Notes

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S_5: An ab Initio Study

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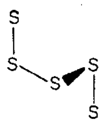
Elemental sulfur,[1,2] which has been known and used for several thousand years, can exist in a polymeric form and as a variety of rings containing different numbers of sulfur atoms. Many of them have been experimentally or theoretically studied and discussed. However, the most stable structure of S_5 remains an interesting unsolved problem.[1,2]

We know very little about the S_5 molecule despite the fact that it has been shown to exist in the sulfur vapor,[3] liquid sulfur,[4] and matrices.[4] Bonding considerations suggest that S_5 may occur as a ring, a diradical chain, a branched chain, and branched rings. Thermodynamic considerations[3,5,6] seem to suggest that S_5 is a ring in the gas phase while semiempirical calculations[1,7] favor the diradical chain.

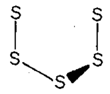
An alternative way to attack this problem which has yet to be applied to S_5 is ab initio molecular orbtial theory. This technique has been described in detail elsewhere.[8,9] In this paper, ab initio molecular orbital theory is employed to investigate the most stable structure of S_5. A similar study on S_4 has recently been reported.[10]

Methods and Results

The results presented here were obtained using the Gaussian 70 system of programs.[11,12] Branched structures are excluded from the present study since the previous study[10] on S_4 has shown that branched ring or chain forms are rather unstable. Three possible conformations (planar, envelope, and half-chair) of the ring form were all examined at the STO-3G level[8] since its small size permits full optimization under reasonable cost for a molecule as large as S_5 (45 basis functions for STO-3G). The obtained STO-3G conformational energy difference is expected to be not much different from those employing extended basis sets.[13] The STO-3G method has proven very useful in structural studies and conformational analysis of sulfides,[14-16] disulfides,[16-18] polysulfides,[16] and elemental sulfur.[16,19,20] In order to compare the relative stabilities of open-chain and ring forms more accurately, the planar ring and the anti open chain (I) were fully optimized at the 44-31G level[9] (vide infra).[10] Full 44-31G optimization of all conformations is too costly in terms of computing economy. (The CPU time required for a single calculation was approximately 8 min for STO-3G and 35 min for 44-31G on UNIVAC 1100/45.)



I



II

The planar ring was chosen because of its inherent high symmetry (D_{5h}) while the choice of the anti form (I) is based on its possible lower energy than the syn form (II). The energy difference between syn and anti forms is expected to be small but may be quite significant. Arrangements similar to the syn form (II) would increase instability by more than 1.8 kcal mol^{-1} for hydrocarbons, thioethers, and ethers.[21] One also notes that the fibrous sulfur (S_∞)[22] seems to have all anti arrangements. Only the open-shell triplet state is considered for the open-chain form since the previous study[10] on S_4 reveals that the singlet is less stable than the triplet by at least 75 kcal mol^{-1} at the STO-3G level of theory. The open-shell system was calculated by the unrestricted Hartree–Fock method of Pople and Nesbet.[23] Each structure is fully geometrically optimized subject only to an overall symmetry constraint with the exception that the dihedral angle of the open chain was assumed to be 90°. Calculated equilibrium geometries and energies (total and relative) for the corresponding structures are all listed in Table I.

Discussion

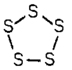
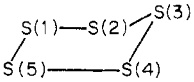
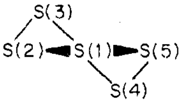
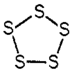
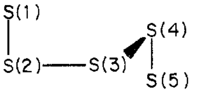
As can be seen from Table I, the envelope conformation is calculated to have the same energy as the half-chair. It is interesting to note that molecular mechanics calculations[19] also give an identical energy for the envelope and the half-chair S_5. Thus, the S_5 ring, like cyclopentane, pseudorotates through a continuum of half-chair and envelope forms. The planar form is predicted to be less stable than the envelope by 18.2 kcal mol^{-1}, which is substantially larger than that obtained by molecular mechanics calculations (11.3 kcal mol^{-1}).[19] The planar-envelope energy gap may even be slightly larger by utilizing more extended basis sets[13] since the recent ab initio study[24] of the ring inversion barrier for cyclobutane using different levels of theory has shown that the STO-3G basis set is less flexible and hence overestimates the angle strain relative to the torsional strain energy. Bond angles obtained by molecular mechanics and STO-3G calculations agree quite well (within 0.5°) although the STO-3G bond lengths are slightly longer than those of molecular mechanics results.[19] But one notes that the S–S bond lengths obtained by the STO-3G method are characteristically longer than (about 0.03 Å) experimental values.[16,17]

At the first glance, the predicted equal stability of the envelope and the half-chair of c-S_5 by both the STO-3G and the molecular mechanics methods may be just fortuitous. However, the envelope and half-chair forms of cyclopentane are also shown to be equally stable experimentally as well as theoretically.[13,25,26] The S–S–S–S torsion has a twofold barrier[10] of 7.6 kcal mol^{-1} while the C–C–C–C torsion is threefold with a barrier height of 2.9 kcal mol^{-1}.[27] These torsional functions represent two distinct classes and the equal stability of envelope and half-chair forms may therefore be generally true. The results presented here support the contention that the existence of an equal stability for the envelope and the half-chair forms is an intrinsic nature of homocyclic five-membered rings, $(AB_n)_5$.

As was found before,[10] the calculated S–S bond lengths using the STO-3G and 44-31G basis sets are quite different. This is consistent with the recent observation[14] that the addition of a full set of valence orbitals to a minimal basis tends to increase bond lengths. It has been proposed that although the absolute errors for 44-31G bond lengths are generally large, the calculated bond lengths are expected to be long consistently.[14]

The terminal atoms for the triplet chain are, as for S_4,[10] predicted to be positively charged (+0.05 e) while the intermediate atoms are negatively charged (−0.04 and −0.01 e, respectively, on S(2) and S(3)). The predicted dipole moment (1.94 D) is hence directed from the S(3) atom to the midpoint

Table I. Calculated Energies and Equilibrium Geometries

Conformation	Symmetry constraint	Structural parameter, Å or deg		Energy	
				Total, au	Relative, kcal mol^{-1}
		STO-3G			
Planar 	D_{5h}	S–S	2.090	−1965.865 50	18.2
Envelope 	C_s	S(1)–S(2)	2.084	−1965.894 48	0
		S(2)–S(3)	2.073		
		S(1)–S(5)	2.110		
		S(2)–S(1)–S(5)	103.3		
		S(1)–S(2)–S(3)	98.9		
		S(2)–S(3)–S(4)[a]	95.4		
Half-chair 	C_2	S(1)–S(2)	2.101	−1965.894 46	0.0
		S(2)–S(3)	2.075		
		S(3)–S(4)	2.073		
		S(2)–S(1)–S(5)	103.8		
		S(1)–S(2)–S(3)	101.6		
		S(2)–S(3)–S(4)[a]	96.5		
		44-31G			
Planar 	D_{5h}	S–S	2.269	−1985.236 23	23.6
Anti 	C_2	S(1)–S(2)	2.225	−1985.273 85	0
		S(2)–S(3)	2.241		
		S(1)–S(2)–S(3)	103.9		
		S(2)–S(3)–S(4)	103.2		
		S(1)–S(2)–S(3)–S(4)	90.0 (assumed)		

[a] Not an independent parameter; shown for easy comparison.

of the S(1)···S(5) line. It is interesting to note that the extended Hückel calculations,[1,7] based on spectroscopic atomic parameters, gave opposite predictions.

On the basis of 44-31G calculations, the planar c-S_5 is predicted to be 23.6 kcal mol^{-1} less stable than the triplet chain. Thus, the envelope or the half-chair of c-S_5 is possibly only 5.4 kcal mol^{-1} less stable than the triplet chain according to the single-determinant theory. However, it would almost certainly be incorrect to assign the triplet chain as the most stable structure in light of the known preference of single determinant methods to favor high-spin multiplicity. For example, the triplet methylene ($^3B_1$) is calculated to be about 31 kcal mol^{-1} lower in energy than the singlet state ($^1A_1$) at the 6-31G* level while experimental estimates favor the triplet by no more than 20 kcal mol^{-1} (but perhaps 10 kcal mol^{-1}).[28,29] The overestimation of the triplet stability relative to that of the singlet is likely mainly due to the unbalanced correlation energy. In going from the $^3B_1$ to the $^1A_1$ state of methylene, two electrons are primarily paired in a σ orbital and the correlation energy is increased. The increase of correlation energy is possibly smaller for S_4 and S_5 since their corresponding molecular orbitals are more diffuse. The preference of triplet over singlet by the 6-31G* method may be partially attributed to the effects of higher multiplet contamination in unrestricted Hartree–Fock calculations.[30–32] However, this is not a serious problem for sulfur chains as evidenced by the calculated expectation values of S^2, the total spin squared operator (2.10 for S_5 and 2.04–2.10 for S_4 compared with 2.00 for a pure triplet).

The ionization potentials of the S_n species ($n = 2, ..., 8$) have been studied by photoionization and electron-impact methods.[5] The photoionization results, which are believed to be more reliable, are uniformly about 0.5–0.6 ev lower than those from electron impact.[5] The reported photoionization potentials are 9.00 and 8.60 eV, respectively, for S_6 and S_5, while those deduced from STO-3G calculations according to Koopmans' theorem[33] are respectively 6.30 and 5.98 eV for c-S_6 and c-S_5. There are notable differences between these two sets of data. However, one notes that (a) the calculated ionization potentials are systematically lower than the corresponding experimental values and (b) the calculated ionization energy difference is in good agreement with the experimental one (0.32 vs. 0.40 eV). This seems to indicate that S_5 is a ring in the gas phase. The lower ionization potential of S_5 may therefore be rationalized in terms of the increasing strain as compared with c-S_6. Furthermore, assuming that there is a linear relationship between the first ionization potential and the strain energy for the species c-S_n, the experimental ionization potentials would seem to suggest that S_4 and S_3 exist as an open chain while S_5 is a ring.

It is believed that the small singlet–triplet splitting obtained here presents a reasonable case to assign a structure (envelope or half-chair) with singlet configuration as the most stable arrangement. But it is also suggested that the triplet chain of S_5 may in reality have energy rather close to that of the envelope or half-chair form. The proposition offered fits the experimental observation which seems to favor the existence of the S_5 chain in the liquid phase and the S_5 ring in the gas phase.[1]

Registry No. S_5, 12597-10-3.

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Phase Relations in the WO_2–V_2WO_6 System

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This work constitutes part of a systematic study of the crystallographic changes in $M^{4+}O_2$–$M^{3+}{}_2M^{6+}O_6$ systems, where M^{4+} = W or V, M^{3+} = V, Fe, Cr, or Al, and M^{6+} = W, Mo, or Te.

The VO_2–$M^{3+}{}_2M^{6+}O_6$ system, where M^{3+} = V, Fe, Cr, or Al and M^{6+} = W, Mo, or Te, has been studied extensively by a number of workers.[1–3] The recent paper by Neurgaonkar and Roy[3] gives a fuller description of the crystallographic changes and the variation of the transition temperature as a function of size of the dopant ions in the VO_2–$M^{3+}{}_2M^{6+}O_6$ system. In the present note, the work on VO_2–V_2WO_6 has been extended by replacing V^{4+} by W^{4+}, and the effects of such replacement on crystalline solubility and structural changes have been studied.

Experimental Section

The starting materials used were WO_3,W (Research in Organic and Inorganic Chemistry Corp.), and V_2O_5 (Fisher Scientific Co.). V_2O_3 was prepared by hydrogen reduction of V_2O_5 for 8 h at 800 °C. The phase $W^{4+}{}_{1-x}V_{2x/3}W^{6+}{}_{x/3}O_2$ has been prepared by substituting vanadium tungstate for WO_2

$$(1-x)WO_2 + \frac{x}{3}V_2WO_6 \rightarrow W_{1-x}V_{2x/3}W_{x/3}O_2 \qquad (1)$$

For the study of the homogeneity range for the different structures, about 25–30 specimens of gradually varying compositions were prepared by mixing WO_3, W, and V_2O_3. The pressed pellets were heated to the desired temperature ranging from 1000 to 1200 °C in evacuated silica tubes. X-ray powder data were obtained using a Picker diffractometer with nickel-filtered Cu Kα radiation. For phase identification a scanning speed of 1° 2θ/min was used. The stoichiometry of each phase was checked by simple gravimetric oxidation to WO_3–V_2WO_6.

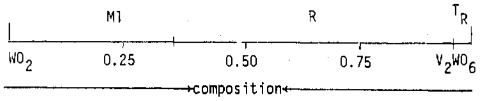

Figure 1. Phases in the system $W_{1-x}V_{2x/3}W_{x/3}O_2$ as observed at room temperature.

Results

A series of these $W_{1-x}V_{2x/3}W_{x/3}O_2$ crystalline solutions exists between the monoclinic WO_2 and the trirutile V_2WO_6 phases. Three structurally related phases have been identified. The results of phase analysis are shown in Figure 1. Here M1 stands for the monoclinic WO_2-type structure, R for the tetragonal rutile structure, and T_R for the trirutile structure. At room temperature, the homogeneity range of the M1 structure is $0.0 \leq x \leq 0.33$, while the R structure appears over a wide compositional range estimated to extend between $0.34 \leq x \leq 0.985$. Only in the samples where $0.985 \leq x \leq 1.0$, superstructure lines indicating the formation of the trirutile solid solution are found.

This study did not find any new phase in the range $W_{1-x}V_{2x/3}W_{x/3}O_2$. WO_2[4] and VO_2[5] are isostructural at room temperature and possess the monoclinically distorted rutile structure. Vanadium dioxide, however, undergoes a structural transformation to the tetragonal rutile at ~67 °C. This fact suggests that the systems WO_2–V_2WO_6 and VO_2–V_2WO_6 should exhibit similar crystallographic changes at room temperature. It is interesting to note that, although the structural changes ($M1 \rightarrow R \rightarrow T_R$) are identical for both the systems, the crystalline solubility of V_2WO_6 in "MO_2" or "MO_2" in V_2WO_6 is entirely different depending on whether "M" is V or W. Recent work on the VO_2–V_2WO_6 system[1] shows that approximately 5 mol % V_2WO_6 dissolves in VO_2. On the other hand, VO_2 dissolves to a large extent in V_2WO_6. It has been shown that 30 mol % of VO_2 can easily be accommodated in V_2WO_6. This interchange of the crystalline solubility in these systems can be explained simply on the basis of the differences in the ionic radii of W^{4+} (0.79 Å) and V^{4+} (0.73 Å).[6]

A notable feature in this system is the occurrence of an undistorted tetragonal rutile-type phase, over a wide range of composition, despite the fact that neither WO_2 nor V_2WO_6 possesses the rutile structure. This large tetragonal rutile crystalline solution field has been reported previously for VO_2–V_2WO_6, VO_2–Cr_2WO_6,[1,2] and some other systems, e.g., VO_2–WO_2, VO_2–MoO_2, and NbO_2–ReO_2, etc.[7,8,9] However, the VO_2–$M^{3+}{}_2TeO_6$ system[3], where M = Fe, Cr or Al, has been shown to be an exception to this rule. No rutile solid solution exists on these binary joins. A comparison between the two systems WO_2–V_2WO_6 and VO_2–V_2WO_6 shows that the homogeneity range of the rutile crystalline solution is exactly similar for the two systems. However, this range does not occur at the same compositional region. For WO_2–V_2WO_6 the rutile solid solution extends in the region $0.34 \leq x \leq 0.985$, while the rutile solid solution is shown to occur in the region $0.06 \leq x \leq 0.70$ in the VO_2–V_2WO_6 system.

Figure 2 gives unit cell parameters, at room temperature, as a function of composition for the rutile-type phase $W_{1-x}V_{2x/3}W_{x/3}P_2$, $0.34 \leq x \leq 0.985$. As shown in Figure 2, the *a* parameter decreases while the *c* parameter increases with increasing amounts of V_2WO_6 in WO_2. It is interesting to note