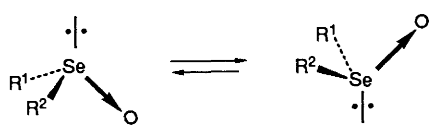
Pyramidal Inversion Energies of Hypervalent Selenoxides. An *Ab Initio* MO Study

Hiroyuki Fueno,[*,a] **Shigeru Ikuta,**[a] **Haruo Matsuyama**[b] **and Nobumasa Kamigata**[b]
[a] *Computer Center, Tokyo Metropolitan University, 1-1 Minami-Ohsawa, Hachioji-shi, Tokyo 192-03, Japan*
[b] *Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, 1-1 Minami-Ohsawa, Hachioji-shi, Tokyo, 192-03, Japan*

Ab initio MO computations on hypervalent selenoxides, R_2SeO (R = H, F and CH_3), have been performed to obtain their accurate pyramidal inversion energies, which are compared with the corresponding sulfoxides. The Se–O bond at the saddle-point in the inversion reactions depends very much on both the basis set and level of theory employed; a method beyond the Hartree–Fock level of theory with an extended basis set is necessary to attain the present purpose. In difluoro selenoxide (F_2SeO) electron correlations greatly decrease the inversion energy, which is smaller than that in the analogous difluoro sulfoxide (F_2SO). The present computations clearly indicate that the pyramidal inversion energies of compounds with a Se atom depend on the substituent R in R_2SeO and that they are not always larger than those with a lower principal quantum number (for example, a S atom) in the same group of the periodic table.

Racemization of selenoxides[1] and sulfoxides[2] occurs through pyramidal inversion. Thus the size of the pyramidal inversion



energies mainly determines their reactivity. The energies usually increase with increasing principal quantum number, if molecules including elements from the same group of the periodic table are compared. This tendency is also believed to be true in the hypervalent species including the main group IVa elements (S and Se).†

Recently one of the present authors observed that the pyramidal inversion energies of the diastereomeric selenoxides may be quite small (*ca.* 20 kcal mol^{-1}),‡ half that of the corresponding sulfoxides.[1]

In the present paper accurate determinations of the pyramidal inversion energies of the model hypervalent compounds R_2SeO (R = H, F and CH_3) will be performed, and the results compared with the corresponding sulfoxides.

The importance of the basis set extension will be noted in the geometry surveys at the saddle-points in the pyramidal inversion reactions of selenoxides. Taking electron correlation (at beyond the Hartree–Fock level of theory) will greatly reduce the inversion energies in difluoro-compounds (F_2SeO and F_2SO). The energy of F_2SeO, being 7–8 kcal mol^{-1} smaller than that of the corresponding sulfoxide (F_2SO), may provide us with very important insights to interpret the experimental activation energy for the pyramidal inversion of diastereomeric selenoxides.

Method

Geometries at global minima and saddle-points in the pyramidal inversion reactions of hypervalent selenoxides (and sulfoxides for comparison) were fully optimized using both Hartree-Fock (HF)[3] and second-order Møller–Plesset perturbation (MP2)[4] methods. Normal vibrational frequencies were calculated to ascertain the geometries and to obtain their zero-point vibrational energies.

Since geometries at the saddle-points of selenoxides depend greatly on the basis sets used, the following two were applied to the geometry surveys: (i) 3-21G(d) for a Se atom and 6-31G(d, p)[5] for other atoms [denoted as the basis set (i), hereafter]; (ii) (20s15p9d/13s10p3d) for a Se atom, (13s8p2d/7s4p2d) for O and F atoms, and (8s2p/5s2p) for H atom[6] [denoted as the basis set (ii) and/or the extended basis set, hereafter].

In sulfoxides the MP2 method with the 6-31G(d, p) basis sets was applied to both the geometry surveys and vibrational analysis.

Final energies at both the global minimum and saddle-point in H_2SeO were obtained by using the following two levels of theory: (*a*) the fourth-order Møller–Plesset perturbation including single, double, triple and quadruple excitations (MP4SDTQ)[7] with the basis set (i), and (*b*) the third-order Møller–Plesset perturbation method (MP3)[8] with the basis set (ii). For F_2SeO the latter level of theory was used. The final energies for the corresponding sulfoxides, H_2SO and F_2SO, were computed by the MP4SDTQ and MP4SDQ methods, respectively, with the 6-311++G(2d, p) basis set.[9] The MP2-optimized geometries were applied to these energy calculations.

The HF method using the basis set (i) was applied to geometry surveys and the MP3 method to final energy computations in $(CH_3)_2XO$ (X = S and Se) owing to the size of the system.

All calculations were performed by using the North-Dakota version of GAMESS[10] and GAUSSIAN90[11] programs at the Computer Center of Tokyo Metropolitan University; the VAX9210VP and IBM RS6000 computers were used.

Results and Discussion

Geometries.—Optimized geometries at global minima and saddle-points in the pyramidal inversion reactions of selenoxides, R_2SeO (R = H and F), are shown in Fig. 1.

H_2SeO *molecule.* The most probable Se–O bond length at the

† For example, optically active sulfur and selenium compounds may be isolated as stable crystals whereas no optically active oxygen compound has been synthesized.
‡ 1 cal = 4.184 J.

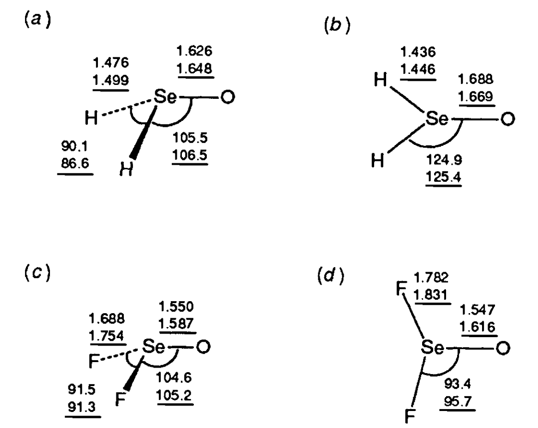


Fig. 1 Geometries at (*a*) the global minimum and (*b*) the saddle-point in the pyramidal inversion reactions of H_2SeO, and at (*c*) the global minimum and (*d*) the saddle-point in the reactions of F_2SeO, optimized by the HF and MP2 methods with the extended basis set [basis set (ii)]. The values underlined are their MP2 parameters. The bond lengths are in angstroms and the bond angles in degrees.

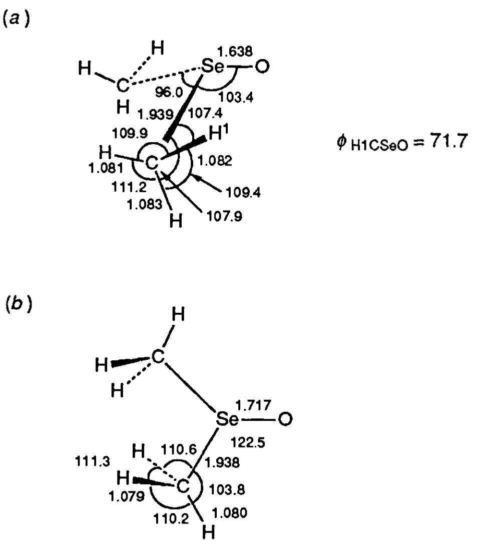


Fig. 2 Geometries at (*a*) the global minimum and (*b*) the saddle-point in the pyramidal inversion reaction of $(CH_3)_2SeO$, optimized by the HF method with the basis set (i). The bond lengths are in angstroms and the bond angles in degrees.

saddle-point of H_2SeO, obtained by the MP2 method with the extended basis set (ii), is 1.67 Å, which is 0.02 Å shorter than that by the corresponding HF level of theory. The bond length of 1.67 Å is shorter by 0.14 and 0.05 Å than those obtained by the HF and MP2 methods, respectively, with the less extended basis set (i). No other geometrical parameters depend on the basis set and level of computation so much.

The Se–O bond length (1.65 Å) and the HSeO angle (106.5°) at the global minimum, calculated by the second-order Møller–Plesset perturbation method (MP2) with the extended basis set (ii), are in good agreement with the experimental values for more complex diaryl selenoxides.[12]

F_2SeO *molecule.* The above discussions also hold good in the F_2SeO system, except that an electron correlation *lengthens* the Hartree–Fock Se–O bond by 0.07 Å at the saddle-point.

$(CH_3)_2SeO$ *molecule.* The geometries at the global minimum and saddle-point in the pyramidal inversion reaction of $(CH_3)_2SeO$ are shown in Fig. 2. These were obtained at the Hartree–Fock level of theory with the basis set (i). Although the geometry optimizations with the extended basis set were not performed owing to the size of the system, these geometries *at the global minimum* are again in good agreement with the

Table 1 Normal vibrational frequencies/cm^{-1} of (*a*) H_2SeO and F_2SeO, and (*b*) H_2SO and F_2SO at their global minima and saddle-points in the pyramidal inversion reactions

(*a*)[a]			
H_2SeO		F_2SeO	
Minimum	Saddle	Minimum	Saddle
a′ 869	b1 1270i	a′ 319	b1 182i
a″ 911	b2 570	a″ 329	a1 314
a′ 965	a1 589	a′ 419	b2 477
a′ 1234	a1 1166	a″ 760	a1 645
a″ 2396	a1 2621	a′ 792	b2 657
a′ 2401	b2 2653	a′ 1154	a1 1187
E_{zp}[b] 12.6	10.9	5.4	4.7
(*b*)[c]			
H_2SO		F_2SO	
Minimum	Saddle	Minimum	Saddle
a″ 1031	b1 1372i	a′ 355	b1 346i
a′ 1115	b2 791	a″ 366	a1 345
a′ 1184	a1 1040	a′ 507	b2 500
a′ 1307	a1 1364	a″ 781	a1 601
a″ 2515	a1 2854	a′ 831	b2 787
a′ 2517	b2 2900	a′ 1370	a1 1156
E_{zp} 13.8	12.8	6.0	4.8

[a] HF method with basis set (i). [b] Zero-point vibrational energies in kcal mol^{-1}. No correction factors were multiplied. [c] MP2 method with the 6-31G(d, p) basis set.

experimental values for large systems like diaryl selenoxide. The Se–O bond-length (1.717 Å) at the saddle-point becomes short, if one applies more accurate levels of theory.

Sulfoxides. The geometries of the corresponding sulfoxides (H_2SO and F_2SO), optimized at both the Hartree–Fock and the MP2 levels of theory with the 6-31G(d, p) basis set are shown in Fig. 3. The MP2 bond lengths are 0.024–0.065 Å longer than the HF ones, except those at the saddle-point of H_2SO, where the MP2 geometry optimization does not change the HF parameters at all.

Vibrational Frequencies and Zero-point Energies.—Normal vibrational frequencies, their symmetry, and zero-point vibrational energies in H_2SeO and F_2SeO at both the global minima and the saddle-points are listed in Table 1(*a*), where the Hartree–Fock level of theory with the basis set (i) was used. No correction factors were multiplied in these values. These data clearly show that each saddle-point has one imaginary frequency, indicating the real saddle-point in the reaction path.

Normal vibrational frequencies and zero-point energies for the corresponding sulfoxides are listed in Table 1(*b*), and were obtained by the MP2 method with the 6-31G(d, p) basis set.

Geometries at both the global minimum and saddle-point in the pyramidal inversion reaction of $(CH_3)_2SO$ are shown in Fig. 4, where the Hartree–Fock method with the 6-31G(d) basis set was used. The vibrational frequencies and zero-point energies are included in the figure caption.

Pyramidal Inversion Energies.—Computed pyramidal inversion energies are listed in Tables 2 and 3.

H_2SeO *molecule.* Pyramidal inversion energies of H_2SeO calculated at various levels of theory with several basis sets are listed in Table 2. The MP3 energy using the extended basis set (ii) is 47 kcal mol^{-1}, which is in fairly good agreement with the MP3 (48 kcal mol^{-1}) and MP4SDTQ values (49 kcal mol^{-1}) with the lower quality basis set (i). An f-function added on the Se atom does not change the energy at all. Thus the probable

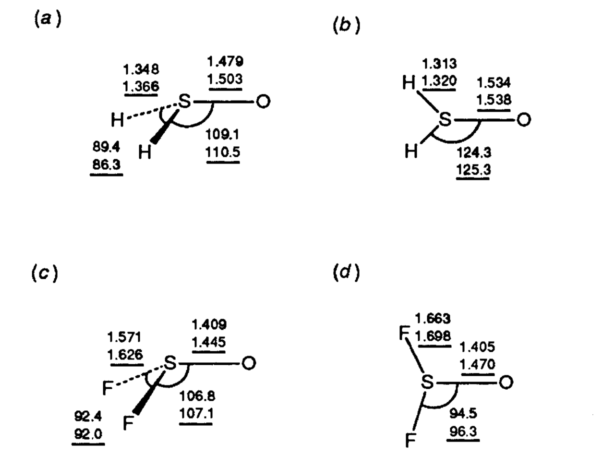


Fig. 3 Geometries at (*a*) the global minimum and (*b*) the saddle-point in the pyramidal inversion reactions of H_2SO, and at (*c*) the global minimum and (*d*) the saddle-point in the reactions of F_2SO, optimized by both the HF and MP2 methods using the 6-31G(d, p) basis set. The values underlined are their MP2 parameters. The bond lengths are in angstroms and the bond angles in degrees.

Table 2 Pyramidal inversion energies (in kcal mol^{-1}) of H_2SeO calculated at various levels of theory[a]

	Basis set				
Method	I[b]	II[c]	III[d]	IV[e]	V[f]
HF	49	49	48	48	
MP2	50	50	49		49
MP3	48	48	47		47
MP4SDQ	49	49			
MP4SDTQ	49	49			

[a] Thermal energy corrections (1.0–1.5 kcal mol^{-1}) should be subtracted from these values. [b] 3-21G(d) for a Se atom and 6-31G(d, p) basis sets for O and H atoms [basis set (i)] at their HF geometries. [c] An f-function is added on the Se atom. Other basis sets and geometries are the same as I. [d] The extended basis set (see the text) was used at the HF geometries optimized with the basis set (i). [e] The extended basis set was used at their HF geometries. [f] The extended basis set was used at their MP2 geometries.

energy, including the thermal energy correction (1–1.5 kcal mol^{-1}), is predicted to be 46–47 kcal mol^{-1}. The electron correlation does not affect the energy at all, contrary to the results on F_2SeO, where an electron correlation decreases the energy greatly.

The inversion energy of H_2SeO (46–47 kcal mol^{-1}) is 7–8 kcal mol^{-1} *larger* than that of the corresponding sulfoxide (H_2SO) listed in Table 3; the energy calculated by the MP4SDTQ method with the 6-311 + G(2d, p) basis set at the MP2/6-31G(d, p) geometries (shown in Fig. 3) is 40 kcal mol^{-1} after the thermal energy correction of *ca.* 1 kcal mol^{-1}.

F_2SeO *molecule.* Pyramidal inversion energies are 29 and 37 kcal mol^{-1} computed by using the MP2 and MP3 levels of theory, respectively, with the extended basis set (ii) (after the thermal energy correction of 0.7 kcal mol^{-1}) at their MP2 geometries. Surprisingly electron correlation drastically reduces the HF energy, by 18 and 11 kcal mol^{-1} at the MP2 and MP3 levels, respectively. Most probable energy of F_2SeO may be *ca.* 34 kcal mol^{-1}, by reference to the data on sulfoxides listed in Table 3, where the MP4SDQ level of computation reduces the MP3 energy by 3 kcal mol^{-1}.

The inversion energies of the corresponding F_2SO, computed by using the HF, MP2, MP3 and MP4SDQ methods with the 6-311 + G(2d) basis set at the MP2/6-31G(d) geometries, are 59, 39, 45 and 42 kcal mol^{-1}, respectively, after the thermal energy correction (1 kcal mol^{-1}).

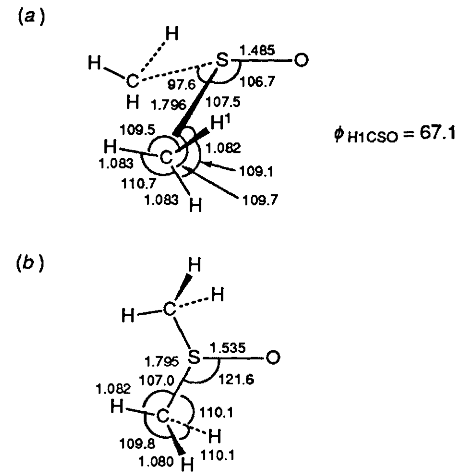


Fig. 4 Geometries at (*a*) the global minimum and (*b*) the saddle-point in the pyramidal inversion reaction of $(CH_3)_2SO$, optimized by the HF method with the 6-31G(d) basis sets. The bond lengths are in angstroms and the bond angles in degrees. Vibrational frequencies/cm^{-1} and zero-point energies/kcal mol^{-1} are as follows: (*a*) 207, 254, 312, 340, 399, 751, 794, 1002, 1053, 1073, 1149, 1175, 1498, 1520, 1589, 1602, 1606, 1623, 3222, 3226, 3315, 3320, 3326, 3326, E_{zp} = 53.9; (*b*) 634*i*, 112, 137, 274, 282, 661, 821, 959, 998, 1089, 1173, 1178, 1502, 1533, 1585, 1586, 1644, 1655, 3238, 3243, 3334, 3337, 3338, 3340, E_{zp} = 52.9.

Table 3 Pyramidal inversion energies (in kcal mol^{-1}) calculated after thermal energy corrections[a] for H_2SO, F_2SeO, F_2SO, $(CH_3)_2SeO$ and $(CH_3)_2SO$

Compound	Basis set	Method	Energy/kcal mol^{-1}
H_2SO	6-311 + G(2d, p)	HF	43
		MP2	40
		MP3	39
		MP4SDQ	40
		MP4SDTQ	40
F_2SeO	(ii)[b]	HF	48
		MP2	29
		MP3	37
F_2SO	6-311 + G(2d)	HF	59
		MP2	39
		MP3	45
		MP4SDQ	42
$(CH_3)_2SeO$	(i)[c]	HF	55
		MP2	52
		MP3	50
$(CH_3)_2SO$	6-31 + G(2d)	HF	52
		MP2	48
		MP3	48

[a] Thermal energy corrections of 0.7–1.0 kcal mol^{-1} were assumed. [b] Extended basis set. See the text. [c] 3-21G(d) for a Se atom and 6-31G(d, p) for other atoms.

The probable energy of 34 kcal mol^{-1} in F_2SeO is 7–8 kcal mol^{-1} *smaller* than that of the corresponding sulfoxide (F_2SO). Although this fact seems somewhat anomalous in a common chemical sense, it may provide us with a very important hint to interpret the Gibbs free energies for the pyramidal inversion of diaryl selenoxides.

$(CH_3)_2SeO$ *molecule.* The pyramidal inversion energy, calculated by the MP3 method with the basis set (i) at their HF geometries, is *ca.* 50 kcal mol^{-1} after the thermal energy correction of 1 kcal mol^{-1}.

This energy of 50 kcal mol^{-1} is very similar to that (*ca.* 48 kcal mol^{-1}) in the corresponding sulfoxide, $(CH_3)_2SO$, calculated by the MP3 method with the 6-31 + G(2d) basis set at their HF/6-31G(d) geometries.

Conclusions

The *present* computations clearly indicate that the pyramidal inversion energies (34–50 kcal mol^{-1}) of compounds with a Se atom depend on the substituent R in R_2SeO, and that they are not always larger than those with a lower principal quantum number (for example a S atom) in the same main group of the periodic table.

References

1 N, Kamigata and T. Shimizu, *Yuki Gosei Kagaku Kyokaishi*, 1990, **48**, 229; N. Kamigata and T. Shimizu, *Reviews on Heteroatom Chemistry*, 1991, **4**, 226.

2 D. R. Rayner, A. J. Gordon and K. Mislow, *J. Am. Chem. Soc.*, 1968, **90**, 4854.

3 C. C. J. Roothaan, *Rev. Mod. Phys.*, 1951, **23**, 69.

4 C. Møller and M. S. Plesset, *Physical Review*, 1934, **46**, 618.

5 W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257; M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, *J. Chem. Phys.*, 1982, **77**, 3654; K. D. Dobbs and W. J. Hehre, *J. Comput. Chem.*, 1986, **7**, 359.

6 R. Poirier, R. Kari and I. G. Csizmadia, *Handbook of Gaussian basis sets*, Elsevier, Amsterdam, 1985.

7 R. Krishnan and J. A. Pople, *Int. J. Quantum Chem.*, 1978, **14**, 91; R. Krishnan, M. J. Frisch and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 4244.

8 J. A. Pople, R. Seeger and R. Krishnan, *Int. J. Quantum Chem. Symp.*, 1977, **11**, 149.

9 R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650; A. D. McLean and G. S. Chandler, *J. Chem. Phys.*, 1980, **72**, 5639; T. Clark, J. Chandrasekhar, G. W. Spitznagel and P. v. R. Schleyer, *J. Comput. Chem.*, 1983, **4**, 294; M. J. Frisch, J. A. Pople and J. S. Binkley, *J. Chem. Phys.*, 1984, **80**, 3265.

10 M. W. Schmidt, K. K. Baldridge, J. A. Boatz, J. H. Jensen, S. Koseki, M. S. Gordon, K. A. Nguyen, T. L. Windus and S. T. Elbert, *QCPE Bulletin*, 1990, **10**, 52.

11 M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. A. Robb, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1990.

12 T. Shimizu, K. Kikuchi, Y. Ishikawa, I. Ikemoto, M. Kobayashi and N. Kamigata, *J. Chem. Soc.*, *Perkin Trans. 1*, 1989, 597.

Paper 2/03016K
Received 8*th June* 1992
Accepted 29*th June* 1992