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MCSCF STUDIES OF THIOXYALLYL INTERMEDIATE

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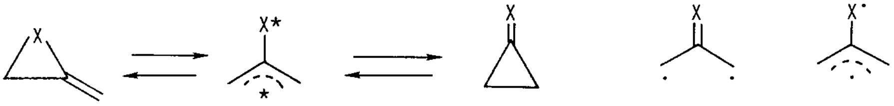
Abstract: The MCSCF studies of thioxyallyl intermediate showed that $^1B_1$ stste is more stable than $^1A_1$ state. The results of F.V.P. of tetramethylallene episulfide and tetramethylpyrazoline-4-thione agreed with that of the MCSCF studies.

Oxyallyl(2b) has been widely accepted as a possible transition state or an intermediate in several reactions,[1] for example, that of cyclopropanone(3b)[2] and allene oxide(1b).[3] The results of semiempirical and ab initio studies for these systems suggest that 3b is more stable than 1b by about 23 kcal mol^{-1}. Depending of whether it is a biradical(singlet and triplet) or not, oxyallyl has been calculated to be 45-232 kcal mol^{-1} higher in energy than 3b.[4] Recently, MCSCF studies of oxyallyl[5] suggest that the intermediate in gas phase is biradical $^1A_1$ state, not $^1B_1$ state. Considerable attention is being given to the tautomeric reaction of sulfur analogous system and some reports are documented on this system,[6,8] however, cyclopropanethione is unknown. There are few theoretical studies on this system[7] and it is found that 1a is 7 kcal mol^{-1} more stable than 3a.[8] We now report the MCSCF studies for $^1A_1$ and $^1B_1$ states of thioxyallyl which agrees with results from pyrolysis of tetramethylallene episulfide and 3,3,5,5-tetramethylpyrazoline-4-thione.



1a:X=S 2a 3a 4a 5a
1b:X=O 2b 3b 4b 5b
($^1A_1$) ($^1B_1$)

The molecular geometries of thioxyallyl were optimized by using the RHF and the UHF built into GAUSSIAN 80 program with STO-3G minimal basis set under the constraint of C_{2v} symmetry in Fig. 1. We used the program GAMESS to determine electronic structure. The electron configurations used in MCSCF calculations were of CAS(complete active space) type and consist of all the configurations generated from all possible occupations of six electrons in a p lone-pair orbital on sulfur, $5b_2(n)$, and four orbitals, $1b_1(\pi_1)$ and $2b_1(\pi_2)$,

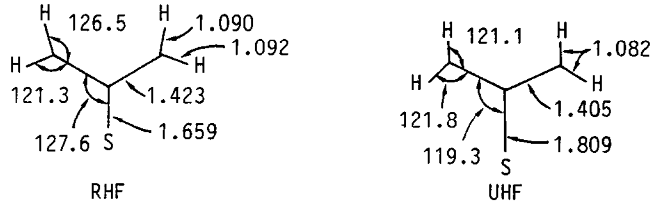
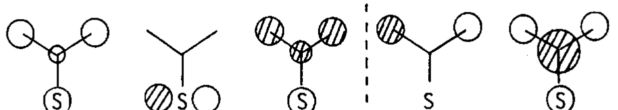


Fig. 1 Optimized Geometries of Thioxyallyl. Values were Determined with The STO-3G Basis set.(in angstroms and degrees)

$1a_2(\pi_3)$ and $3b_1(\pi_4)$. The number of configurations for singlet states is 50 without symmetry restriction. The MCSCF calculations of thioxyallyl were studied for three singlets, $^1A_1$, $^1B_1$, and $^1B_2$ with split-valence 3-21G[9] basis set by use of optimized RHF and UHF geometry, respectively. Shapes of active molecular orbitals and their electron occupation numbers are shown in Fig. 2. The relative energies of the states in thioxyallyl are summarized in Table 1.

In the MCSCF study, we used two molecular geometries of thioxyallyl by using the RHF and UHF. The optimized geometry by using RHF is closed to the structure of thioxyally which has an ionic character and geometry by using UHF is closed to its which has a biradical character. Although the respective optimized geometries of thioxyallyl were insufficient for the MCSCF study, there is a tendency that $^1B_1$ state(5a) is more stable than $^1A_1$ state(4a) in each result using both geometries. The lowest singlet state of thioxyallyl intermediate is $^1B_1$ shows striking contrast with that of oxyallyl intermediate

Fig. 2 Shapes and Electron Occupation Numbers of Active MO's in MCSCF Wave Functions with the 3-21G Basis set.



		$1b_1(\pi_1)$	$5b_2(n)$	$2b_1(\pi_2)$	$1a_2(\pi_3)$	$3b_1(\pi_4)$
$^1A_1$	a	1.816	1.999	1.659	0.433	0.092
	b	1.867	1.999	1.484	0.480	0.170
$^1B_1$	a	1.921	1.000	1.921	1.000	0.159
	b	1.917	1.000	1.903	1.000	0.180
$^1B_2$	a	1.836	2.000	0.985	1.000	0.179
	b	1.837	2.000	0.977	1.000	0.186

a: The result was obtained by using optimized RHF geometry.
b: The result was obtained by using optimized UHF geometry.

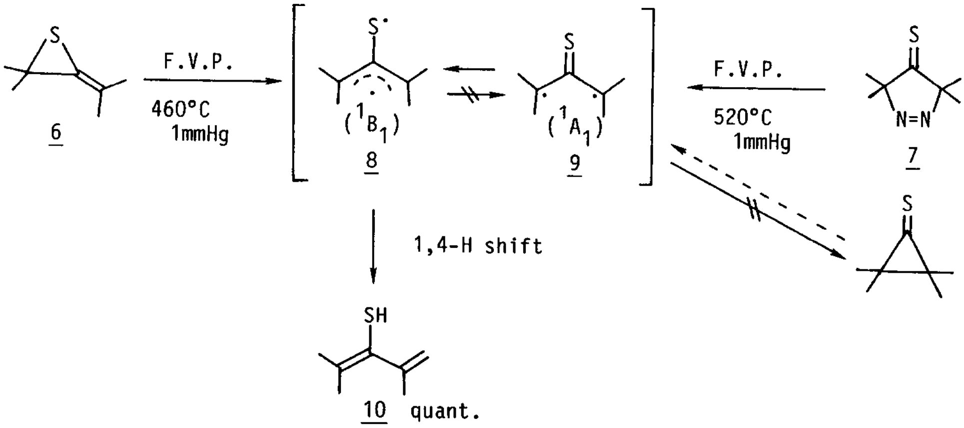
Table 1 MCSCF Relative Energies(in kcal mol^{-1}) for States of Thioxyallyl at Respectively Optimized Geometry.

geometry	State $^1A_1$	$^1B_1$	$^1B_2$
RHF geometry	3.8	0.0^a	8.5
UHF geometry	24.8	0.0^b	3.7

a: Absolute energy is -510.77296 hartree.
b: Absolute energy is -510.80612 hartree.

is $^1A_1$ state(4b), not $^1B_1$ state(5b)[5]; this may be attributed to the difference between the strength of C-S π bond(bond energy:129.9 kcal mol^{-1}) and that of C-O π bond(173.0 kcal mol^{-1}).

Now, we attempted to generate $^1A_1$ and $^1B_1$ states by the route of thermolyses of tetramethylallene episulfide(6) and 3,3,5,5-tetramethyl-pyrazoline-4-thione(7), which may inform us the stability of thioxyallyl although cyclopropanethione is unknown. Flash vaccum pyrolysis of 8 at 460°C under 1mmHg afforded a thermally stable 2,4-dimethyl-3-mercaptpenta-1,3-diene (10) in 88% yield. The formation of 10 can be accounted by initial C-S bond cleavage to give $^1B_1$ state of thioxyallyl(8) followed by intramolecular hydrogen abstraction. Flash vaccum pyrolysis of 7 at 520°C under 1mmHg also gave 10 quantitatively. Initial denitrogenation of 7 gave thioxyallyl(9) corresponds to $^1A_1$ state, then subsequent isomerization of $^1A_1$ state would give 10 through $^1B_1$ state. These results agreed well with that of the MCSCF studies.



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9) On the basis set of 3-21G*, the calculation was very completed and overflowed the ability of computer.

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