Activation energies for pyramidal inversion of sulfonium, selenonium and telluronium ylides based on *ab initio* MO calculations

Toshio Shimizu,[a] Ayumi Matsuhisa,[a] Nobumasa Kamigata [*,a] and Shigeru Ikuta [b]

[a] *Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Minami-ohsawa, Hachioji, Tokyo 192-03, Japan*

[b] *Computer Center, Tokyo Metropolitan University, Minami-ohsawa, Hachioji, Tokyo 192-03, Japan*

Ab initio MO calculations of sulfonium, selenonium and telluronium ylides $R^1_2X^+-C^-R^2_2$ (X = S, Se, Te; R^1 = H, Me; R^2 = H, CN) have been performed to estimate their thermal stabilities toward the pyramidal inversion (vertex inversion) reaction. Geometrical parameters at both the global minima and the saddle-points are independent of the levels of theory employed. However, the activation energies for the pyramidal inversion reaction depend on the levels of theory employed; a method superior to the Hartree–Fock level of theory was necessary for the present purposes. The activation energies for the pyramidal inversion were also found to depend on the substituents. The present computations clearly indicate that the telluronium ylides require higher activation energies for the pyramidal inversion reaction than those of the sulfonium and selenonium ylides.

Many optically active tricoordinate tetravalent sulfur compounds such as sulfoxides, sulfonium salts and sulfonium imides have been synthesized and their stereochemistry and kinetics for the pyramidal inversion reaction have been investigated.[1–3] Recently our interests have focussed on the synthesis of optically active tricoordinate tetravalent selenium and tellurium compounds and the study of their stereochemistry. Previously we reported the synthesis and stereochemistry of optically active selenoxides,[4] selenonium salts[5] and selenonium imides.[6] The pyramidal inversion reaction is important for these optically active selenium compounds as a process for racemization. Recently we reported the theoretical studies on the kinetics for the pyramidal inversion of selenoxides.[7] Although optically active sulfonium ylides have been synthesized and their kinetics for racemization have been studied,[8,9] no paper on the synthesis of selenonium and telluronium ylides (which are considered to have analogous structures to the corresponding sulfonium ylide) had appeared for a long time. Very recently, we succeeded in synthesizing optically active selenonium[10] and telluronium[11] ylides. We also studied the kinetics of racemization *via* pyramidal inversion. However, comparison of the optical stabilities of sulfonium, selenonium and telluronium ylides toward the racemization was impracticable because the synthesis of optically active sulfonium, selenonium and telluronium ylides possessing the same substituents was difficult. Therefore, we have calculated the activation energies for pyramidal inversion (vertex inversion) reactions of sulfonium, selenonium and telluronium ylides by *ab initio* molecular orbital calculations. In this paper geometries and activation energies for the pyramidal inversion of sulfonium, selenonium and telluronium ylides with several substituents are reported.

Method

Geometries at both the global minima and the saddle-points in the pyramidal inversion of the sulfonium, selenonium and telluronium ylides were fully optimized using the Hartree–Fock (HF)[12] and the second-order Møller–Plesset perturbation (MP2)[13] methods. Normal vibrational frequencies were calculated in order to characterize their stationary points and to obtain their zero-point vibrational energies. Final energies at
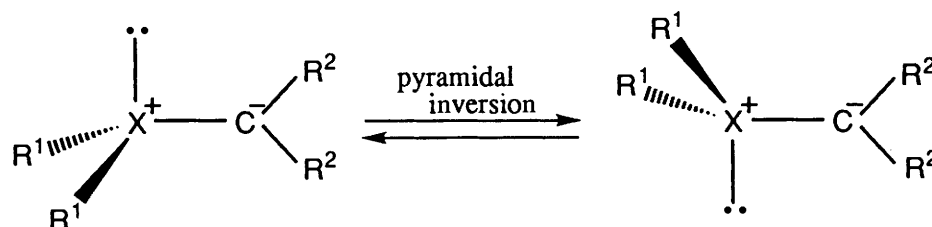
1a:	X=S,	$R^1=R^2=H$	
1b:	X=Se,	$R^1=R^2=H$	
1c:	X=Te,	$R^1=R^2=H$	
2a:	X=S,	$R^1=H$,	$R^2=CN$
2b:	X=Se,	$R^1=H$,	$R^2=CN$
2c:	X=Te,	$R^1=H$,	$R^2=CN$
3a:	X=S,	$R^1=Me$,	$R^2=CN$
3b:	X=Se,	$R^1=Me$,	$R^2=CN$
3c:	X=Te,	$R^1=Me$,	$R^2=CN$

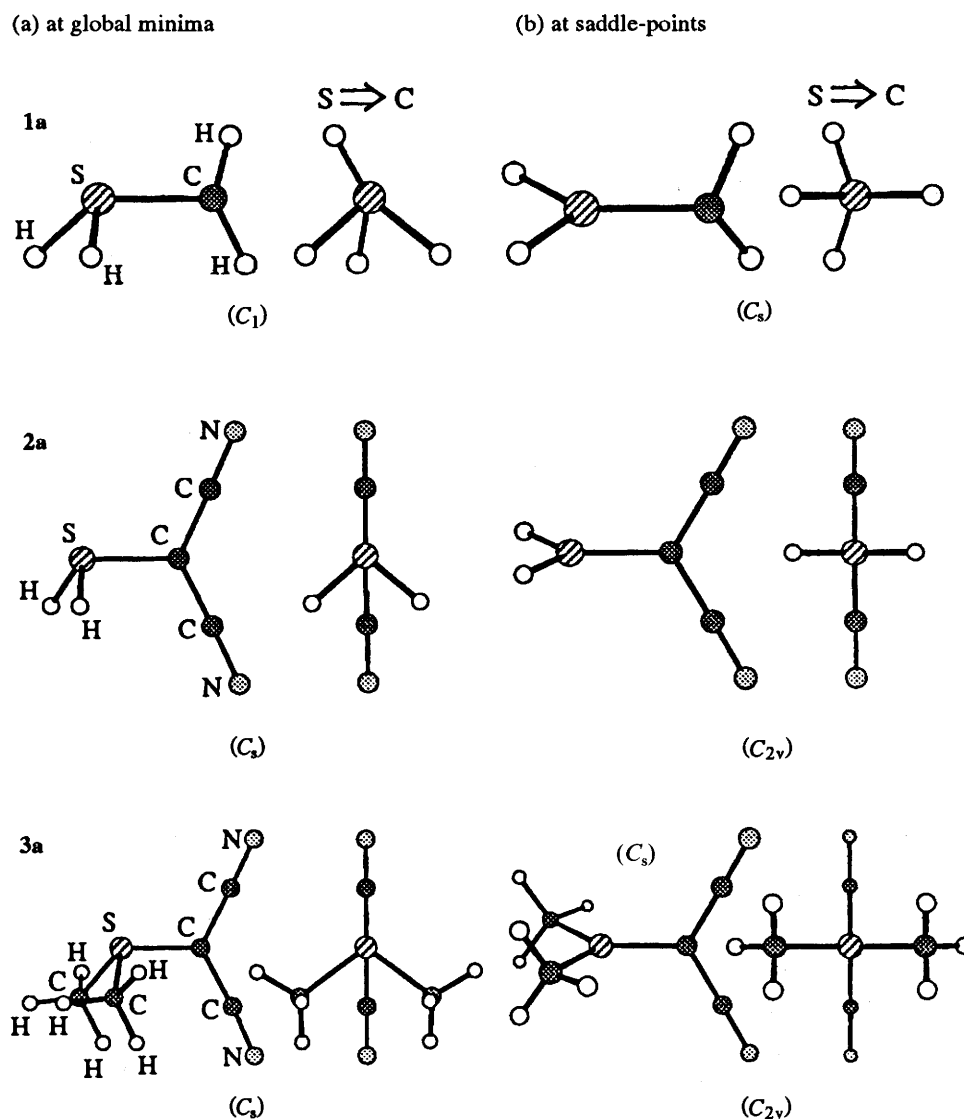(a) at global minima   (b) at saddle-points

Fig. 1 Geometries at (a) the global minima and (b) the saddle-points in the pyramidal inversion reactions of sulfonium ylides (**1a, 2a** and **3a**) optimized by the MP2 (**1a** and **2a**) and the HF (**3a**) methods

both the global minima and the saddle-points were calculated by using the Hartree–Fock (HF), the second-order Møller–Plesset perturbation (MP2)[13] and the third-order Møller–Plesset perturbation (MP3)[14] methods. The following basis sets were used for all calculations. The double-zeta plus polarization basis set[15,16] of hydrogen, carbon, nitrogen and sulfur atoms was used. The (5s4p2d/12s8p5d) and (10s8p-4d/16s11p6d) basis sets were also used for the selenium and tellurium atoms, respectively.[17] All calculations were performed by using GAUSSIAN90 and GAUSSIAN92 programs on the IBM 3090-30J, IBM RS/6000 and VAX9210VP computers at the Computer Center of Tokyo Metropolitan University.

Results and discussion

Geometries

Optimized geometries at both the global minima and the saddle-points in the pyramidal inversion reactions of sulfonium ylides **1a, 2a** and **3a** by MP2 (**1a** and **2a**) and HF (**3a**) methods are shown in Fig. 1. No geometrical parameter of **1a** and **2a** at both the global minima and the saddle-points was found to depend on the levels of theory (HF and MP2 methods) and **3a** showed similar geometrical parameters on several basis sets (STO-3G, 3-21G and double-zeta plus polarization basis sets). Sulfonium

ylide **1a** showed C_1 symmetry, whereas both the sulfonium ylides **2a** and **3a** showed C_s symmetry at the global minima. Lack of planarity of the carbanion of **1a** might be explained by the instability of the carbanion; carbanions of sulfonium ylides **2a** and **3a** are stabilized by electron-withdrawing cyano groups while the ylide **1a** is not stabilized by any substituent. It was also found that the sulfonium ylides **1a, 2a** and **3a** at the saddle-points in the pyramidal inversion via sp² square geometries (vertex inversion) showed C_s, C_{2v} and C_2 symmetries, respectively. Selenonium (**1b, 2b** and **3b**) and telluronium (**1c, 2c** and **3c**) ylides also showed similar symmetries with the corresponding sulfonium ylides. Calculated bond lengths and angles around the chalcogen atoms of the sulfonium, selenonium and telluronium ylides are shown in Fig. 2. Bond lengths of S–C (carbanion) bonds range between 1.68 and 1.71 Å for the six geometries. Bond lengths of the corresponding Se–C and Te–C bonds have values 1.8 and 2.0 Å, respectively. The sum of the bond angles around the tellurium atoms are smaller than those of sulfur and selenium atoms at the global minima, indicating that the telluronium ylides have sharper pyramidal structures compared with those of the sulfonium and the selenonium ylides. This phenomenon is explained by the decline in the valence shell repulsion and the decrease in the steric repulsion of the substituents; this decrease in the repulsion is considered to be caused by the long Te–C and Te–H bond
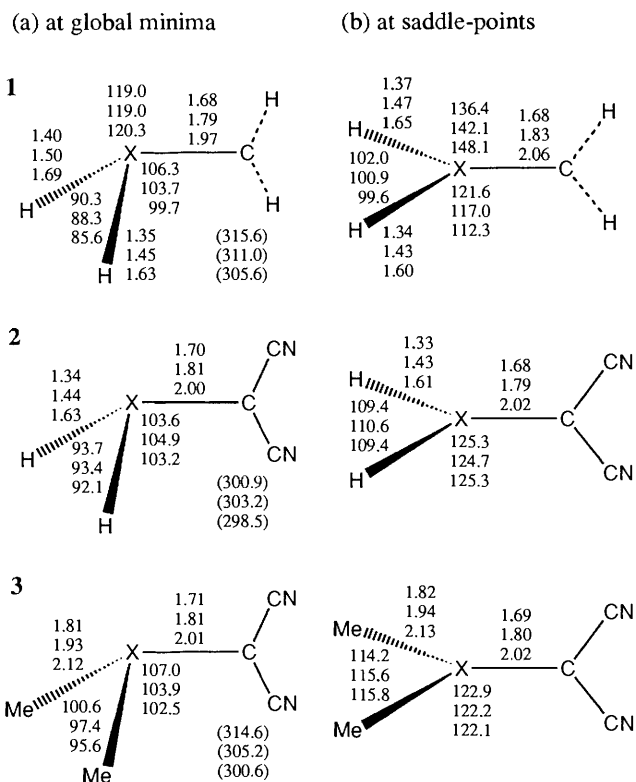
(a) at global minima   (b) at saddle-points

Fig. 2 Bond lengths (Å) and angles (degrees) around the chalcogen atoms of sulfonium, selenonium and telluronium ylides at (a) the global minima and (b) the saddle-points optimized by the MP2 (1 and 2) and the HF (3) methods. Parameters of the sulfonium ylides are on the first line, those of the selenonium ylides on the second line and those of the telluronium ylides on the third line. The sum of the bond angles around the chalcogen atoms are in parentheses, respectively.
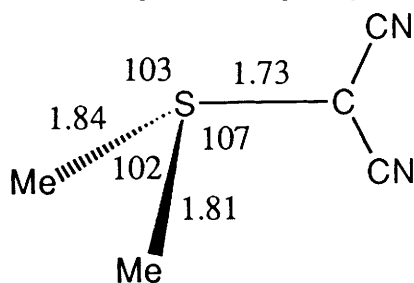
Fig. 3 X-Ray crystal structure of **3a** by A. T. Christensen and Witmore[18]

lengths. The calculated structure of **3a** at the global minimum shows good agreement with the X-ray structure determined by Christensen and Witmore (Fig. 3).[18]

Vibrational frequencies and zero-point energies

Vibrational frequency analysis of each geometry at the saddle-point showed one imaginary frequency which corresponds to the pyramidal inversion mode, clearly indicating the real saddle-point in the reaction pathway. Differences in the zero-point vibrational energies between the global minimum and the saddle-point are within 1.1 kcal mol^{-1} † in each ylide.

Atomic charges

Atomic charges of the chalcogen and the carbanion carbon atoms calculated by the HF method are summarized in Table 1. Positive atomic charges of the tellurium atom are much larger than those of the sulfur and the selenium atoms at both the

† 1 cal = 4.184 J.

Table 1 Selected atomic charges of sulfonium, selenonium and telluronium ylides calculated by the HF method at the global minima and the saddle-points for the pyramidal inversion reactions

	Atomic charge			
	Minimum		Saddle-points	
Compound	X$^+$	C$^-$	X$^+$	C$^-$
1a	0.127	−0.791	−0.088	−0.709
1b	0.210	−0.586	0.035	−0.535
1c	1.049	−0.920	0.643	−0.707
2a	0.128	−0.262	−0.091	−0.144
2b	0.396	−0.494	0.267	−0.486
2c	1.268	−0.851	0.967	−0.736
3a	0.372	−0.243	0.131	−0.171
3b	0.568	−0.499	0.473	−0.506
3c	1.634	−0.876	1.236	−0.775

Table 2 Activation energies calculated for pyramidal inversion reactions of sulfonium, selenonium and telluronium ylides

Compound				Energy/kcal mol^{-1}		
	X	R^1	R^2	HF^a	MP2^b	MP3^c
1a	S	H	H	19.9	17.8	17.7
1b	Se	H	H	19.9	19.3	18.8
1c	Te	H	H	17.6	25.9	24.0
2a	S	H	CN	24.5	21.7	21.7
2b	Se	H	CN	27.4	24.9	25.1
2c	Te	H	CN	33.4	34.4	34.8
3a	S	Me	CN	27.3	27.1	—
3b	Se	Me	CN	33.4	33.0	—
3c	Te	Me	CN	38.2	42.1	—

^{a} HF-geometries were used for 2 and 3 and MP2-geometries were used for 1. ^{b} HF-geometries were used for 3 and MP2-geometries were used for 1 and 2. ^{c} MP2-geometries were used.

global minima and the saddle-points. This result is comprehensible based on the electronegativity of sulfur, selenium and tellurium atoms of 2.5, 2.4 and 2.1 (Pauling), respectively. In particular, the atomic charge of the tellurium atom of the ylide **3c** is 1.6 at the global minimum. It was also found that the differences in the atomic charges of the tellurium atoms between the global minima and the saddle-points are larger than those of the sulfur and selenium atoms.

Activation energies for pyramidal inversion reactions

Calculated pyramidal inversion energies for the sulfonium, selenonium and telluronium ylides at several levels of theory are listed in Table 2. By using the HF and the MP methods the gaps of the energies are comparatively small, except for the case of **1c**, and the MP2 energies are in fairly good agreement with the MP3 values. The activation energies of **3a** are calculated to be 27.3 and 27.1 kcal mol^{-1} by using the HF and MP2 methods, respectively, and these values agree comparatively well with the experimental values (ca. 24 kcal mol^{-1}) of several dialkylsulfonium ylides reported by Campbell and Darwish.[8] The MP2 energies of the dimethylsulfonium, dimethylselenonium and dimethyltelluronium dicyanomethylides **3a**, **3b** and **3c** are 27.1, 33.0 and 42.1 kcal mol^{-1}, respectively. This trend in activation energies is also observed for the ylides 1 and 2 at the MP level. The HF energies for 1 showed the opposite tendency, however this result is considered to be caused by using the MP2 geometries; the geometry for **1c** at the saddle-point could not be optimized by using the HF method. The telluronium ylides were calculated to have the highest activation energies for the pyramidal inversion reactions among the sulfonium, selenonium

and telluronium ylides. Furthermore, it was found that introduction of electron-withdrawing groups on the ylide carbons increases their activation energies.

Conclusions

The present computations clearly indicate that the activation energies for the pyramidal inversion of ylides with chalcogen atoms depend on the substituents and that the activation energy of the ylide with a higher principal quantum number is larger than those of the ylide with a lower principal quantum number in group 6 of the periodic table.

Acknowledgements

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