in all of the dimer cation systems. For example, the extrusion of ethylene from thiirane dimer radical cation **5** (reaction 6d) requires roughly 160 kJ mol^{-1} while to cleave the S–S hemibond (reverse of reaction 5d) requires only 127 kJ mol^{-1} (Figure 2). However, the differences between the reaction energies for extrusion and sulfur–sulfur cleavage are not very great with the result that, at our highest level of theory, the sulfur-transfer reactions (4a–4d) are all predicted to be only slightly endothermic (typically by 20–30 kJ mol^{-1}). Apparently, for example, the energy that is released when the S–S bond and the C–C π-bond are formed in reaction 4d is almost sufficient to compensate for the loss of two thiirane C–S bonds. The observation that the sulfur-transfer reactions are almost thermoneutral is consistent with the finding that reaction 4d involving ethylene extrusion in the thiirane system is very fast in the gas phase (the second-order rate constant $k \simeq 1.3 \times 10^{-10}$ cm^3 s^{-1} molecule^{-1},

---

[21] The 6-311G(MC)(d,p) basis set is described in: Wong, M. W.; Gill, P. M. W.; Nobes, R. H.; Radom, L. *J. Phys. Chem.* **1988**, *92*, 4875.

according to BWH[1]). However, we have found that, unlike the ethylene-extrusion reactions (6b and 6d), both of the reactions (6a and 6c) in which H_2 is extruded occur with reverse activation energy. Consequently, the barriers to H_2 loss from **6** and **7** will be greater than the corresponding reaction energies (131 and 76 kJ mol^{-1}, respectively) shown in Table II.

In order to gain some measure of the reliability of our calculated energies for the extrusion fragmentations, we have performed higher-level calculations for the simplest reaction of this type, $H_2S\cdots SH_2^{\bullet+}$ (**6**) $\rightarrow$ $H_2SS^{\bullet+}$ (**11**) + H_2. These were carried out at the same level of theory as used previously[5,6] to calculate the hemibond energy (vide supra), namely MP4/6-311G(MC)(d,p)//MP2/6-31G(d) plus zero-point vibrational correction. The extrusion energy calculated in this manner (148 kJ mol^{-1}) is slightly higher than the value (131 kJ mol^{-1}) obtained at the highest level of theory used for the remaining systems in this paper (MP2/6-31G(d)//HF/6-31G(d) + ZPVE, Table II).

Our theoretical results appear to rationalize both the ease with which the sulfur-transfer reaction 1 takes place and the facile formation (reaction 3) of the thiirane dimer radical cation **5**. However, the finding[3a] that **5** is apparently thermally unstable in some matrices at only 105 K is somewhat puzzling in the light of our moderately large calculated barrier (160 kJ mol^{-1}) for extrusion of ethylene. It is possible that the observed behavior may be associated with a matrix effect, a suggestion supported by the fact that the decomposition is strongly matrix dependent.[3a] Alternatively, it is possible that there may be a lower-energy pathway for production of ethylene that we have not yet investigated.[22]

Conclusions

In this paper, we have demonstrated that the experimental report of the formation of the hemibonded dimer radical cation of thiirane (**5**) is consistent with the theoretical prediction that sulfur–sulfur hemibonds of the type found in **5** are generally rather strong. Although fission of the sulfur–sulfur hemibond is probably the lowest-energy fragmentation pathway (127 kJ mol^{-1}), our calculations indicate that an alternative, and only slightly more energetically costly, unimolecular fragmentation is the recently observed ethylene-extrusion decomposition (160 kJ mol^{-1}). Both of these processes are predicted to occur without reverse activation energy. The mixed H_2S–thiirane dimer cation (**7**) is predicted to be a much less stable species than either the thiirane dimer cation (**5**) or the hydrogen sulfide dimer cation (**6**), principally because of the comparatively low barrier (47 kJ mol^{-1}) to the fission of its hemibond.

Acknowledgment. We thank Professor Ffrancon Williams for a preprint of ref 3a and gratefully acknowledge the award of an ANU Vacation Scholarship to P.W. and a generous allocation of time on the Fujitsu FACOM VP-100 of the Australian National University Supercomputer Facility.

Registry No. 1, 420-12-2; **2**, 119273-76-6; **3**, 119273-77-7; **4**, 74-85-1; **8**, 7783-06-4; **9**, 26453-60-1; **10**, 1333-74-0; **11**, 119273-78-8.

---

[22] For example, in related gas-phase experiments involving thiirane *anions*, the proposed mechanism for extrusion of ethylene involved *ring-opened* sulfur-containing species: de Koning, L. J.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1988**, *110*, 2066.

Ab Initio Studies of the C_3H_4 Surface. 2. MCSCF and CI Study of Structures of Vinylmethylene and Ring Opening of Cyclopropene

M. Yoshimine,* J. Pacansky, and N. Honjou[†]

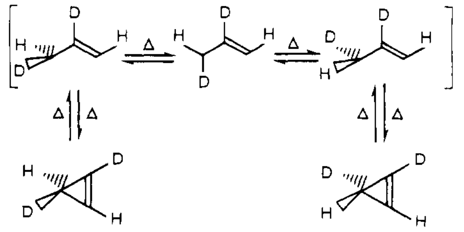
Contribution from the IBM Almaden Research Center, San Jose, California 95120.
Received August 1, 1988

Abstract: MCSCF and CI calculations have been performed to investigate the potential energy surface of vinylmethylene and rearrangement paths from cyclopropene to vinylmethylene and propenylidene. The results show that triplet vinylmethylene has two isoenergetic minima (trans and cis) that have allylic planar structures and lie 45.9 kcal/mol above the X $^1A_1$ state of methylacetylene. Singlet vinylmethylene has four isoenergetic local minima (two for cis and two for trans) that have allylic-like nonplanar structures and lie 12 kcal/mol above triplet vinylmethylene. These singlet species are rather unstable with respect to the ring closures to cyclopropene, with potential energy barriers of 1.3 and 4.7 kcal/mol for the cis and trans species, respectively. It is found that a direct reaction path from cyclopropene to *cis*-vinylmethylene exists with the potential energy barrier of 36.5 kcal/mol while the barrier for the cyclopropene to *trans*-vinylmethylene is 40.2 kcal/mol. The rearrangement of cyclopropene to propenylidene is a concerted reaction with the potential energy barrier of 41.5 kcal/mol, in which ring opening is accompanied by a 1,2-hydrogen migration, and the barrier for the reverse reaction is 20.5 kcal/mol, indicating that this ring-opening process is product forming. We also found a surface crossing between the singlet excited and ground states of C_3H_4 occurring in the vicinity of the singlet vinylmethylene structure, providing a mechanism for radiationless decay of excited cyclopropene species.

I. Introduction

In the first paper of this series[1] (hereafter referred to as paper 1), we reported SCF and CI calculations for the structures and relative energies of the C_3H_4 isomers. In this paper we report MCSCF and CI calculations on the reaction paths among various vinylmethylene structures, which are sketched in Figure 1, and reaction paths for the reversible ring closure to cyclopropene (**1**).[2] In addition we present a study on the reaction path for the ring opening of cyclopropene to propenylidene (**2**), which has been proposed in paper 1 as a possible low-energy path to methylacetylene.

Scheme I



It has been suggested that vinylmethylene plays a central role in the thermal interconversions on the C_3H_4 surface. The in-

---

[†] Present address: IBM Tokyo Research Laboratory, Tokyo 102, Japan.

0002-7863/89/1511-2785$01.50/0 © 1989 American Chemical Society