Reactivities of 2,6-dimethoxyphenyl methyl sulfide, selenide and telluride with their onium salts

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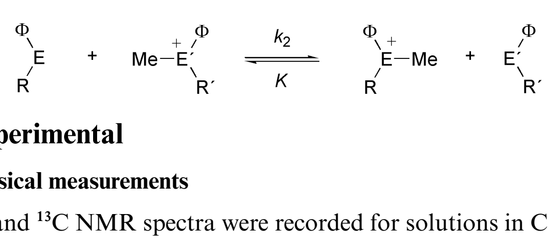
2,6-Dimethoxyphenyl derivatives of sulfur, selenium and tellurium, such as MeΦE, EtΦE, $[Me_2ΦE]X$, [MeEtΦE]X {Φ = $2,6\text{-}(MeO)_2C_6H_3$; E = S, Se, Te; X = $MeSO_4$, ClO_4, or PF_6} have been prepared, mostly as crystals. The reaction rates and the equilibrium constants for methyl abstraction by MeΦE from [MeRΦE′]ClO_4 {R = Me, Et, Φ; E, E′ = S, Se, Te} were measured by means of ^{1}H NMR spectra. Some representative results include: (1) RΦE (R = Me, Φ; E = S, Se) react commonly with $[MeRΦE]^+$ (R = Me, Et, Φ; E = S, Se) to give the equilibrium mixture, except that MeΦS does not react with $[MeEtΦS]^+$; (2) RΦE (R = Me, Φ; E = S, Se) do not react with $[MeRΦTe]^+$ (R = Me, Et, Φ); (3) RΦTe (R = Me, Φ) react with $[MeRΦE]^+$ (R = Me, Et, Φ; E = S, Se, Te) to complete the methyl abstraction (E = S, Se) or to give the equilibrium mixture (E = Te); (4) the reaction rate of MeΦE with $[MeRΦE']^+$ (R = Me, Et, Φ) increases in the orders E = S < Se < Te and E′ = S ~ Te < Se; (5) reactions of $[Me_2ΦE]^+$ are faster than those of $[MeEtΦE]^+$, which react faster than $[MeΦ_2E]^+$; (6) Me–E bond strength of $[MeΦ_2E]^+$ increases in the order E = S ≤ Se < Te, but those of $[Me_2ΦE]^+$ and $[MeEtΦE]^+$ increase in the order E = Se ≤ S < Te; (7) Me–E bond strength of $[MeRΦE]^+$ (E = S, Se) increases in the order R = Φ < Me < Et or Me < Φ < Et, while Me–Te bond strength of $[MeRΦTe]^+$ increases in the order R = Φ < Et < Me.

Introduction

It is one of the basic chemical interests to compare the chemical and physical properties of compounds among elements as well as among the substituents. 2,6-Dimethoxyphenyl derivatives of chalcogenides in general have prominent properties such as odorless character, higher crystallinity, and higher nucleophilicity than common phenyl derivatives. As part of our systematic investigation on the chemistry of 2,6-dimethoxyphenyl derivatives of main group elements, we have recently reported the reactivity of bis(2,6-dimethoxyphenyl) chalcogenides, $Φ_2E$ {Φ = $2,6\text{-}(MeO)_2C_6H_3$; E = S, Se, Te}.[1] The reaction rates of $Φ_2E$ with dimethyl sulfate and butyl bromide increased in the order E = S < Se < Te, while the E^+–Me bond strengths of $[Φ_2E–Me]^+$ salts were estimated to increase in the order E = Se < S < Te. With the hope of obtaining more distinctive results, we further studied the reactions of 2,6-dimethoxyphenyl sulfide, selenide, and telluride, RΦE, with their onium salts, [MeR′ΦE′]ClO_4 (R = Me, Φ; R′ = Me, Et, Φ; E, E′ = S, Se, Te), [eqn. (1)] by means of ^{1}H NMR experiments.



(1)

Experimental

Physical measurements

^{1}H and ^{13}C NMR spectra were recorded for solutions in $CDCl_3$ using a JEOL model JNM-GX-270 spectrometer. IR spectra were recorded for Nujol® mull using a Shimadzu FTIR-4200 spectrophotometer. GC–MS spectra were recorded for acetone or toluene solutions using a Shimadzu QP-5000 mass spectrometer (gasified at 250 °C). UV–vis spectra were recorded using a Shimadzu UV-160 spectrophotometer. The ^{1}H and ^{13}C NMR spectral data are summarized in Tables 1 and 2, respectively.

2,6-Dimethoxyphenyl derivatives ΦSH, ΦSeH, ΦEEΦ, $Φ_2E$, $[MeΦ_2E]ClO_4$ (E = S, Se, Te) were prepared as described elsewhere.[1,2]

Preparations of alkyl 2,6-dimethoxyphenyl sulfides, RΦS (R = Me, Et)

MeΦS. To a solution of ΦSH (50 mmol) in methanol (250 cm^3) were added iodomethane (3.4 cm^3, 52 mmol) and triethylamine (7.3 cm^3, 52 mmol). The mixture was stirred at room temperature for 1 h. Water was added at 0 °C, and the resultant precipitates were recrystallized from hexane to give crystals of MeΦS in 66–84% yield; mp 77–78 °C (81–82 °C);[3] MS: *m*/*z* (%) 184 (M^+; 100) (Found: C, 58.46; H, 6.54%. $C_9H_{12}O_2S_1$ requires C, 58.67; H, 6.56%).

EtΦS. To a solution of ΦSH (5 mmol) in ethanol (40 cm^3) was added bromoethane (0.4 cm^3, 5.4 mmol) and 1 M (1 M = 1 mol dm^{-3}) sodium hydroxide (6 cm^3). The mixture was stirred at room temperature for 2 h, and it was treated with hexane (100 cm^3) and water (100 cm^3). The hexane layer was separated and was concentrated under reduced pressure to afford crystals of EtΦS in 45% yield; mp 39–40 °C (45–46 °C)[3]; MS: *m*/*z* (%) 198 (M^+; 100). This product was characterized by ^{1}H and ^{13}C NMR spectra.

Preparations of alkyl 2,6-dimethoxyphenyl selenides, RΦSe (R = Me, Et)

MeΦSe. To a mixture of ΦSeSeΦ (4.32 g, 10 mmol) and sodium borohydride (0.95 g, 25 mmol) was added ethanol (100 cm^3) with stirring, followed by addition of iodomethane

Table 1 ^{1}H NMR spectral data for 2,6-dimethoxyphenyl derivatives of sulfur, selenium and tellurium[a]

Compounds	δ(4-H)[b]	δ(3,5-H)[c]	δ(2,6-MeO)[d]	δ(Others)[e]
MeΦS	7.23	6.58	3.90	2.37s
MeΦSe	7.23	6.56	3.88	2.27s[13(Se)]
MeΦTe	7.23	6.50	3.85	2.14s[26(Te)]
EtΦS	7.24	6.57	3.88	2.85q[7], 1.17t[7]
EtΦSe	7.23	6.56	3.87	2.92q[7], 1.32t[7]
EtΦTe	7.23	6.51	3.85	2.96q[8], 1.56t[8]
[Me$_2$ΦS]ClO$_4$	7.63	6.73	4.02	3.37s
[Me$_2$ΦSe]ClO$_4$	7.56	6.71	3.98	3.23s[11(Se)]
[Me$_2$ΦTe]ClO$_4$	7.51	6.66	3.93	2.77s[27(Te)]
[MeEtΦS]ClO$_4$	7.66	6.75	4.02	3.90dq[7][15], 3.88dq[7][15], 3.33s, 1.34t[7]
[MeEtΦSe]ClO$_4$	7.59	6.73	3.98	3.90m, 3.19s[11(Se)], 1.42t[8]
[MeEtΦTe]ClO$_4$	7.54	6.68	3.93	3.50m, 2.57s[27(Te)], 1.51t[8]
[Et$_2$ΦS]ClO$_4$	7.67	6.77	4.01	3.95dq[7][12], 3.84dq[7][12], 1.34t[7]
[Et$_2$ΦSe]ClO$_4$	7.62	6.76	3.98	3.89m, 1.44t[7]
[Et$_2$ΦTe]ClO$_4$	7.57	6.71	3.94	3.53m, 1.54t[8]

[a] In chloroform-d_1; $\Phi = 2,6\text{-}(\mathrm{MeO})_2\mathrm{C}_6\mathrm{H}_3$; s = singlet, t = triplet, q = quartet, dq = double quartet, m = multiplet; spectral data for Φ_2E and [MeΦ_2E]ClO$_4$ (E = S, Se, Te) have been reported elsewhere.[1] [b] Triplet with $J_{\mathrm{H-H}} = 8–9$ Hz. [c] Doublet with $J_{\mathrm{H-H}} = 8–9$ Hz. [d] Singlet. [e] The coupling constants $J_{\mathrm{H-H}}$, $J_{\mathrm{Se-H}}$ or $J_{\mathrm{Te-H}}$ (in Hz) are given in square brackets.

Table 2 ^{13}C NMR spectral data for 2,6-dimethoxyphenyl derivatives of sulfur, selenium and tellurium[a]

Compounds	δ[b]				
MeΦS	112.3,	160.7,	104.2,	129.2,	56.2; 17.8
MeΦSe	107.6,	160.5,	104.1,	129.3,	56.2; 7.6
MeΦTe	91.8,	161.7,	103.7,	129.8,	56.1; −17.6
EtΦS	110.4,	161.2,	104.2,	129.4,	56.2; 28.1, 14.7
EtΦSe	106.4,	160.7,	104.1,	129.4,	56.2; 20.5[59(Se)], 15.5
EtΦTe	92.0,	161.7,	103.7,	129.9,	56.1; 17.4, −0.9
[Me$_2$ΦS]ClO$_4$	—,[c]	161.5,	105.4,	137.9,	57.0; 45.2
[Me$_2$ΦSe]ClO$_4$	99.6,	160.9,	105.5,	136.4,	56.9; 22.6[53(Se)]
[Me$_2$ΦTe]ClO$_4$	94.2,	162.3,	105.0,	135.9,	56.7; 6.2
[MeEtΦS]ClO$_4$	94.8,	162.0,	105.4,	138.2,	57.1; 37.7, 24.8, 10.1
[MeEtΦSe]ClO$_4$	97.2,	161.3,	105.5,	136.7,	56.9; 36.4[51(Se)], 20.8, 10.9
[MeEtΦTe]ClO$_4$	99.5,	162.5,	105.1,	136.1,	56.7; 21.3, 11.3, 4.6
[Et$_2$ΦS]ClO$_4$	92.4,	162.5,	105.4,	138.3,	57.1; 36.3, 10.2
[Et$_2$ΦSe]ClO$_4$	95.3,	161.6,	105.5,	136.9,	57.0; 35.1[53(Se)], 11.1
[Et$_2$ΦTe]ClO$_4$	92.3,	162.8,	105.1,	136.3,	56.7; 20.6[147(Te)], 11.5

[a] In chloroform-d_1; $\Phi = 2,6\text{-}(\mathrm{MeO})_2\mathrm{C}_6\mathrm{H}_3$; spectral data for Φ_2E and [MeΦ_2E]ClO$_4$ (E = S, Se, Te) have been reported elsewhere.[1] [b] In the order of C(1), C(2,6), C(3,5), 2,6-MeO; and others, of which the coupling constants $J_{\mathrm{H-H}}$, $J_{\mathrm{Se-H}}$ or $J_{\mathrm{Te-H}}$ (in Hz) are given in square brackets when observed. [c] The C(1) resonance could not be observed.

(1.56 cm^3, 25 mmol) to give a clear solution. After stirring for 2 h, water was added at 0 °C, and the resultant precipitates were recrystallized from aqueous methanol to give white crystals of MeΦSe in 74% yield; mp 69–70 °C; MS: *m*/*z* (%) 232 (M$^+$; 100) (Found: C, 46.84; H, 5.31%. $\mathrm{C_9H_{12}O_2Se_1}$ requires C, 46.76; H, 5.23%).

EtΦSe. Using iodoethane, EtΦSe was prepared in 74% yield as a brown liquid. It was characterized by ^{1}H and ^{13}C NMR spectra.

Preparations of alkyl 2,6-dimethoxyphenyl tellurides, RΦTe (R = Me, Et)

MeΦTe. To a mixture of ΦTeTeΦ (1.06 g, 2 mmol) and sodium borohydride (0.22 g, 5.8 mmol) was added ethanol (20 cm^3) with stirring, followed by addition of iodomethane (0.3 cm^3, 4.6 mmol). After stirring for 3 h, water was added at 0 °C, and the resultant precipitates were recrystallized from hexane to give light yellow crystals of MeΦTe in 58% yield; mp 41–42 °C; MS: *m*/*z* (%) 280 (M$^+$; 77), 137 (Φ$^+$, 100) (Found: C, 38.25; H, 4.35%. $\mathrm{C_9H_{12}O_2Te_1}$ requires C, 38.64; H, 4.32%). MeΦTe is soluble in alcohols, acetone, benzene and hexane.

EtΦTe. Using iodoethane, EtΦTe was prepared in 46% yield as a brown liquid. It was characterized by ^{1}H and ^{13}C NMR spectra.

Preparations of dialkyl(2,6-dimethoxyphenyl)sulfonium salts, [MeRΦS]X (R = Me, Et) and [Et$_2$ΦS]X (X = ClO$_4$, PF$_6$)

[Me$_2$ΦS]X. A mixture of MeΦS (1.84 g, 10 mmol) and dimethyl sulfate (1.2 cm^3, 12 mmol) was stirred at room temperature for 15 h to give an oily mixture. It was washed with diethyl ether, repeatedly, and the residual solid was dissolved in water (70 cm^3). Aqueous 1 M perchloric acid (15 cm^3) was added, and the resultant precipitates were recrystallized from ethanol to afford colorless crystals of [Me$_2$ΦS]ClO$_4$ in 63% yield; mp 164–165 °C; IR 1100 and 625 cm^{-1} (ClO$_4$) (Found: C, 40.06; H, 5.03%. $\mathrm{C_{10}H_{15}Cl_1O_6S_1}$ requires C, 40.21; H, 5.06%).

When aqueous ammonium hexafluorophosphate was used in place of perchloric acid, colorless crystals of [Me$_2$ΦS]PF$_6$ were obtained in 56% yield; mp 187–189 °C (after recrystallization from ethanol); IR 840 cm^{-1} (PF$_6$).

[MeEtΦS]X. A mixture of EtΦS (1.58 g, 8 mmol) and dimethyl sulfate (0.8 cm^3, 8 mmol) was heated at 50 °C for 3 h. On working up as above, colorless crystals of [MeEtΦS]ClO$_4$ were obtained in 64% yield; mp 146–147 °C; IR 1100 and 625 cm^{-1} (ClO$_4$) (Found: C, 42.06; H, 5.43%. $\mathrm{C_{11}H_{17}Cl_1O_6S_1}$ requires C, 42.24; H, 5.48%). This salt could be obtained in 58% yield by an analogous treatment of MeΦS and diethyl sulfate. When aqueous ammonium hexafluorophosphate was used in place of perchloric acid, colorless crystals of [MeEtΦS]PF$_6$ were obtained in 70% yield; mp 159.5–160.5 °C (after recrystallization from ethanol); IR 840 cm^{-1} (PF$_6$).

$[Et_2\Phi S]X$. A treatment of EtΦS and diethyl sulfate at 50 °C for 24 h afforded colorless crystals of $[Et_2\Phi S]ClO_4$ in 40% yield; mp 94–95 °C; IR 1100 and 625 cm^{-1} (ClO_4) (Found: C, 43.87; H, 5.90%. $C_{12}H_{19}Cl_1O_6S_1$requires C, 44.10; H, 5.86%).

Preparations of dialkyl(2,6-dimethoxyphenyl)selenonium salts, $[MeR\Phi Se]X$ (R = Me, Et) and $[Et_2\Phi Se]X$ (X = ClO_4, PF_6)

$[Me_2\Phi Se]X$. A mixture of MeΦSe (0.51 g, 2 mmol) and dimethyl sulfate (0.2 cm^3) was stirred at room temperature for 2–6 h to give a yellow oil. It was washed with diethyl ether (1 cm^3 × 3), and the residue was dissolved in water (2 cm^3). Aqueous solution of ammonium hexafluorophosphate (0.33 g, 2 mmol in 6 cm^3) was added, and the resultant precipitates were recrystallized from ethanol to give colorless crystals of $[Me_2\Phi Se]PF_6$ in 87% yield; mp 166–168 °C; IR 840 cm^{-1} (PF_6) (Found: C, 30.80; H, 3.80%. $C_{10}H_{15}F_6O_2P_1Se_1$ requires C, 30.71; H, 3.87%).

When aqueous perchloric acid was added in place of ammonium hexafluorophosphate, precipitates of $[Me_2\Phi Se]ClO_4$ were obtained in 34% yield; mp 126–128 °C (after recrystallization from ethanol); IR 1100 and 625 cm^{-1} (ClO_4) (Found: C, 34.87; H, 4.48%. $C_{10}H_{15}Cl_1O_6Se_1$ requires C, 34.75; H, 4.37%).

$[MeEt\Phi Se]X$. A mixture of EtΦSe (0.35 g, 1.43 mmol) and dimethyl sulfate (0.2 cm^3) was stirred for 7 h. It was washed with diethyl ether (1 cm^3 × 3), and the residue was dissolved in water (1 cm^3). Aqueous solution of ammonium hexafluorophosphate (1.5 mmol in 4.5 cm^3) was added, and the resultant precipitates were recrystallized from ethanol to give colorless crystals of $[MeEt\Phi Se]PF_6$ in 58% yield; mp 141–142 °C; IR 840 cm^{-1} (PF_6) (Found: C, 32.80; H, 4.33%. $C_{11}H_{17}F_6O_2P_1Se_1$ requires C, 32.61; H, 4.23%).

An analogous treatment of MeΦSe with diethyl sulfate resulted in a mixture of $[Me_2\Phi Se]PF_6$, $[MeEt\Phi Se]PF_6$ and $[Et_2\Phi Se]PF_6$.

$[Et_2\Phi Se]X$. A mixture of EtΦSe and diethyl sulfate was heated at 50 °C for 20 h. It was washed well with diethyl ether, and the residue was dissolved in water (1 cm^3). Aqueous solution of ammonium hexafluorophosphate (4 mmol in 5 cm^3) was added, and the resultant precipitates were recrystallized from ethanol to give $[Et_2\Phi Se]PF_6$ in 55% yield; mp 114 °C; IR 840 cm^{-1} (PF_6) (Found: C, 34.49; H, 4.53%. $C_{12}H_{19}F_6O_2P_1Se_1$ requires C, 34.38; H, 4.57%).

Preparations of dialkyl(2,6-dimethoxyphenyl)telluronium salts, $[MeR\Phi Te]X$ (R = Me, Et) and $[Et_2\Phi Te]X$ (X = $MeSO_4$, ClO_4)

$[Me_2\Phi Te]X$. An analogous mixture of MeΦTe and dimethyl sulfate was treated as above. The mixture was washed with diethyl ether repeatedly to give gray crystals of $[Me_2\Phi Te]MeSO_4$ in 87% yield; mp 40–41 °C; IR 1255 cm^{-1} ($MeSO_4$).

Its aqueous solution was treated with aqueous perchloric acid, and the resultant precipitates were recrystallized from propan-2-ol to give colorless crystals of $[Me_2\Phi Te]ClO_4$ in 39% yield; mp 140 °C; IR 1100 cm^{-1} (ClO_4) (Found: C, 30.31; H, 3.88%. $C_{10}H_{15}Cl_1O_6Te_1$ requires C, 30.46; H, 3.83%).

$[MeEt\Phi Te]X$. In a manner analogous to that described above, a mixture of EtΦTe and dimethyl sulfate was treated with aqueous perchloric acid to give colorless crystals of $[MeEt\Phi Te]ClO_4$ in 40% yield after recrystallization from ethanol; mp 82–83 °C; IR 1100 and 625 cm^{-1} (ClO_4) (Found: C, 32.20; H, 4.24%. $C_{11}H_{17}Cl_1O_6Te_1$ requires C, 32.36; H, 4.20%).

An analogous mixture of MeΦTe and diethyl sulfate was treated with aqueous perchloric acid to give a mixture of $[Me_2\Phi Te]ClO_4$, $[MeEt\Phi Te]ClO_4$, and $[Et_2\Phi Te]ClO_4$.

$[Et_2\Phi Te]X$. An analogous mixture of EtΦTe and diethyl sulfate was treated with aqueous perchloric acid to give $[Et_2\Phi Te]ClO_4$ in 47% yield after recrystallization from ethanol; mp 102–103 °C; IR 1100 and 625 cm^{-1} (ClO_4) (Found: C, 33.86; H, 4.49%. $C_{12}H_{19}Cl_1O_6Te_1$ requires C, 34.13; H, 4.54%).

Rate and equilibrium measurements

The reaction rates for eqn. (1) were measured by ^{1}H NMR spectroscopy by the method of initial rates and by conventional second-order kinetics for the solutions containing MeΦE and $[MeR\Phi E']ClO_4$ at 50 °C, where the concentrations of both reactants were identical (0.04 mmol each) in 0.5 cm^3 of acetone-d_6. The equilibrium constants were measured at the end of reactions. The results are summarized in Table 3.

Results and discussion

Preparation and properties of 2,6-dimethoxyphenyl chalcogenides and their onium salts

Some alkyl 2,6-dimethoxyphenyl sulfides, RΦS (R = Me, Et), have been prepared as crystalline compounds by the reactions of 2,6-dimethoxybenzenethiol, ΦSH, and iodoalkanes in the presence of base or by the reaction of ΦLi with dialkyl disulfide.[3] In the present work, 2,6-dimethoxyphenyl methyl selenide and telluride, MeΦE (E = Se, Te), were prepared also as crystalline compounds, while the ethyl selenide and telluride, EtΦE (E = Se, Te), were obtained as viscous oils at room temperature. Because of this property, these compounds were characterized only by ^{1}H and ^{13}C NMR spectra. They could be used successfully for the preparation of the following onium compounds but not for precise measurements such as those given in Table 3.

The sulfonium, selenonium and telluronium salts, $[MeR\Phi E]X$ (R = Me, Et; E = S, Se, Te; X = $MeSO_4$, ClO_4, PF_6), could be prepared best by the reactions of RΦE with dimethyl sulfate or by the reaction of MeΦS with diethyl sulfate, followed by anion exchange in water. However, the reaction of MeΦSe with diethyl sulfate resulted in a mixture containing both $[Me_2\Phi Se]X$ and $[Et_2\Phi Se]X$ [eqns. (2) and (3)], implying

$$R\Phi E + (MeO)_2SO_2 \longrightarrow [MeR\Phi E](MeSO_4)\ (E = S, Se, Te;\ R = Me, Et) \quad (2)$$

$$Me\Phi E + (EtO)_2SO_2 \longrightarrow [MeEt\Phi E](EtSO_4) + [Me_2\Phi E](EtSO_4) + [Et_2\Phi E](EtSO_4)\ (E = Se, Te) \quad (3)$$

that the initially formed onium ion, $[MeEt\Phi Se]^+$, methylated MeΦSe to give EtΦSe and $[Me_2\Phi Se]^+$ very fast and that EtΦSe reacted also with diethyl sulfate to give $[Et_2\Phi Se]^+$. An analogous formation of mixture was observed for the reaction of MeΦTe with diethyl sulfate to give a mixture containing $[Me_2\Phi Te]ClO_4$, $[MeEt\Phi Te]ClO_4$, and $[Et_2\Phi Te]ClO_4$.

The ^{1}H NMR spectra of 2,6-dimethoxyphenyl derivatives (Table 1) showed a triplet due to 4-proton, a doublet due to 3,5-protons and a very sharp singlet due to 2,6-methoxy protons. The methylene proton resonances of ethyl group in $[MeEt\Phi E]X$ were observed as multiplets or double AB quartets due to the pyramidal arrangement of three organic groups on element E. In spite of the well-known electronegativity order of chalcogenides $S \leq Se > Te$, most of the ^{1}H NMR chemical shifts were observed in the normal orders of these elements, $S < Se < Te$ or $S > Se > Te$. The chemical shifts of sulfonium and selenonium protons were quite similar in value, but those of CH_3- and CH_2-Te protons in $[MeR\Phi Te]X$ were observed at much higher magnetic fields.

The ^{13}C NMR spectra of 2,6-dimethoxyphenyl derivatives (Table 2) showed five resonances due to the Φ-group. The *ipso*-carbon, C(1), resonance of the Φ-group was often too weak to be observed or it was observed in the region of δ 91~112. It shifted to higher magnetic field in the order $E = S < Se < Te$

Table 3 Rate constants and equilibrium constants for the reactions,[a] RΦE [A] + $[MeR'\Phi E']ClO_4$ [B] $\rightleftarrows$ $[MeR\Phi E]ClO_4$ [C] + R′ΦE′ [D] (1)

Entry	RΦE	$[MeR'\Phi E']ClO_4$	k_2/l mol^{-1} s^{-1}	A : C or B : D[b]	Eq. time/h[c]	*K*
1	MeΦS	$[Me\Phi_2S]ClO_4$	4.7×10^{-5}	11 : 89	384	*ca.* 100
2	MeΦS	$[Me\Phi_2Se]ClO_4$	4.2×10^{-4}	32 : 68	138	4.5
3	MeΦS	$[Me\Phi_2Te]ClO_4$	0.0	100 : 0	980	0.0
4	MeΦS	$[Me_2\Phi Se]ClO_4$	5.0×10^{-5}	34 : 66	288	4.3
5	MeΦS	$[Me_2\Phi Te]ClO_4$	0.0	100 : 0	360	0.0
6	MeΦS	$[MeEt\Phi S]ClO_4$	0.0	100 : 0	336	0.0
7	MeΦS	$[MeEt\Phi Se]ClO_4$	2.4×10^{-5}	(47 : 53)[d]	336	(1.3)[d]
8	MeΦS	$[MeEt\Phi Te]ClO_4$	0.0	100 : 0	336	0.0
9	Φ_2S	$[Me_2\Phi S]ClO_4$	—[e]	93 : 7	117	*ca.* 0.01
10	Φ_2S	$[Me_2\Phi Se]ClO_4$	—[e]	89 : 11	180	*ca.* 0.01
11	Φ_2S	$[Me_2\Phi Te]ClO_4$	0.0	100 : 0	500	0.0
12	MeΦSe	$[Me\Phi_2S]ClO_4$	2.1×10^{-4}	7 : 93	257	*ca.* 100
13	MeΦSe	$[Me\Phi_2Se]ClO_4$	3.1×10^{-3}	12 : 88	17	54
14	MeΦSe	$[Me\Phi_2Te]ClO_4$	0.0	100 : 0	258	0.0
15	MeΦSe	$[Me_2\Phi S]ClO_4$	8.9×10^{-6}	69 : 31	360	0.23
16	MeΦSe	$[Me_2\Phi Te]ClO_4$	0.0	100 : 0	360	0.0
17	MeΦSe	$[MeEt\Phi S]ClO_4$	6.9×10^{-6}	80 : 20	336	0.06
18	MeΦSe	$[MeEt\Phi Se]ClO_4$	1.6×10^{-4}	67 : 33	64	0.24
19	MeΦSe	$[MeEt\Phi Te]ClO_4$	0.0	100 : 0	336	0.0
20	Φ_2Se	$[Me_2\Phi S]ClO_4$	—[e]	(89 : 11)[f]	117	(0.015)[f]
21	Φ_2Se	$[Me_2\Phi Se]ClO_4$	—[e]	(91 : 9)[f]	20	(0.01)[f]
22	Φ_2Se	$[Me_2\Phi Te]ClO_4$	0.0	100 : 0	87	0.0
23	MeΦTe	$[Me\Phi_2S]ClO_4$	2.0×10^{-3}	0 : 100	8	$> 10^4$
24	MeΦTe	$[Me\Phi_2Se]ClO_4$	$\sim 1.0 \times 10^{-1}$	0 : 100	2	$> 10^4$
25	MeΦTe	$[Me\Phi_2Te]ClO_4$	2.2×10^{-3}	14 : 86	74	32
26	MeΦTe	$[Me_2\Phi S]ClO_4$	3.3×10^{-4}	0 : 100	476	$> 10^4$
27	MeΦTe	$[Me_2\Phi Se]ClO_4$	4.1×10^{-2}	0 : 100	7	$> 10^4$
28	MeΦTe	$[MeEt\Phi S]ClO_4$	2.1×10^{-4}	0 : 100	546	$> 10^4$
29	MeΦTe	$[MeEt\Phi Se]ClO_4$	6.9×10^{-3}	0 : 100	10	$> 10^4$
30	MeΦTe	$[MeEt\Phi Te]ClO_4$	5.6×10^{-4}	(31 : 69)[d]	408	(5.0)[d]
31	Φ_2Te	$[Me_2\Phi S]ClO_4$	2.5×10^{-4}	0 : 100	284	$> 10^4$
32	Φ_2Te	$[Me_2\Phi Se]ClO_4$	$< 1.2 \times 10^{-2}$	0 : 100	7	$> 10^4$
33	Φ_2Te	$[Me_2\Phi Te]ClO_4$	1.3×10^{-5}	84 : 16	500	0.031

[a] In acetone-d_6 at 50 °C; $\Phi = 2,6\text{-}(MeO)_2C_6H_3$. [b] Molar ratio at the equilibrium. [c] Final hour of measurement. [d] Ethyl group transfer products also formed in very small amounts. [e] The rate constant could not be obtained due to the very small change. [f] Some unknown products were contaminated.

for RΦE (R = Me, Et), but it shifted in the reverse order for $[MeEt\Phi E]ClO_4$ or in the order S > Se < Te for $[Et_2\Phi E]ClO_4$. The other four resonances due to the Φ-group were far less sensitive to the change of E. In contrast, α-carbons in R–E were quite sensitive to the change of E, and they shifted, in general, to higher magnetic field in the order E = S < Se < Te, an exception being methyl carbon in EtΦE.

Oxidation potentials of Ph_2E {electrochemical E_0/V *vs.* NHE = 1.56 (S), 1.38 (Se), 0.95 (Te)},[4] $Me(4\text{-}RC_6H_4)E$,[4,5] Me_2E,[5] MePhE,[5,6] and ΦEEΦ[7] have been reported to decrease in the order E = S > Se > Te, while those of phenoxachalcogenides, $C_{12}H_8OE$,[8] and chalcanthrenes, $C_{12}H_8E_2$,[9,10] studied both by photoelectron spectroscopy and semiempirical MO calculation, have been reported to show somewhat different orders such as Se > S > Te. The former order (S > Se > Te) paralleled the rate order of reactions between Φ_2E and dimethyl sulfate (S < Se < Te), while the latter paralleled the Me–E$^+$ bond strength order of $[Me\Phi_2E]^+$ (Se < S < Te).[1]

Reaction rates and equilibrium constants for the reactions of alkyl 2,6-dimethoxyphenyl chalcogenides with their onium salts

The reactions of alkyl 2,6-dimethoxyphenyl chalcogenides, RΦE, with the onium salts, $[MeR'\Phi E']ClO_4$ (R = Me, Φ; R′ = Me, Et, Φ; E, E′ = S, Se, Te) [eqn. (1)] were followed by measuring the ^{1}H NMR spectra of acetone-d_6 solutions containing equimolar amounts of MeΦE and $[MeR'\Phi E']ClO_4$ at 50 °C (Table 3). Because of the sharpness of methoxy proton resonance, the reactions could easily be followed. Among the three organic groups in $[MeEt\Phi E']ClO_4$, the methyl group predominantly transferred to MeΦE, although ethyl transfer products also formed in very small amounts (entries 7 and 30 in Table 3). The relative reactivities of alkyl methylphenylsulfonium perchlorates with iodide anion in acetone at 50 °C have been reported to be Me (1.0) > Et (0.20) > i-Pr (0.05).[11–13] Generally, the relative reactivity of the alkyl groups of alkyl halides toward nucleophiles has been known to be Me : Et : i-Pr = 1.0 : 0.05 : 0.01.[14] Although data are not shown, essentially identical results for k_2 and *K* were obtained for the reactions in $CDCl_3$ solutions. These observations are indicative that the present reactions [(eqn. 1)] are of typical S_N2 reactions.[13,15]

The reaction between MeΦS and $[Me\Phi_2S]ClO_4$ was very slow but it gradually formed $[Me_2\Phi S]ClO_4$ and Φ_2S (entry 1 in Table 3). The second order rate constant, k_2, was calculated from the time-dependent ^{1}H NMR spectra at the early stage of reaction. In fifteen days, it attained an equilibrium containing 89% of the products. The equilibration was confirmed by observation of the reverse reaction (entry 9), although the rate could not be followed with precision due to the minority of the products. The equilibrium constants of entries 1 *vs.* 9, 4 *vs.* 15, 10 *vs.* 12, and 25 *vs.* 33 in Table 3 were the mean value estimated from these reversal reactions. The reaction of MeΦS with $[Me\Phi_2Se]ClO_4$ was faster than that with $[Me\Phi_2S]ClO_4$, but, interestingly, the former reaction attained an equilibrium with less amount of the products in spite of the faster forward rate (entry 2). The reverse reaction (entry 20) was also observed, but the rate constant could not be obtained due to the minority of the products and because some unknown products were contaminants. The mixture of MeΦS and $[Me\Phi_2Te]ClO_4$ did not react (entry 3), as confirmed by the reverse reaction (entry 31).

MeΦS reacted also with $[Me_2\Phi Se]ClO_4$ to give an equilibrium mixture containing $[Me_2\Phi S]ClO_4$ and MeΦSe (entry 4), but it did not react with $[Me_2\Phi Te]ClO_4$ (entry 5). These reactivities also were confirmed by the reverse reactions (entries 15 and 26). It is impossible to follow the reaction of MeΦS with

[Me$_2$ΦS]ClO$_4$ due to the identity of the products, and the equilibrium constant must be 1.0, naturally, if there is methyl group exchange. It was unexpected that MeΦS did not react with [MeEtΦS]ClO$_4$ (entry 6), while MeΦS reacted with [MeEtΦSe]ClO$_4$ to give an equilibrium mixture (entry 7). MeΦS also did not react with [MeEtΦTe]ClO$_4$ (entry 8). These results indicate that the Me–E bond strength of [MeΦ$_2$E]ClO$_4$ increases in the order $E = S \leq Se < Te$, but that the strength of [Me$_2$ΦE]ClO$_4$ and [MeEtΦS]ClO$_4$ increases in the order $E = Se \leq S < Te$. Reactions of Φ$_2$S with [Me$_2$ΦE]ClO$_4$ confirmed the last order (entries 9–11). As observed for MeΦS, the reaction of MeΦSe with [Me$_2$ΦS]ClO$_4$ was slower than that with [Me$_2$ΦSe]ClO$_4$ (entries 12 and 13).

The larger equilibrium constant of the reaction between MeΦSe and [MeΦ$_2$S]ClO$_4$ (entry 12) than that between MeΦS and [MeΦ$_2$S]ClO$_4$ (entry 1) or that between MeΦSe and [MeΦ$_2$Se]ClO$_4$ (entry 13) also confirmed the Me–E bond strength order of [MeΦ$_2$E]ClO$_4$ ($E = S \leq Se$). The equilibrium constant for the reaction of MeΦSe with [Me$_2$ΦSe]ClO$_4$ also must be 1.0, naturally. By comparison of this value and the equilibrium constants observed for the reactions of MeΦSe with [Me$_2$ΦE]ClO$_4$ (entries 15 and 16) or with [MeEtΦE]ClO$_4$ (entries 17–19), it was confirmed that the Me–E bond strength of [Me$_2$ΦE]ClO$_4$ and [MeEtΦE]ClO$_4$ increases in the order $E = Se \leq S < Te$. It was also found that Φ$_2$S and Φ$_2$Se are weaker nucleophiles than MeΦE (E = S, Se, Te) (entries 9–11, 20–22). Tellurides, MeΦTe and Φ$_2$Te, were stronger nucleophiles than MeΦE and Φ$_2$E (E = S, Se), and they reacted with [MeΦ$_2$E]ClO$_4$, [Me$_2$ΦE]ClO$_4$ and [MeEtΦE]ClO$_4$ (E = S, Se) to complete the reactions (entries 23, 24, 26–29, 31, 32). The reaction rate was faster with selenonium salts than with sulfonium salts irrespective of the type of onium salts. MeΦTe reacted with [MeΦ$_2$Te]ClO$_4$ and [MeEtΦTe]ClO$_4$ to give the equilibrium mixtures (entries 25 and 30). Thus, MeΦTe must react with [Me$_2$ΦTe]ClO$_4$, although the reaction cannot be followed by ^{1}H NMR spectrometry. Φ$_2$Te also reacted with [Me$_2$ΦTe]ClO$_4$ (entry 33), which was the reverse reaction of MeΦTe with [MeΦ$_2$Te]ClO$_4$ (entry 25). By comparison of these equilibrium constants, the Me–Te bond strength of [MeRΦTe]ClO$_4$ is expected to increase in the order [MeΦ$_2$Te]ClO$_4$ < [MeEtΦTe]ClO$_4$ < [Me$_2$ΦTe]ClO$_4$.

Some important results are summarized as follows:

1) RΦE (R = Me, Φ; E = S, Se) react commonly with [MeRΦE]$^+$ (R = Me, Et, Φ; E = S, Se) to give the equilibrium mixture, except that MeΦS does not react with [MeEtΦS]$^+$.

2) RΦE (R = Me, Φ; E = S, Se) do not react with [MeRΦTe]$^+$ (R = Me, Et, Φ).

3) RΦTe react with [MeRΦE]$^+$ (R = Me, Et, Φ; E = S, Se, Te) to complete the methyl abstraction (E = S, Se) or to give the equilibrium mixture (E = Te).

4) The reaction rate of MeΦE with [MeRΦE′]$^+$ (R = Me, Et, Φ) increases in the orders $E = S < Se < Te$ and $E' = S \sim Te < Se$.

5) Reactions of [Me$_2$ΦE]$^+$ are faster than those of [MeEtΦE]$^+$, which react faster than [MeΦ$_2$E]$^+$.

6) The Me–E bond strength of [MeΦ$_2$E]$^+$ increases in the order $E = S \leq Se < Te$, but those of [Me$_2$ΦE]$^+$ and [MeEtΦE]$^+$ increase in the order $E = Se \leq S < Te$.

7) The Me–E bond strength of [MeRΦE]$^+$ (E = S, Se) increases in the orders R = Φ < Me < Et or Me < Φ < Et, while the Me–Te bond strength of [MeRΦTe]$^+$ increases in the order R = Φ < Et < Me.

The results for the reactivity of MeΦE with [MeRΦE′]$^+$ are quite complicated, being influenced by E and E′, as well as R. The results 4), 6), and 7) are especially interesting because they contain unusual orders of elements.

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