Energetics of the Lighter Chalcogen Analogues of Carboxylic Acid Esters[†]

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In the current paper we present the results of our quantum chemical (G2, G2(MP2), and G3) study of the structure and energetics of carboxylic acids and their chalcogen analogues. In the particular, calculations and accompanying natural bond orbital (NBO) and atoms in molecules (AIM) analyses were performed on all species with the generic formula $RC(=X)YR'$ (X, Y = O, S, Se and R = R' = CH$_3$). Energies, enthalpies, and free energies of formation, resonance energies, interchalcogen methyl transfer energies and their energies of activation, and heavy atom bond lengths and angles are all discussed. A comparison of the calculated results with the sparse experimentally available data shows good agreement. Trends are also presented.

Introduction

Carboxylic acid esters [$RC(=O)OR'$] are nearly ubiquitous. They are found in foods as definitional components of fats (cf. triglycerides) and in flavorings (e.g., methyl anthranilate and grapes). They are found in plastics as monomeric components, (e.g., methyl methacrylate, vinyl acetate) and as plasticizers (e.g., dibutyl phthalate). They are found in drugs, both legal (e.g., lidocaine) and illegal (e.g., heroin). It is thus not surprising that they have also caught the attention of the thermochemical community: a quick look at diverse data compendia—Domalski,[1] Stull et al.,[2] Pedley,[3] and the WebBook (Afeefy, Liebman, Stein chapter)[4]—shows data for well over a hundred esters. Carboxylic acid esters containing sulfur are rather much rarer in any of their three incarnations, *S*-thiocarboxylate esters (thiolesters, [$RC(=O)SR'$]), *O*-thiocarboxylate esters (thionesters, [$RC(=S)OR'$]), and dithioesters [$RC(=S)SR'$], respectively. Of these, *S*-thiocarboxylate esters (thiolesters), as perhaps befits their relevance to biochemical energetics and coenzyme A,[5] have been studied by calorimetrists, but these efforts have been dominated by thiolacetates.[6–9] Exclusive of carbamic acid derivatives,[10–15] *O*-thioesters (thionesters) have seemingly been ignored by this community. Nonetheless, some qualitative inferences may be drawn, such as *O*-thioesters are less stable than the corresponding isomeric *S*-thioester as evidenced by the rearrangement for the former into the latter.[16–19] This oversight is surprising, indeed disappointing, given the extensive chemical interest in sulfur-containing species. Selenium-containing esters (with one or two

seleniums, and if but one, with the other element oxygen or sulfur) likewise remain unstudied by thermochemical researchers. This omission is less surprising given the paucity of such studies with selenium compounds in general as compared to those containing its lighter chalcogen congeners, as in the brief review in the "Patai series" on organoselenium and organotellurium thermochemistry,[20] as opposed to that on general sulfur compounds,[21] and the earlier, but more specialized one, on sulfonic acids and derivatives.[22]

As befits our earlier studies of the energetics of chalcogen-containing 16 valence electron triatomics and pentaatomics[23–25] and of a pair of thiocarbamate and dithiocarbamate heterocycles,[15,16] we now report our computational study of *S*- and *O*-thiocarboxylate esters (thiol and thiocarboxylates), dithiocarboxylate esters, and their selenium counterparts. In particular, we have investigated the structures and energetics of the nine compounds, $H_3CC(=X)YCH_3$ (X, Y = O, S, Se), at the G2, G2(MP2), and G3 levels of theory. The focus of this work is on the following properties of these compounds: resonance energies, enthalpies of formation, barrier heights for intramolecular 1,3-methyl migration, and syn (*Z*) vs anti (*E*) relative stabilities. We are interested in how these properties differ down the group and between the C(=X)Y and the C(=Y)X arrangements.

Relatively few previous quantum mechanical studies of sulfur-containing esters have appeared in the literature. Moreover, although the relative energies of HC(=Se)OH and HC(=O)SeH and the barrier for O→Se hydrogen transfer have been examined computationally,[26] as have the gas-phase acidities of the series of selenocarboxylic acids RCSeOH and RCOSeH, R = H, F, Cl, NH$_2$, CH$_3$,[27] we have found no computational studies performed on selenoesters. The theoretical work with the most

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CHART 1

syn (Z)   anti (E)
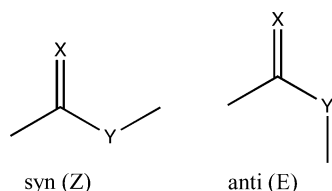
overlap with this work is a MNDO investigation of the ketene−thioketene formation and 1,3-methyl transfer reactions of methyl acetate $H_3CC(=O)OCH_3$, *S*-methyl thioacetate $H_3CC(=O)SCH_3$, *O*-methyl thioacetate $H_3CC(=S)OCH_3$, and methyl dithioacetate $H_3CC(=S)SCH_3$.[28] The 1,3-methyl transfer reaction was found to be preferred for all compounds but *S*-methyl thioacetate. The majority of the remaining calculations discussed below involve the sulfur-containing compounds as models for thioesters.

The energy difference between the *Z* and the *E* rotamers (Chart 1) and the barrier to internal rotation for the model *S*-thiocarboxylate ester $H_3CC(=O)SCH_3$ have been evaluated by several research groups.[29−32] The destabilization of the *E* conformer compared with the *Z* has generally been rationalized in terms of its less effective $n_S→π*_{C=O}$ electron delocalization, less favorable dipole−dipole interactions, and larger steric strain.

S-methyl thioacetate and methyl dithioacetate $H_3CC(=S)SCH_3$ have also been used as model compounds to assay C−S versus C−O bond polarities, relevant to the higher reaction rates of thiol esters with respect to dithio esters in the deacylation of the cysteine protease papain.[33] The reactivities of oxoesters and thioesters in nucleophilic acyl transfer reactions have been probed by a comparison of the model reactions of methyl acetate and *S*-methyl thioacetate with hydroxide, ammonia, and methylcyanoacetate carbanion.[34] The relative reactivities correlate with the net loss of delocalization energy accompanying the formation of the transition state. Substituent effects on the gas-phase basicities of the *O*-thiocarboxylate $H_3CC(=S)OCH_3$ and $H_3CC(=S)OC_2H_5$ have been examined as part of a combined mass spectrometric and computational study of the intrinsic reactivities of carbonyl versus thiocarbonyl compounds.[35] Again, differences in electron delocalization effects, in this case from the substituent lone pairs to the C=O or C=S π-orbitals, help to elucidate the greater sensitivity of the carbonyl compounds to substitution. The greater basicity of the S counterparts was attributed to the lower electronegativity and greater polarizability of S than O. (Similar effects were seen when the carbonyl compounds were compared with the selenocarbonyl derivatives.[26]) The ^{33}S NMR properties of $H_3CC(=O)SCH_3$, $H_3CC(=S)OCH_3$, and $H_3CC(=S)SCH_3$ have also been calculated.[36]

G3[37] and G2[38] energies have been evaluated for methyl acetate to determine the proton affinity of $[CH_2COOCH_3]^-$ and the enthalpy of formation of methyl peroxy acetate (via an isodesmic reaction), respectively. A G3 energy has also been evaluated for *S*-methyl thioacetate[39] to determine the homolytic bond dissociation energy of the C−S bond. However, no systematic study of the entire series of $H_3CC(=X)YCH_3$ (X, Y = O, S, Se) molecules has been carried out at any level of calculation. In addition, *Z* and *E* relative stabilities were not reported in the earlier investigations.

Calculational Details

The calculations on the nine chalcogen-containing compounds $H_3CC(=X)YCH_3$ (X, Y = O, S, Se) were performed with Gaussian 03[40] and Gaussian 09[41] using the G3[42] and G2[43]

composite methods. Ethane and the three corresponding $H_3CC(=X)CH_3$ and H_3CYCH_3 compounds (eq 1 below) have been studied previously at these levels of calculation.[26,38,39,42−45] All possible arrangements of the hydrogens within the *Z* and *E* C(=X)YC configurations of $H_3CC(=X)YCH_3$ (Chart 1) were examined for each X, Y pair. Structures with both C_S and C_1 symmetry were considered. (The C(=X)YC gauche conformations tested relaxed to syn or anti.) Transition structures were located for the Y→X intramolecular 1,3-methyl shifts for all six relevant combinations of X and Y. The designation **TS−YX** has been used to more easily differentiate among the various interconversions. For the transition structures, normal-mode vibrational frequencies were reevaluated at the MP2/6-31G(d) calculational level to verify that the structures had one imaginary frequency at that level. Intrinsic reaction coordinate calculations (IRC)[46] were carried out for the transition structures to confirm that they connected the desired reactants and products. The Cartesian coordinates for the nine *Z* and nine *E* equilibrium structures and for the six transition structures can be found in Table S1 of the Supporting Information (SI). The G2, G2(MP2), and G3 energies, enthalpies, and free energies of these molecules and the reference molecules are listed in Table S2 of the SI.

As our measure of the resonance energies associated with these compounds, for each X, Y pair, where X, Y = O, S, Se, we have computed the enthalpy change for the following isodesmic group separation reaction (eq 1).

$$H_3C-C(=X)-Y-CH_3 + H_3C-CH_3 \rightarrow$$
$$H_3C-C(=X)-CH_3 + H_3C-Y-CH_3 \quad (1)$$
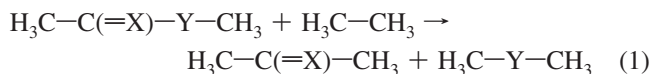
This reaction has also been used to compare the resonance energy and rotational barriers of esters and amides (Y = NCH_3).[47] Together with the experimental enthalpies of formation[4,48] of C_2H_6, $H_3C-C(=X)-CH_3$ and $H_3C-Y-CH_3$, the above reaction enthalpies allow us to obtain enthalpies of formation for the $H_3CC(=X)YCH_3$ (X, Y = O, S, Se) species. When experimental enthalpies of formation are not available for the products, we have estimated some enthalpies of formation for $H_3CC(=X)YCH_3$ from the following rearrangement reaction (eq 2).

$$H_3C-C(=Y)-X-CH_3 \rightarrow H_3C-C(=X)-Y-CH_3$$
$$(2)$$
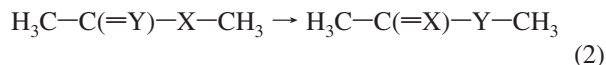
Natural bond orbital (NBO)[49,50] and atoms in molecules (AIM)[51] analyses were performed for the nine $H_3CC(=X)YCH_3$ systems to elucidate the influence of electron delocalization effects on the relative conformational and group separation energies of these systems. The AIM analysis provides bond critical point densities ($ρ_b$), which we use as a measure of bond strength.[26,51−55] The NBO analysis examines deviations of the molecule from the strictly localized Lewis structure. For these molecules, the Lewis NBOs describe about 99% of the total electron density. We utilized the NBO analysis of the Hartree−Fock orbitals to examine the role of the $n_X→σ*(C−Y)$, $n_Y→σ*(C=X)$, and $n_Y→π*(C=X)$ hyperconjugations in governing the above relative energies. Each of these orbital interactions involves a lone pair on atom X(Y) delocalizing into an unfilled C−Y(C=X) NBO. The energies of the individual orbital interactions $ΔE^{(2)}$(donor→acceptor) were estimated with the second-order NBO perturbation approach.[50]

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TABLE 1: Relative Enthalpies and Free Energies, Dipole Moments, and %Y$_s$ Character

molecule	$\Delta H_{298}{}^a$	$\Delta G_{298}{}^a$	μ^b (Z)	μ^b (E)	%Y$_s{}^c$ (C(X)−Y)	%Y$_s{}^c$ (Y−CH$_3$)
H$_3$CC(=O)OCH$_3$	30.6 [31.2]	30.7 [31.2]	1.95	5.07	32.6	29.3
H$_3$CC(=S)OCH$_3$	32.5 [33.4]	32.1 [33.0]	2.52	5.43	34.8	29.6
H$_3$CC(=Se)OCH$_3$	32.0 [33.1]	31.6 [33.0]	2.57	5.47	35.3	29.5
H$_3$CC(=O)SCH$_3$	17.7 [17.7]	25.0 [24.5]	1.51	4.70	17.5	18.0
H$_3$CC(=S)SCH$_3$	17.9 [18.1]	20.1 [20.3]	2.07	4.87	19.4	18.2
H$_3$CC(=Se)SCH$_3$	17.1 [17.4]	18.1 [19.0]	2.13	4.83	20.0	18.2
H$_3$CC(=O)SeCH$_3$	13.4 [14.0]	15.1 [17.3]	1.46	4.48	13.9	14.7
H$_3$CC(=S)SeCH$_3$	13.3 [13.9]	14.4 [17.2]	2.00	4.63	15.4	15.0
H$_3$CC(=Se)SeCH$_3$	12.6 [13.2]	13.9 [21.2]	2.04	4.59	16.0	15.0

^{a} G2 and G3 (square brackets) thermochemical data (kJ/mol) for the E local minimum relative to the Z global minimum. ^{b} Calculated dipole moments in Debye. ^{c} % contribution from the s-orbitals of atom Y to the C(X)−Y or Y−CH$_3$ σ-bond of the Z rotamer.

Results and Analysis of Results

The thermochemical data reported in this work was evaluated at the G2, G2(MP2), and G3 levels of calculation. Because the G2(MP2) and G2 values vary by no more than 3 kJ/mol and usually by less than 1 kJ/mol, the G2(MP2) values have not been tabulated. The G2 and G3 ΔE_0 and ΔH_{298} values deviate by 4 kJ/mol or less, but the ΔG_{298} values deviate by as much as 10 kJ/mol. Another general trend is that all ΔE_0 and ΔH_{298} thermochemical quantities are essentially equal. Thus, we can concentrate on solely the stereoelectronic aspects of the chemical energetics.

Z versus E Conformers. The conformational preference of the X=C−Y−Z backbone in RC(=X)YR′ compounds (Chart 1) has been of interest for some time. For example, the relative stability of the two possible conformations has been important in interpreting spectral data[31,56−59] and photodecomposition data.[30] The previous experimental[30,31,59−63] and computational[30,31,38,59,63−65] studies on a variety of RC(=X)YR′ species indicate that the Z conformation is preferred over the E conformation (Chart 1), although the difference in stability varies with the R and R′ substituents. The IR and (resonance) Raman investigations of methyl acetate H$_3$CC-(=O)OCH$_3$,[59] S-methyl thioacetate H$_3$CC(=O)SCH$_3$,[30,58] O-methylthioacetate H$_3$CC(=S)OCH$_3$,[57] and methyl dithioacetate H$_3$CC(=S)SCH$_3$[56,60,62] also suggest that all of the heavy atoms lie in the same plane. In agreement with these results and those from earlier computational work on H$_3$CC(=O)OCH$_3$,[59,64] H$_3$CC(=O)SCH$_3$,[29−32] and H$_3$CC(=S)OCH$_3$,[35] the G2 and G3 results for these compounds show that the Z conformer, with C$_S$ symmetry, is the more stable of the two conformers (Table 1). We found the same preferred symmetry and conformation for Se-methyl selenoacetate H$_3$CC(=O)SeCH$_3$, O-methyl selenoacetate H$_3$CC(=Se)OCH$_3$, Se-methyl thioacetate H$_3$CC(=S)-SeCH$_3$, and methyl diselenoacetate H$_3$CC(=Se)SeCH$_3$. However, the Z global minima of methyl dithioacetate H$_3$CC-(=S)SCH$_3$ and S-methyl selenoacetate H$_3$CC(=Se)SCH$_3$ have C$_1$ symmetry at these levels of calculation. The 1−2° deviation from planarity of the X = C−S−C backbone and twisting of the H$_3$CC hydrogens observed for these C$_1$ structures (Table 2) were confirmed with MP2(full)/6-31G(d) vibrational frequency calculations for both molecules and with higher level MP2/6-311+G(d,p), MP2/cc-pVDZ, and MP2/aug-cc-pVDZ optimizations and frequencies for H$_3$CC(=S)SCH$_3$. For all nine compounds, the E local minima have C$_S$ symmetry.

The primary determining factor in the energy difference between the Z and the E conformations (Chart 1) appears to be the nature of the Y atom in the X=C−Y−C framework. The thermochemical data summarized in Table 1 show that, for each X, as Y proceeds from O to S to Se the E form is increasingly favored with respect to the Z. The calculated Z/E enthalpy difference (31 kJ/mol) for H$_3$CC(=O)OCH$_3$ is in good agreement with the experimental measurement of about 36 ± 4 kJ/mol[59] and with the MP2/6-311+G(d,p) ΔE value of 35 kJ/mol.[65] The ca. 25 kJ/mol greater stability of the Z conformer of H$_3$CC(=O)SCH$_3$ is comparable to the value of about 22 kJ/mol obtained at the MP2/6-31+G(d)[30] and MP2/6-31G(d)[31] levels of calculation. S-Methyl thioacetate and methyl diselenoacetate are the only compounds for which the effect of the X atom on any thermochemical value is larger than 1−2 kJ/mol. Again with the exceptions of H$_3$CC(=O)SCH$_3$ and H$_3$CC-(=Se)SeCH$_3$ the ΔH_{298} and ΔG_{298} values are within 3 kJ/mol of each other (Table 1), indicating that, generally, entropy does not play a significant role in the relative stabilities of the two conformations. The larger 7 kJ/mol contribution of the $-T\Delta S$ term to ΔG_{298} for H$_3$CC(=O)SCH$_3$ was also obtained with the B3LYP/6-311+G(d,p) calculations of Nagy et al. and can be explained by the difference in the vibrational frequencies of the methyl torsions for the two forms.[65]

Selected MP2(full)/6-31G(d) geometrical parameters are collected in Table 2 for the Z forms of the nine H$_3$CC(=X)YCH$_3$ molecules and for the transition structures for the 1,3-methyl migrations among them. Because the overall structures of the minima are so similar for the nine systems, only the optimized structures of the Z and E rotamers of H$_3$CC(=Se)SCH$_3$ are displayed in Figure 1. The optimized structures of the transition structures for the three symmetric and three asymmetric interconversions are also depicted in the figure. Experimental geometries are available for H$_3$CC(=O)OCH$_3$[59] and H$_3$CC-(=O)SCH$_3$,[31] and as has been reported previously for methyl thioacetate, there is good agreement between the theoretical and the experimental results. However, the gas electron diffraction data for H$_3$CC(=O)SCH$_3$ were refined by fixing two of the tilt angles and a dihedral angle to their MP2/6-31G(d) calculated values.[31] Also, only the mean S−C distance and the difference in the two S−C distances were determined from the experimental data. Nevertheless, the resulting values of 1.793 Å and 0.024 Å, respectively, are in excellent agreement with the MP2/6-31G(d) values.[31]

Several patterns emerge from the geometrical parameters for the Z conformers. Whether X = O, S, or Se, the C=X bond length is the same within 0.006 Å for all three compounds containing that bond. Similarly small differences are found for the Y−CH$_3$ bonds. There is more diversity among the C(X)−Y bond distances, with a range of 0.017 Å for Y = O, 0.050 Å for Y = S, and 0.057 Å for Y = Se. These changes in C=X and C(X)−Y bond lengths are reminiscent of the behavior of amide bonds upon rotation about the C−N bond.[64] For formamide, for example, Wiberg and Laidig have shown that the rotation elongates the C−N bond by 0.08 Å but shortens the C=O bond by only 0.01 Å.[64]

TABLE 2: Selected Geometrical Parameters of the Z Rotamers and the Transition Structures[a]

molecule	bond lengths	bond angles	dihedral angles
$H_3CC(=O)OCH_3$, C_S	C=O: 1.218 [1.206][b] C(O)–O: 1.356 [1.357] O–CH$_3$: 1.439 [1.438] O⋯CH$_3$: 2.632	O=C–O: 123.4 [123.0] C–O–CH$_3$: 114.1 [116.4] O⋯CH$_3$–O: 59.4	
$H_3CC(=S)OCH_3$, C_S	C=S: 1.631 C(S)–O: 1.345 O–CH$_3$: 1.437 S⋯CH$_3$: 2.960	S=C–O: 125.4 C–O–CH$_3$: 117.8 S⋯CH$_3$–O: 63.4	
$H_3CC(=Se)OCH_3$, C_S	C=Se: 1.768 C(Se)=O: 1.339 O–CH$_3$: 1.438 Se⋯CH$_3$: 3.040	Se=C–O: 125.4 C–O–CH$_3$: 117.8 Se⋯CH$_3$–O: 65.3	
$H_3CC(=O)SCH_3$, C_S	C=O: 1.222 [1.214][c] C(O)–S: 1.781 [1.781] S–CH$_3$: 1.806 [1.805] O⋯CH$_3$: 2.790	O=C–S: 122.1 [122.8] C–S–CH$_3$: 98.2 [99.2] O⋯CH$_3$–S: 66.2	
$H_3CC(=S)SCH_3$, C_1	C=S: 1.633 C(S)–S: 1.744 S–CH$_3$: 1.797 S⋯CH$_3$: 3.110	S=C–S: 125.3 C–S–CH$_3$: 102.7 S⋯CH$_3$–S: 69.6	S=C–S–C: 1.4
$H_3CC(=Se)SCH_3$, C_1	C=Se: 1.771 C(Se)–S: 1.731 S–CH$_3$: 1.796 Se⋯CH$_3$: 3.167	Se=C–S: 125.4 C–S–CH$_3$: 102.7 Se⋯CH$_3$–S: 71.7	Se=C–S–C: 0.9
$H_3CC(=O)SeCH_3$, C_S	C=O: 1.218 C(O)–Se: 1.935 Se–CH$_3$: 1.944 O⋯CH$_3$: 2.886	O=C–Se: 121.7 C–Se–CH$_3$: 94.9 O⋯CH$_3$–Se: 66.9	
$H_3CC(=S)SeCH_3$, C_S	C=S: 1.627 C(S)–Se: 1.893 Se–CH$_3$: 1.936 S⋯CH$_3$: 3.202	S=C–Se: 124.9 C–Se–CH$_3$: 99.7 S⋯CH$_3$–Se: 70.0	
$H_3CC(=Se)SeCH_3$, C_S	C=Se: 1.765 C(Se)–Se: 1.878 Se–CH$_3$: 1.935 Se⋯CH$_3$: 3.248	Se=C–Se: 124.8 C–Se–CH$_3$: 99.8 Se⋯CH$_3$–Se: 72.1	
TS–OO, C_S	C–O: 1.265 O⋯CH$_3$: 2.001	O–C–O: 117.7 C–O⋯CH$_3$: 88.4 O⋯CH$_3$⋯O: 65.5	O–C–O⋯CH$_3$: 1.1
TS–OS, C_1	C–S: 1.668 C(S)–O: 1.267 O⋯CH$_3$: 2.006 S⋯CH$_3$: 2.482	S–C–O: 118.2 C–O⋯CH$_3$: 100.7 S⋯CH$_3$⋯O: 67.6	O–C–S⋯CH$_3$: 1.6
TS–OSe, C_1	C–Se: 1.806 C(Se)–O: 1.263 O⋯CH$_3$: 2.022 Se⋯CH$_3$: 2.611	Se–C–O: 117.9 C–O⋯CH$_3$: 103.6 Se⋯CH$_3$⋯O: 68.2	O–C–Se⋯CH$_3$: 1.6
TS–SS, C_S	C–S: 1.662 S⋯CH$_3$: 2.470	S–C–S: 119.4 C–S⋯CH$_3$: 84.7 S⋯CH$_3$⋯S: 71.0	S–C–S⋯CH$_3$: 2.7
TS–SSe, C_1	C–Se: 1.800 C(Se)–S: 1.656 S⋯CH$_3$: 2.482 Se⋯CH$_3$: 2.596	Se–C–S: 119.4 C–S⋯CH$_3$: 89.0 Se⋯CH$_3$⋯S: 72.0	S–C–Se⋯CH$_3$: 1.8
TS–SeSe, C_S	C–Se: 1.793 Se⋯CH$_3$: 2.604	Se–C–Se: 119.1 C–Se⋯CH$_3$: 84.0 Se⋯CH$_3$⋯S: 72.8	Se–C–Se⋯CH$_3$: 3.0

[a] MP2(full)/6-31G(d) distances in Å and angles in degrees. [b] Experimental data in brackets from ref 59. [c] Experimental data (in brackets) and calculated data from ref 31.

Comparing the C(X)–Y and Y–CH$_3$ distances within the same species (Table 2), the variations decrease in the order Y = O ($\leq$0.099 Å) > Y = S ($\leq$0.065 Å) > Y = Se ($\leq$0.057 Å). For a particular Y, $\Delta r((Y-CH_3)-(C(X)-Y))$ increases as X changes from O to S to Se. With respect to the bond angles, <XCY is remarkably similar regardless of the identity of X or Y; it differs by less than 3.5° among the nine compounds. On the other hand, <CYC ranges from 95°–118° with, as expected, the smallest angles for Y = Se and the largest for Y = O. Also,

when Y is fixed <CYC is smallest when X = O and essentially identical when X = S, Se.

Isodesmic Group Separation Reaction Energies: Resonance Energies. One objective of the normal coordinate analysis El-Assar et al.[58] undertook for *S*-methyl thioacetate was to determine if the low vibrational frequency of the carbonyl bond in this molecule arises from electron delocalization into the bond. Because the force constant for the C=O bond in liquid $H_3CC(=O)SCH_3$ (9.8 mdyn/Å) is very similar to that of liquid
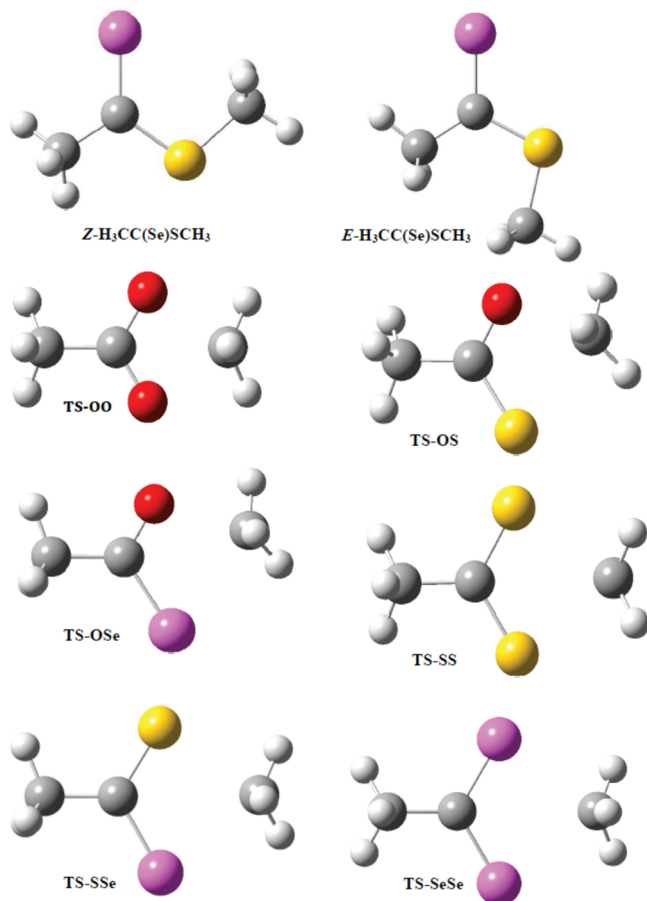
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Figure 1. Diagram of the *Z* and *E* minima of $H_3CC(=Se)SCH_3$ and the six 1,3-methyl migration transition structures located on the G2 and G3 potential energy surfaces. Color scheme: O, red; S, yellow; Se, fuchsia; C, gray; H, white.

TABLE 3: AIM Bond Critical Point Densities, ρ_b

molecule	$\rho_b(C=X)$	$\rho_b(C(X)-Y)$	$\rho_b(Y-CH_3)$
$H_3CC(=O)OCH_3$	0.414	0.299	0.232
$H_3CC(=S)OCH_3$	0.226	0.303	0.231
$H_3CC(=Se)OCH_3$	0.185	0.306	0.229
$H_3CC(=O)SCH_3$	0.405	0.206	0.190
$H_3CC(=S)SCH_3$	0.225	0.215	0.194
$H_3CC(=Se)SCH_3$	0.182	0.219	0.195
$H_3CC(=O)SeCH_3$	0.408	0.158	0.153
$H_3CC(=S)SeCH_3$	0.227	0.164	0.155
$H_3CC(=Se)SeCH_3$	0.185	0.168	0.156

acetone (9.6 mdyn/Å), El-Aasar et al. argued against significant double bond character in the C(O)—S bond and thus against significant $n_S \rightarrow \pi^*_{C=O}$ or $n_S \rightarrow \sigma^*_{C=O}$ electron delocalization. Their conclusion was supported by the result that the force constant for the C(O)—S bond (3.0 mdyn/Å) is the same as that of the S—CH₃ bond (3.1 mdyn/Å) within experimental error.[58] A comparison of the AIM[51] bond critical point densities (ρ_b, Table 3) of the C(X)—Y and Y—CH₃ bonds also indicates that these two C—S bonds have similar strengths. In sharp contrast to the C(O)—O and O—CH₃ bonds of methyl acetate, for which the ρ_b values differ by 0.067, the ρ_b values for the two C—S bonds of *S*-methyl thioacetate differ by only 0.016. The variation in the ρ_b values for the C(O)—Se and Se—CH₃ bonds of $H_3CC(=O)SeCH_3$ is even smaller (0.005), implying that the strengths of these two C—Se bonds are similar as well. On the basis of the ρ_b data for the remaining molecules in Table 3, the above conclusions on relative Y—CH₃ and C(X)—Y bond strengths can be drawn for all compounds with a given Y,

regardless of the identity of X. Note also the remarkably similar values of ρ_b for any given C=X bond, whether Y = O, S, or Se. This is especially the case when X = S or Se, as is also observed for the C=X bond lengths (Table 2).

As El-Assar et al.[58] point out, the preceding results are consistent with Wadsö's finding, on the basis of gas-phase hydrolysis enthalpies and thermodynamic bond energies,[66] that the resonance energy in thioesters drops by about 54−59 kJ/mol with respect to that in the all-oxygen carboyxlate esters. Although Wadsö's estimate was determined for ethyl acetate and *S*-ethyl thioacetate, the drop in resonance energy we obtain from the group separation reactions for methyl acetate and *S*-methyl thioacetate (58−60 kJ/mol (Table 4)) is in excellent agreement with his value. Predictably, Se-methyl selenoacetate shows a somewhat larger loss in resonance energy of about 70 kJ/mol. Compared to the corresponding Y = O systems, the reduction in resonance energy for the remaining Y = S systems is about 30−35 kJ/mol, and that for the remaining Y = Se systems is about 40−45 kJ/mol. Thus, the interesting result that the Y atom groups the relative conformational energies of these systems is repeated for the resonance energies (Tables 1 and 4). For a given Y, only the resonance energy for methyl acetate differs by more than 4 kJ/mol as X proceeds down the periodic table. Again the thermochemical values calculated for Y = S are about one-half those for Y = O, and the thermochemical values calculated for Y = Se are about one-third those for Y = O, making the results for S and Se closer to each other than either set of results is to those for oxygen (Tables 1 and 4). As expected for these bond separation reactions, the $T\Delta S$ contribution to ΔG is small and uniform at about 3−5 kJ/mol (Table 4).

NBO Analyses. For both the *Z* and *E* conformations of the $H_3CC(=X)YCH_3$ compounds, the two largest components of the NBO total delocalization energy are associated with the $n_Y \rightarrow \pi^*_{C=X}$ and $n_X \rightarrow \sigma^*_{C-Y}$ orbital interactions (this work and refs 34 and 67). Although the $\Delta E^{(2)}(n_Y \rightarrow \sigma^*_{C=X})$ component is about an order of magnitude smaller than the above components, it is not always negligible, and we have added this anomeric contribution to the $\Delta E^{(2)}(n_Y \rightarrow \pi^*_{C=X})$ contribution to give a combined $\Delta E^{(2)}(n_Y \rightarrow (C=X)^*)$ contribution. The latter energy and $\Delta E^{(2)}(n_X \rightarrow \sigma^*_{C-Y})$ are given in Table 5 for the two conformers. In each case the contributions from both lone pairs on the X or Y atom have also been summed together in the tabulated interaction energies. Other, less important, hyperconjugations include the delocalization of the lone pair electrons into C_1 Rydberg orbitals, into the C_1-C_2 unfilled orbital and into C−H unfilled orbitals. The contribution to the delocalization energy from the former hyperconjugation is significant only when X = O, and the contributions from the latter hyperconjugations are similar for the comparisons made below.

Several of the trends discussed earlier in this section for the $H_3CC(=X)YCH_3$ species can be rationalized on the basis of the lone pair donation into the C=X and C−Y unfilled orbitals (Table 5). For example, while there is not a one-to-one correspondence in the difference in the summed delocalization energy and stability of the *Z* and *E* minima, the lower value of the summed delocalization energy for the *E* conformer is consistent with its lower stability (Table 1). Likewise, for a given X the drop in summed delocalization energy as Y changes from O to Se is consistent with the drop in resonance energy (Table 4). Finally, the bond length changes observed for the C=X and C(X)−Y bonds can be rationalized on the basis of the competition between the $n_Y \rightarrow \pi^*_{C=X}$ and the $n_X \rightarrow \sigma^*_{C-Y}$ hyperconjugations.

TABLE 4: Isodesmic Group Separation Reaction Thermochemistry: Resonance Energies[a]

reaction	ΔH_{298}	ΔG_{298}
$H_3CC(=O)OCH_3 + H_3CCH_3 \rightarrow H_3CC(=O)CH_3 + H_3COCH_3$	94.4 [96.6]	89.5 [91.7]
$H_3CC(=S)OCH_3 + H_3CCH_3 \rightarrow H_3CC(=S)CH_3 + H_3COCH_3$	72.7 [75.2]	68.6 [71.0]
$H_3CC(=Se)OCH_3 + H_3CCH_3 \rightarrow H_3CC(=Se)CH_3 + H_3COCH_3$	69.9 [72.8]	65.9 [69.2]
$H_3CC(=O)SCH_3 + H_3CCH_3 \rightarrow H_3CC(=O)CH_3 + H_3CSCH_3$	35.5 [35.8]	36.8 [36.5]
$H_3CC(=S)SCH_3 + H_3CCH_3 \rightarrow H_3CC(=S)CH_3 + H_3CSCH_3$	37.5 [39.5]	34.5 [36.6]
$H_3CC(=Se)SCH_3 + H_3CCH_3 \rightarrow H_3CC(=Se)CH_3 + H_3CSCH_3$	39.7 [42.3]	35.7 [38.9]
$H_3CC(=O)SeCH_3 + H_3CCH_3 \rightarrow H_3CC(=O)CH_3 + H_3CSeCH_3$	24.7 [26.4]	20.4 [23.6]
$H_3CC(=S)SeCH_3 + H_3CCH_3 \rightarrow H_3CC(=S)CH_3 + H_3CSeCH_3$	25.2 [28.7]	21.1 [26.7]
$H_3CC(=Se)SeCH_3 + H_3CCH_3 \rightarrow H_3CC(=Se)CH_3 + H_3CSeCH_3$	26.8 [30.6]	22.8 [33.3]

[a] G2 and G3 (square brackets) thermochemical data in kJ/mol.

TABLE 5: NBO Analysis[a]

molecule	$\Delta E_0{}^b$	$\Delta E^{(2)}(n_Y \rightarrow (C=X)^*)^c$	$\Delta E^{(2)}(n_X \rightarrow \sigma^*_{C-Y})$	total
$H_3CC(=O)OCH_3$	−94.0 (30.8)	305.7 (254.1)	188.2 (186.7)	493.9 (440.9)
$H_3CC(=S)OCH_3$	−72.4 (32.4)	353.0 (287.1)	119.3 (112.0)	472.3 (399.2)
$H_3CC(=Se)OCH_3$	−69.6 (31.9)	371.7 (306.5)	95.1 (89.1)	466.8 (395.6)
$H_3CC(=O)SCH_3$	−35.9 (18.5)	210.2 (180.1)	168.4 (154.1)	378.6 (334.2)
$H_3CC(=S)SCH_3$	−37.7 (18.3)	284.7 (245.1)	105.2 (81.9)	389.9 (326.9)
$H_3CC(=Se)SCH_3$	−39.8 (17.2)	305.9 (277.1)	85.9 (63.6)	391.9 (340.7)
$H_3CC(=O)SeCH_3$	−24.9 (13.8)	158.4 (138.7)	184.0 (169.5)	342.4 (308.2)
$H_3CC(=S)SeCH_3$	−25.6 (13.5)	225.3 (195.9)	112.0 (86.9)	337.3 (282.8)
$H_3CC(=Se)SeCH_3$	−27.2 (12.8)	255.2 (225.3)	89.9 (65.9)	345.1 (291.2)

[a] All values in kJ/mol. [b] Either the G2 change in energy for reaction 1 or, in parentheses, the energy of the *E* form relative to the *Z* form, at 0 K. [c] Sum of the $n_Y \rightarrow \pi^*_{C=X}$ and $n_Y \rightarrow \sigma^*_{C=X}$ hyperconjugations. The values in parentheses are for the *E* form.

According to the NBO analysis, the preference for the *Z* conformation generally results from enhanced lone pair delocalization into both the C=X and C—Y unfilled orbitals for that conformation (Table 5, this work and ref 31). It is only when Y = O that the latter delocalization plays a lesser role in destabilizing the *E* conformer. On the other hand, the observed decrease in resonance energy for the *Z* conformers as Y proceeds down the periodic table is dominated by diminished $n_Y \rightarrow \pi^*_{C=X}$ and $n_Y \rightarrow \sigma^*_{C=X}$ interactions, which has been reported previously for $H_3CC(=O)OCH_3/H_3CC(=O)SCH_3$.[34] The changes in $n_X \rightarrow \sigma^*_{C-Y}$ interactions are not only smaller; there is also no smooth trend in the changes from O to S to Se. The combination of these two patterns leads to the two most striking sets of results in Table 5, namely, that the difference in the magnitudes of the $\Delta E^{(2)}$ contributions are at least 70 kJ/mol smaller for $H_3CC(=O)SCH_3$ and $H_3CC(=O)SeCH_3$ than for those of the other systems. In fact, the relative magnitudes of the two contributions are reversed for $H_3CC(=O)SeCH_3$. The more competitive $n_X \rightarrow \sigma^*_{C-Y}$ electron delocalization as Y varies for a given X helps to explain the near equivalency of both the bond lengths and bond strengths for (1) the C=X bonds for a given X and (2) the C(X)—Y and Y—CH_3 bonds of $H_3CC(=O)SCH_3$ and $H_3CC(=O)SeCH_3$ (Tables 2 and 3). Regardless of the conformer, there are also opposing trends in the $\Delta E^{(2)}$ values as X goes from O to Se for a specific Y. The charge transfer from the lone pairs on Y into the C=X bonds increases in the order O < S < Se, whereas the charge transfer from the lone pairs on X into the C—Y bond follows the reverse order. The less competitive $n_X \rightarrow \sigma^*_{C-Y}$ electron delocalization as X varies for a given Y correlates with the shortening of the C(X)—Y bond lengths (Table 2). Interestingly, overall, the sums of the delocalization energies are grouped by Y atom and, with the exception of methyl acetate, are nearly independent of atom X, just as are the *Z/E* stabilities and group separation energies.

Other factors that have been shown to influence the relative stabilities of *Z* and *E* conformers of oxo- and thioesters and may play a significant role here include lone pair—lone pair, dipole—dipole, and steric interactions.[31,64,68−70] As Della Védova

et al.[31] have pointed out for methyl thioacetate, both the interactions between the bond dipoles, as measured by the dipole moments, and steric effects, as measured by the C—S—C bond angles, favor the *Z* rotamer. For the remaining eight compounds studied in this work, the dipole moments (Table 1) and C—Y—C bond angles (data not shown) are also smaller for the *Z* form than the *E*, indicating that the same preferential effects are operative in all nine of the $H_3CC(=X)YCH_3$ compounds. Moreover, the decrease in $\Delta\mu(E−Z)$ as Y progresses down group 16 parallels the decrease in *E*−*Z* energy difference (Table 1). Another factor that correlates with the C(X)—Y and Y—CH_3 bond length changes is the % s-character on the Y atom in these bonds, that is, the percent contribution from the s-orbitals of atom Y to the C(X)—Y or Y—CH_3 σ-bond. The data in Tables 1 and 2 obtained from the NBO analysis demonstrate that C(X)—Y bond shortening is accompanied by an increase in % s-character on the Y atom. Because the bond distance and Y-atom % s-character are independent of the nature of X for the Y—CH_3 bonds, there is also a direct relationship between the difference in bond length and the difference in Y-atom % s-character when the C(X)—Y and Y—CH_3 bonds are compared.

Rearrangement Thermochemistry and Barriers to Rearrangement. Analogously to the Schönberg rearrangement for diaryl thioncarbonates[71−73] and to the Newman—Kwart rearrangement for *O*-aryl thiocarbamates,[9,74] a gas-phase thione to thiol rearrangement has been observed experimentally for thioesters, including $H_3CC(=S)OCH_3$.[16−19,75] That the reverse rearrangement from the thermodynamically more favorable *S*-methyl thioacetate to *O*-methyl thioacetate is not observed is consonant with the relatively large difference in stability between the two isomers. The value of 63−66 kJ/mol for the free energy change associated with this rearrangement (Table 6) is in reasonable agreement with the experimental estimate of about 80 kJ/mol.[18,75] Perhaps surprisingly, our calculated enthalpy of reaction (54−56 kJ/mol) is in excellent agreement with the MNDO value of 59 kJ/mol calculated by Lebrilla and Schwarz in their investigation of the unimolecular reactions of the four X, Y = O, S systems.[28] The interconversion from H_3CC-

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TABLE 6: Rearrangement Thermochemistry[a]

reaction	ΔH_{298}	ΔG_{298}
$H_3CC(=S)OCH_3 \rightarrow H_3CC(=O)SCH_3$	−56.3 [−54.2]	−65.6 [−63.0]
$H_3CC(=Se)OCH_3 \rightarrow H_3CC(=O)SeCH_3$	−63.6 [−60.2]	−68.6 [−66.6]
$H_3CC(=Se)SCH_3 \rightarrow H_3CC(=S)SeCH_3$	−0.9 [0.5]	−2.1 [−2.5]

[a] G2 and G3 (square brackets) thermochemical data in kJ/mol.

(=Se)OCH$_3$ to H$_3$CC(=O)SeCH$_3$ is slightly more exothermic and exoergic than that for the analogous sulfur systems; in contrast, the H$_3$CC(=Se)SCH$_3$ to H$_3$CC(=S)SeCH$_3$ interconversion is essentially thermoneutral (Table 6).

Contrary to what has been assumed in the literature,[18,76] the only 1,3-methyl transfer for which $\Delta H \approx \Delta G$ at 298 K is the S→Se transfer (Table 6). At this temperature, the discrepancy between ΔH and ΔG is 9−10 kJ/mol for the O→S methyl transfer but is only 5−6 kJ/mol for O→Se. Because ΔS is positive for all three of these asymmetric rearrangements, the calculations indicate that ΔG will become even more negative with respect to ΔH as the temperature increases.

A generally accepted explanation for the greater stability of carbonyl compounds compared with thiocarbonyl compounds is that there is a relatively poor $\pi_{C,2p}$−$\pi_{S,3p}$ orbital overlap in C−S multiple bonds.[19,77,78] This explanation is supported by the force constant data obtained for methyl acetate and methyl dithioacetate from the normal coordinate analyses performed by Teixeira−Dias et al.[56] In the dioxo case, there is a significant disparity in the force constants associated with the C=O and C(O)−O bonds (10.8 and 6.1 mdyn/Å); in the dithio case there is little disparity in the force constants for the C=S and C(S)−S bonds (4.9 and 4.4 mdyn/Å). These results suggest that the difference in bond order is significantly smaller for the formal CS single and double bonds than for the formal CO single and double bonds.[56] The same conclusion is drawn from the bond critical point densities of the relevant C=X and C−Y bonds (Table 3). At 0.115 the difference in ρ_b for the C=O and C(O)−O bonds of methyl acetate is an order of magnitude larger than that for the C=S and C(S)−S bonds of methyl dithioacetate. Applying the same analysis to methyl diselenoacetate yields the not unexpected $\Delta\rho_b$ = 0.017 for the C=Se and C(Se)−Se bonds, strengthening the rationalization of the greater stability of the carbonyl compounds in terms of more efficient π−π orbital overlap. Correspondingly, the gain in ρ_b for the CO bonds in the H$_3$C(=Y)OCH$_3$ to H$_3$CC(=O)YCH$_3$ (Y = S, Se) rearrangements is an order of magnitude greater than the decrease in ρ_b for the CY bonds. In contrast, the net change in ρ_b is nearly zero for the H$_3$CC(=Se)SCH$_3$ to H$_3$CC(=S)SeCH$_3$ rearrangement, and the individual $\Delta\rho_b$'s are essentially identical to their values in dithioacetate and diselenoacetate. Inasmuch as the bond critical point densities relate to the bond strengths, the above results are consistent with the observed exothermicity of the former reactions and the near thermoneutrality of the latter (Tables 3 and 6). The observed exothermicity and thermoneutrality also correlate with the differential in the attractive interactions between bond dipoles in the two isomeric forms. The $\Delta\mu$ is about ten times smaller for the H$_3$CC(=Se)SCH$_3$ to H$_3$CC(=S)SeCH$_3$ interconversion than for the other two interconversions (Tables 1 and 6).

It should be noted that, according to the NBO analysis, enhanced electron delocalization does not account for the observed X=C−Y and Y=C−X relative isomer energies. In all three cases the resonance energy is smaller for the more stable isomer, as is the total delocalization energy (Tables 5 and 6), implying that π-bond energy dominates over resonance in the relative stabilities of these isomers. This interpretation was also

TABLE 7: Barrier Heights for C−Y ↔ C=X Me-Group Transfers[a]

reaction	$\Delta(E + Z \text{ PE})$	ΔG_{298}
$H_3CC(=O)OCH_3 \rightarrow H_3CC(=O)OCH_3$	222 [223]	219 [219]
$H_3CC(=S)OCH_3 \rightarrow H_3CC(=O)SCH_3$	201 [202]	199 [199]
$H_3CC(=O)SCH_3 \rightarrow H_3CC(=S)OCH_3$	259 [258]	264 [263]
$H_3CC(=Se)OCH_3 \rightarrow H_3CC(=O)SeCH_3$	192 [193]	190 [191]
$H_3CC(=O)SeCH_3 \rightarrow H_3CC(=Se)OCH_3$	257 [255]	259 [257]
$H_3CC(=S)SCH_3 \rightarrow H_3CC(=S)SCH_3$	241 [239]	241 [239]
$H_3CC(=Se)SCH_3 \rightarrow H_3CC(=S)SeCH_3$	233 [232]	232 [228]
$H_3CC(=S)SeCH_3 \rightarrow H_3CC(=Se)SCH_3$	235 [232]	234 [230]
$H_3CC(=Se)SeCH_3 \rightarrow H_3CC(=Se)SeCH_3$	227 [225]	226 [230]

[a] G2 and G3 (square brackets) data in kJ/mol.

invoked to explain the facility with which keto−enol tautomerism occurs for a series of H$_3$CC(=X)Y molecules, including X = O, S, Se, Te and Y = H, CH$_3$.[45,79] In the keto−enol equilibrium, the competition for the π electrons is between C=X and C=C bonds, and the equilibrium shifts toward the enol as X advances from O to Te. For the related HC(=Se)OH system, the enol isomer is more stable by 17.5 kJ/mol at the G2 level of theory.[26] Similarly, in accord with the experimental results, B3LYP/cc-pVTZ(-f) calculations indicate that the C(=Se)NH backbone of the selone tautomer of 1-mesityl-1,3-dihydro-imidazole-2-selone is preferred over the C(SeH)N backbone of the selenol tautomer, by 45 kJ/mol.[80]

The two most likely mechanisms by which the rearrangement reactions occur are (1) an intramolecular methyl group transfer and (2) a homolytic cleavage of the Y−CH$_3$ bond and subsequent X−CH$_3$ bond formation. The latter mechanism has been excluded by several research groups[17,75,81] because, for example, cothermolysis of a mixture of H$_3$CC(^{18}O)OCH$_3$ and [^{2}H$_3$] methyl acetate showed no crossover of the methyl group[81] and cothermolysis of a series of thionacetates with cyclohexene showed no reduction in reaction rate.[17] Hence, only the concerted pathway via a four-centered cyclic transition state has been considered in this work. The barrier heights associated with the three symmetric and three asymmetric rearrangements (Figure 1) are listed in Table 7. The designation **TS−YX** indicates the preferred Y→X direction of methyl transfer for the asymmetric reactions, but for convenience and to help detect trends, barrier heights in both directions have been tabulated for those reactions.

The transition structures for the three X→X 1,3-methyl migrations have C$_S$ symmetry and equal H$_3$C···X distances; the transition structures for the three Y→X methyl migrations have C$_1$ symmetry and H$_3$C···X and H$_3$C···Y distances within 0.01 Å of those in the corresponding transition structures for the symmetric reactions (Table 2). Likewise, the C−X and C−Y distances of the stationary carbon to X and Y in **TS−OS**, **TS−OSe**, and **TS−SSe** are within 0.01 Å of the two equal corresponding C−X distances in **TS−OO**, **TS−SS**, and **TS−SeSe**. Analogous XCY and X···H$_3$C···Y bond angles are within 3° of each other. In all cases, the reaction proceeds through an asynchronous transition structure with a nearly planar four-membered ring (Table 2 and Figure 1). The breaking of the CX double bond (23−34%) significantly trails the forming of the CY double bond (65−75%). In agreement with the Hammond−Leffler postulate,[82] the transition structures for the O→S and O→Se 1,3-methyl shifts are early, with short breaking H$_3$C···Y bonds (42 and 40%, respectively) and long forming H$_3$C···X bonds (41 and 39%, respectively).

The only activation parameters derived from the experiment for these rearrangement reactions are those for the H$_3$CC(=S)OCH$_3$ to H$_3$CC(=O)SCH$_3$ 1,3-methyl switch. The experi-

TABLE 8: Enthalpies of Formation[a]

molecule	$\Delta_f H_{298}$(calc)	$\Delta_f H_{298}$(exp)
$H_3CC(=O)OCH_3$	−413 [−415]	−410[b]
$H_3CC(=S)OCH_3$	−149 [−150]	
$H_3CC(=Se)OCH_3$	−78[c] [−83][c]	
$H_3CC(=O)SCH_3$	−208 [−208]	
$H_3CC(=S)SCH_3$	32 [32]	
$H_3CC(=Se)SCH_3$	101[c] [96][c]	
$H_3CC(=O)SeCH_3$	−142 [−144]	
$H_3CC(=S)SeCH_3$	100 [96]	

[a] G2 and G3 (square brackets) data in kJ/mol calculated from reaction 1, unless otherwise noted. [b] Ref 4. [c] Calculated from reaction 2.

mental activation energies of 195 kJ/mol[75] and 192 kJ/mol[17] are reproduced well by our computed barrier height of about 200 kJ/mol (Table 7). The 20 kJ/mol higher barrier for the O→O exchange than for the O→S exchange is consistent with the experimentally observed smaller percentage of methyl migration for the former process than for the latter at the same temperature.[18,81] That the barrier height for the S→S methyl transfer is some 20 kJ/mol above that for the O→O transfer (Table 7) may help to clarify the lack of intramolecular exchange and preferred thioketene formation found by Carlsen and Egsgaard in their gas-phase pyrolysis of $H_3C(^{34}S)SCH_3$.[83] Our support of the experimental results for methyl dithioacetate is not duplicated by the MNDO calculations of Lebrilla and Schwarz.[28] At 249 kJ/mol, the MNDO barrier height obtained for the 1,3-methyl migration in this compound is in good agreement with our value of about 240 kJ/mol. However, the MNDO calculations do not predict the same trend in barrier heights as do the G2 and G3 calculations. The MNDO barriers for O-methyl thioacetate and methyl acetate are some 45 and 100 kJ/mol larger than that for methyl dithioacetate. The MNDO results also indicate that intramolecular exchange has the lowest barrier of the pathways examined for the unimolecular reactions of $H_3CC(=S)SCH_3$.[28]

The 1,3-methyl shift with the lowest computed barrier height is that from O→Se, suggesting that the rearrangement for $H_3CC(=Se)OCH_3$ may be more facile than that for $H_3CC(=S)OCH_3$ (Table 7). Nonetheless, the barrier for the O→Se methyl shift is more than 2.5 times larger in magnitude than the G2 barrier for the O→Se hydrogen shift in $HC(=Se)OH$ (72 kJ/mol).[26] The height of the methyl transfer barrier for $H_3C(=Se)SeCH_3$ is some 5 kJ/mol higher than that for $H_3CC(=O)OCH_3$; thus, the transfer might be observed within the same temperature range studied for methyl acetate and O-methyl thioacetate.[18,81] On the other hand, the barrier for the essentially thermoneutral $H_3CC(=Se)SCH_3$ to $H_3CC(=S)SeCH_3$ interconversion is the second largest for the forward reactions, and formation of thioketene or selenoketene via a 1,3-hydrogen shift may be preferred over a methyl shift. Overall, for a given X, methyl transfer from oxygen is favored by about 40 kJ/mol compared with that from sulfur or selenium. For a given Y methyl transfer to oxygen is least favored, and the barrier heights decrease by about 10−20 kJ/mol as X proceeds down the group.

Enthalpies of Formation. Enthalpies of formation have been calculated for all compounds other than methyl diselenoacetate (Table 8, this work and refs 4 and 48). Because no enthalpy of formation is available for $(CH_3)_2CSe$, only $\Delta_f H_{298}$ values for the systems with X ≠ Se could be evaluated using the isodesmic group separation reactions (eq 1, Table 4). The values for $H_3CC(=Se)OCH_3$ and $H_3CC(=Se)SCH_3$ were then estimated from the rearrangement reactions (eq 2, Table 6) and the calculated enthalpies of formation for the relevant Y = Se

products. As a measure of the error in the enthalpies of formation determined with the latter approach, we have computed the enthalpy of formation of $H_3CC(=S)OCH_3$ using both methods. The two values concur to within 4 kJ/mol (G2: −149 vs −152, G3: −150 vs −154 kJ/mol).

As seen in Table 8 for methyl acetate, the one compound for which a comparison can be made, the agreement between the theoretical and the experimental enthalpies of formation is excellent. One may ask, however, whether the predicted enthalpies of formation of the remaining diverse S and Se containing derivatives of methyl acetate are plausible. The paucity of archival experimental data restricts this comparison to just S-methyl thioacetate and the suggested value of −208 kJ/mol. A reasonable assumption is that there is a nearly constant difference between the enthalpies of formation of S-alkyl thioacetates and alkyl methyl thioethers, at least for n-alkyl species. This is equivalent to the assumption that the following isodesmic reaction is thermoneutral.

$$CH_3C(=O)-S-R + CH_3-S-CH_3 \rightarrow$$
$$CH_3C(=O)-S-CH_3 + CH_3-S-R \quad (3)$$
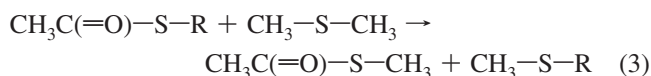
Using Pedley's compendium[3] as a unified source of data for these species, this assumption is confirmed for the ethyl, n-propyl, and n-butyl species: the three values are 168.5 ± 1.4, 168.2 ± 1.3, and 168.2 ± 1.3 kJ/mol, resulting in an average difference of −168.3 ± 2.3 kJ/mol. Combined with the archival enthalpy of formation of dimethyl sulfide of −37.4 ± 0.6 kJ/mol, the derived value is −206 kJ/mol, and with an uncertainty of almost 3 kJ/mol, quantum chemical calculation and estimate concur giving confidence in the remaining newly suggested values. Alternatively, one could assume that there is a nearly constant difference between the enthalpies of formation of S-alkyl thioacetates and alkyl methyl ketones (2-alkanones), at least for n-alkyl species. This is equivalent to the assumption that the following isodesmic reaction is thermoneutral.

$$CH_3C(=O)-S-R + CH_3-C(=O)-CH_3 \rightarrow$$
$$CH_3C(=O)-S-CH_3 + CH_3-C(=O)-R \quad (4)$$
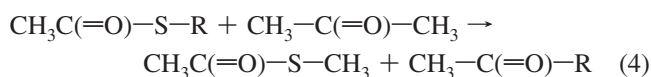
Again, from Pedley,[3] this assumption is confirmed: the three values are 10.4 ± 0.9, 8.1 ± 1.3, and 8.3 ± 1.5, resulting in an average difference of 8.9 ± 2.2 kJ/mol. Combined with the archival enthalpy of formation of dimethyl ketone (acetone) of −37.4 ± 0.6 kJ/mol, the derived value is −208 kJ/mol, and with an uncertainty of again almost 3 kJ/mol, quantum chemical calculation and estimate again concur giving confidence in the remaining newly suggested values.

The $\Delta_f H_{298}$ values become more positive as the chalcogen changes from oxygen to selenium when either X or Y is held constant. Moreover, for this set of compounds, the change in the magnitude of $\Delta_f H_{298}$ from sulfur to selenium is essentially independent of the identity of X (∼65 kJ/mol). Extending this pattern to $H_3CC(=Se)SeCH_3$ allows us to approximate its enthalpy of formation as ∼165 kJ/mol.

The same trend in the enthalpies of formation of $H_3CC(=O)OCH_3$, $H_3CC(=O)SCH_3$, $H_3CC(=S)OCH_3$, and $H_3CC(=S)SCH_3$ was obtained with the MNDO calculations.[28] Although the MNDO values tend to be too negative with respect to the G2 and G3 values, the Gn values are reproduced to within 15 kJ/mol.

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Conclusions

Two key results of this work on $H_3CC(=X)YCH_3$ (X, Y = O, S, Se) are that the resonance energies and relative *Z/E* conformer energies of the compounds are grouped by the Y atom in the X=C—Y framework and that, as has been found previously, the thermodynamic properties of the compounds containing third- and fourth-row atoms are close to each other and different from those containing second-row atoms. The changes in resonance energies, C=X and C(X)—Y bond lengths, and rotamer stabilities correlate with the magnitudes of the $n_Y{\rightarrow}\pi^*_{C=X}$, $n_Y{\rightarrow}\sigma^*_{C=X}$, and $n_X{\rightarrow}\sigma^*_{C-Y}$ electron delocalizations, whereas the dominant factor in the relative stabilities of $H_3CC(=X)YCH_3$ and $H_3CC(=Y)XCH_3$, $X \neq Y$, appears to be the competition between the C=X and C=Y π-bond energies. The intramolecular 1,3-methyl transfer reactions of these compounds proceed through asynchronous transition structures with nearly planar four-membered rings. The relative barrier heights for the O→O, O→S, and S→S methyl transfers are consistent with the lack of intramolecular exchange and preferred thioketene formation found experimentally for $H_3C(=S)SCH_3$. The calculations also suggest that interconversion is less likely to occur from S to Se than from O to Se or from Se to Se. The enthalpies of formation obtained for these compounds become more positive as the chalcogen goes down group 16.

Supporting Information Available: Tables S1 and S2 listing Cartesian coordinates and thermochemical data (energies, enthalpies, and free energies), respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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