Theoretical studies on thiocarbonyl group transfer reactions†

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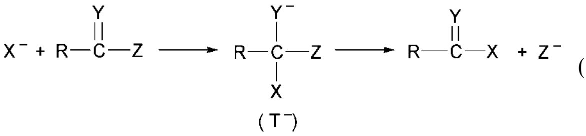
The gas-phase thiocarbonyl transfer reactions $X^- + RC(=S)Z \rightleftharpoons RC(=S)X + Z^-$ have been investigated with X, Z = Cl, Br and R = H, CH_3 at the MP2 and G2(+) levels using the MP2/6-311+G** optimized geometries. The thiocarbonyl transfers proceed by a stepwise mechanism through a triple-well potential energy surface involving a tetrahedral intermediate, T^-. The strong proclivity toward the stepwise path is caused mainly by the low-lying $\pi^*_{C=S}$ level coupled with the high energy σ^*_{C-Z} orbital. The reaction barriers, $\Delta G^{\neq}$, are higher than the corresponding values for the carbonyl transfers, excepting for the X = Z = Cl case at the G2(+) level. The major factors for these elevated barriers, despite the low deformation energies (ΔE_{def}), are lower proximate σ–σ* charge transfer energies ($\delta\Delta E^{(2)}_{\sigma-\sigma^*}$) and the relatively high electrostatic repulsion ($\Delta E_{es} > 0$) in the transition state due to the highly polarized structure with a large negative charge on the S atom. The occurrence of a well-defined intermediate, T^-, in the reaction coordinate leads to a relatively early transition state with a low degree of bond making and breaking in the transition state.

Carbonyl addition reactions have been extensively studied in the gas phase as well as in solution.[1] Experimental results suggested that acyl transfer reactions proceed through a tetrahedral adduct, T^-, which can be either a stable intermediate (stepwise mechanism) or a transition state (concerted mechanism).[2] Theoretical analyses[1,3] have shown that the stepwise mechanism through an out-of-plane π-attack ($S_N\pi$) is favored by a large orbital energy gap between the $\pi^*_{C=O}$ (Y = O) and σ^*_{C-Z} levels; the wider the gap, $\Delta\varepsilon = \varepsilon_{\sigma^*} - \varepsilon_{\pi^*}$, the greater is the possibility of proceeding by the stepwise mechanism involving a tetrahedral intermediate.[4]



$$X^- + R-\overset{\overset{\displaystyle Y}{\|}}{C}-Z \longrightarrow R-\underset{\underset{\displaystyle X}{|}}{\overset{\overset{\displaystyle Y^-}{|}}{C}}-Z \longrightarrow R-\overset{\overset{\displaystyle Y}{\|}}{C}-X + Z^- \quad (1)$$

On the other hand, experimental results of thiocarbonyl [Y = S in eqn. (1)] transfer reactions in solution have shown a greater proclivity toward a stepwise mechanism than the carbonyl (Y = O) transfers, mainly due to the greater stability of the tetrahedral adducts.[5] We are not aware of any reports on gas-phase experiments for the thiocarbonyl transfers. However, limited theoretical as well as experimental results have shown that there are important similarities and differences between the carbonyl and thiocarbonyl group transfer mechanisms, such that a detailed high-level MO theoretical analysis of the thiocarbonyl transfer reactions is warranted to shed more light on the thiocarbonyl transfer mechanism. In this work, we carried out a G2(+)//MP2/6-311+G** level investigation on the thiocarbonyl group transfer reactions with X, Z = Cl, Br and R = H, CH_3 in eqn. (1) where Y = S.

Calculations

Calculations were carried out using the GAUSSIAN 98 set of programs.[6] Geometries of reactants, products and stationary point structures were fully optimized at the MP2/6-311+G** level. Stationary points were characterized by harmonic vibrational analysis employing energy Hessians at the same level. Energies (ΔE) were obtained at the MP2 and G2(+) levels[7] and corrected for zero point energies (ZPE) by application of appropriate scaling factors,[8] and thermal energies (ΔH), and applied entropies (ΔS) to arrive at free energy changes (ΔG) at 298 K. All the energy changes reported (ΔE, ΔH and ΔG) are relative to the separated reactants level. The natural bond orbital (NBO) analyses[9] were performed to determine π* and σ* levels, formal charges and the proximate σ–σ* (including *n*–σ*, *n*–π*, *etc.*) charge transfer energies. The percentage bond order changes, $\%\Delta n^{\neq}$,[10] at the stationary points, that is, transition states (TSs) and intermediates [int.(T^-)], were calculated using eqn. (2), where $r^{\neq}$, r_R and r_P are the bond lengths in the TS (or intermediate), reactant and product, respectively. The value $a = 0.6$ was used for r_{C-X} and r_{C-Z}, and $a = 0.3$ for $r_{C=S}$.[10]

$$\%\Delta n^{\neq} = \frac{\exp(-r^{\neq}/a) - \exp(-r_R/a)}{\exp(-r_P/a) - \exp(-r_R/a)} \times 100 \qquad (2)$$

Results and discussion

Comparison of the C–Z (C–Cl and C–Br) bond lengths in the carbonyl and thiocarbonyl compounds shows that the C–Z bonds in the thiocarbonyl are uniformly shorter by *ca.* 0.03–0.04 Å than those in the carbonyl halides. This is mainly due to the greater ionic bond character[11] in the thiocarbonyl than carbonyl since the C=S bond is partially polarized to $C^{\delta+}$–$S^{\delta-}$ and this leads to $C^{\delta+}$–$Z^{\delta-}$ charge separation. In contrast, both the C=Y and C–Z bonds are longer by *ca.* 0.01–0.02 Å with R = CH_3 than with R = H, reflecting the electron-donating effect of the methyl group, which reduces the positive charge on the carbon and weakens the charge separation.

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† Electronic supplementary information (ESI) available: structures and energies of the reaction complexes (RCs), deformation energies, MO level energies and charge densities. See http://www.rsc.org/suppdata/nj/b0/b010202o/

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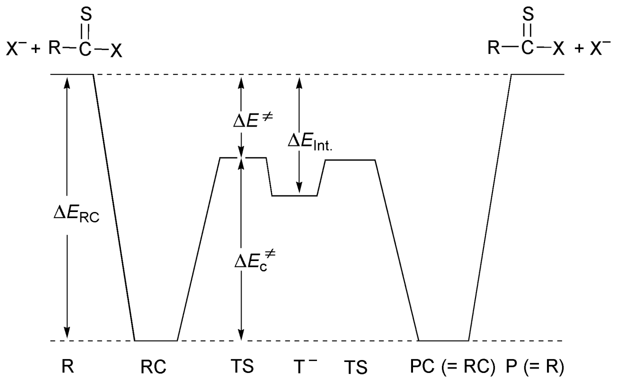


Scheme 1

Loose ion-dipole complexes (RCs) are formed electrostatically between the nucleophile (X^-) and the reactants. The structures and energies relative to the separated reactants (ΔE_{RC}) are given in the ESI. The well depths (ΔE_{RC}) are *ca.* 3 kcal mol^{-1} shallower with $R = CH_3$ than with R = H, reflecting again the electron-donating effect of the methyl group, which weakens the charge separation within the substrate and leads to a decrease in the electrostatic energy. Since in the identity exchanges (X = Z) of the thiocarbonyl group between the halides (Scheme 1), intermediates (T^-) are formed in all cases (albeit stabilities are low), the barriers, $\Delta E_c^{\neq}(=E_{TS} - E_{RC})$, do not represent the intrinsic barriers ($\Delta E_c^{\neq} \neq \Delta E_o^{\neq}$) since the TS is not located at the central position due to the presence of the adduct T^-. The intrinsic barriers $\Delta E_o^{\neq}$ corresponds to the central barrier in the case of the thermoneutral reaction without the stable adduct T^-. The well depths, $\Delta E^{\neq} - \Delta E_{Int.}$, are *ca.* 2 kcal mol^{-1} for X = Z = Cl but are much shallower at *ca.* 0.6 kcal mol^{-1} for X = Z = Br at the G2(+) level. Nevertheless, these are distinctly non-zero and the gas-phase thiocarbonyl transfer (with R = H and CH_3) proceeds stepwise through a triple-well potential energy surface (PES) involving a tetrahedral intermediate, T^-. This triple-well PES was confirmed and it was found that the TS was located on the reaction path from RC to T^- for the reaction with R = H and X = Z = Cl by performing intrinsic reaction coordinate calculations[12] at the MP2 level. This is in contrast to the corresponding carbonyl transfers[1,3] in which the transition structure regions were quite flat with hardly recognizable well depths ($\Delta E^{\neq} - \Delta E_{Int.} \leq 0.01$ kcal mol^{-1}) so that the reactions exhibit a borderline behavior with a double-well type PES.

The energetics at the MP2/6-311+G** and G2(+) levels are summarized in Tables 1 and 2, respectively. All the energy changes, $\Delta E^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$, are relative to the separated reactants level. In all cases, the stronger nucleophile, X = Cl, leads to a lower barrier, $\Delta G^{\neq}$, as well as a more stable intermediate, $\Delta G_{Int.}$ than X = Br, the weaker nucleophile. For the symmetric exchanges, X = Z, the TSs have C_1 and the intermediates C_s symmetries for the out-of-plane π-attack ($S_N\pi$)

Table 1 Energetics at the MP2/6-311+G** level in kcal mol^{-1}

R	X	Z	Adduct	Sym.	$\Delta E^{\neq}$	$\Delta E^{\neq}$(ZPE)	$\Delta H^{\neq}$	$T\Delta S^{\neq}$	$\Delta G^{\neq}$	$\Delta G^{\circ a}$
H	Cl	Cl	π-int.(T^-)	C_s	−10.56	−9.64	−10.27	−8.07	−2.20	0
			π-TS	C_1	−8.09	−7.66	−8.47	−8.20	−0.27	
			σ	C_{2v}	18.69	16.89	16.52	−7.24	23.75	
	Br	Br	π-int.(T^-)	C_s	−6.07	−5.75	−5.96	−7.07	1.12	0
			π-TS	C_1	−5.91	−5.67	−6.36	−8.24	1.87	
			σ	C_{2v}	13.57	11.90	11.59	−7.13	18.72	
	Cl	Br	π-TS	C_1	−9.04	−8.73	−9.43	−7.99	−1.44	−10.63
			σ	C_s	10.40	8.89	8.50	−6.81	15.30	
	Br	Cl	π-TS	C_1	2.06	1.93	1.34	−7.85	9.19	10.63
			σ	C_s	21.51	19.55	19.26	−6.68	25.93	
CH_3	Cl	Cl	π-int.(T^-)	C_s	−9.38	−8.68	−9.34	−8.82	−0.51	0
			π-TS	C_1	−6.83	−6.44	−7.25	−8.85	1.60	
	Br	Br	π-int.(T^-)	C_s	−4.36	−4.16	−4.36	−7.72	3.34	0
			π-TS	C_1	−4.22	−4.03	−4.72	−8.90	4.17	
	Cl	Br	π-TS	C_1	−7.81	−7.44	−8.15	−8.63	0.48	−10.71
	Br	Cl	π-TS	C_1	3.33	3.29	2.71	−8.48	11.19	10.71

[a] ΔG = Gibbs free energy difference between products and reactants.

Table 2 Energetics at the G2(+) level in kcal mol^{-1}

R	X	Z	Adduct	Sym.	$\Delta E^{\neq}$(ZPE)	$\Delta H^{\neq}$	$T\Delta S^{\neq}$	$\Delta G^{\neq}$	$\Delta G^{\circ a}$
H	Cl	Cl	π-int.(T^-)	C_s	−12.54	−13.16	−8.07	−5.10	0
			π-TS	C_1	−10.37	−11.17	−8.20	−2.98	
			σ	C_{2v}	14.31	13.93	−7.24	21.17	
	Br	Br	π-int.(T^-)	C_s	−7.16	−7.37	−7.07	−0.30	0
			π-TS	C_1	−7.14	−7.84	−8.24	0.40	
			σ	C_{2v}	10.78	10.47	−7.13	17.59	
	Cl	Br	π-TS	C_1	−11.37	−12.07	−7.99	−4.08	−11.13
			σ	C_s	6.59	6.20	−6.81	13.01	
	Br	Cl	π-TS	C_1	−0.20	−0.80	−7.85	7.05	11.13
			σ	C_s	17.76	17.47	−6.68	24.14	
CH_3	Cl	Cl	π-int.(T^-)	C_s	−10.03	−10.69	−8.82	−1.87	0
			π-TS	C_1	−8.15	−8.96	−8.85	−0.11	
	Br	Br	π-int.(T^-)	C_s	−4.29	−4.49	−7.72	3.22	0
			π-TS	C_1	−4.40	−5.09	−8.90	3.80	
	Cl	Br	π-TS	C_1	−9.27	−9.98	−8.63	−1.35	−11.21
	Br	Cl	π-TS	C_1	1.95	1.37	−8.48	9.86	11.21

[a] ΔG = Gibbs free energy difference between products and reactants.

Table 3 Second-order σ–σ* charge transfer energy changes, $\delta\Delta E^{(2)}_{\sigma\text{–}\sigma^*} = \Sigma\Delta E^{(2)}_{\sigma\text{–}\sigma^*}(\mathrm{T}^-) - \Sigma\Delta E^{(2)}_{\sigma\text{–}\sigma^*}(\mathrm{R})$, and electrostatic interaction energies, $\Sigma\Delta E_{\mathrm{es}}$, in kcal mol^{-1}

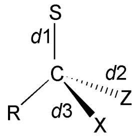
R	X	Z	Adduct	Sym.	$\delta\Delta E^{(2)}_{\sigma\text{–}\sigma^*}$	$\Sigma\Delta E_{\mathrm{es}}$
H	Cl	Cl	π-int.(T$^-$)	C_s	−43	37.25
			π-TS	C_1	−129(−212)[a]	33.78
			σ	C_{2v}	−33	−50.55
	Br	Br	π-int.(T$^-$)	C_s	−102	43.55
			π-TS	C_1	−166(−259)	41.10
			σ	C_{2v}	−33	−42.12
	Cl	Br	π-TS	C_1	−88	31.02
			σ	C_1	−42	−45.79
	Br	Cl	π-TS	C_1	−83	29.07
			σ	C_1	−37	−47.74
CH_3	Cl	Cl	π-int.(T$^-$)	C_s	−36	33.94
			π-TS	C_1	−106(−221)	33.53
	Br	Br	π-int.(T$^-$)	C_s	−107	44.90
			π-TS	C_1	−167(−293)	42.98
	Cl	Br	π-TS	C_1	−73	33.03
	Br	Cl	π-TS	C_1	−70	28.85

[a] The values in parentheses are those for the corresponding carbonyl transfers.

processes. The in-plane σ-attack processes with C_{2v} symmetry ($S_N\sigma$) have much larger barriers ($\Delta G^{\neq} > 16$ kcal mol^{-1}) than the corresponding $S_N\pi$ processes. Characterization of the TS for the $S_N\sigma$ process has shown that there are two imaginary vibrational frequencies, that is, it is a second-order saddle point,[13] corresponding to a species in the inversion profile of the $S_N\pi$-type TSs (C_1 symmetry) and located at a maximum with respect to two mutually perpendicular directions.[13] This was confirmed by the normal mode analysis. The imaginary frequency corresponding to the inversion mode arises from the constraint of keeping the C_{2v} symmetry in the TS for the $S_N\sigma$ process.

The activation barriers $\Delta G^{\neq}$ to the thiocarbonyl transfers (*e.g.*, $\Delta G^{\neq} = -0.3$ kcal mol^{-1} for X = Z = Cl with R = H) are higher in all cases than for the corresponding carbonyl transfers ($\Delta G^{\neq} = -1.9$ kcal mol^{-1} for X = Z = Cl with R = H)[1] at the MP2 level. However, at the G2(+) level, the barrier heights for the symmetric chloride exchanges (X = Z = Cl) become lower for the thiocarbonyl ($\Delta G^{\neq} = -3.0$ and -1.9 kcal mol^{-1} for R = H and CH_3, respectively) than for the carbonyl transfers ($\Delta G^{\neq} = -1.6$ and $+0.6$ kcal mol^{-1} for R = H and CH_3, respectively).[1] It has been shown that the major stabilizing factor within the relatively tight $S_N\pi$ TSs is the proximate σ–σ* charge transfer interactions, ΔE_{ct}.[1,3,4] This stabilization appears to be much less for the thiocarbonyl than for the carbonyl transfers (Table 3, $\delta\Delta E^{(2)}_{\sigma\text{–}\sigma^*}$) due mainly to the greater initial σ–σ* charge transfer stabilization, $\Delta E^{(2)}_{\sigma\text{–}\sigma^*}(\mathrm{R})$, within the reactants, which leads to a lesser

Table 4 Bond lengths (in Å) and percentage bond order changes, calculated at the MP2/6-311+G** level



R	X	Z	Bond	Reactant	π-int.(T$^-$)	π-TS	σ	%Δ*n*[π-int.(T$^-$)]	%Δ*n*(π-TS)	%Δ*n*(σ)
H	Cl	Cl	*d*1	1.603	1.699	1.632	1.523	27.4	9.2	−30.6
			*d*2	1.737	1.895	1.794	2.594	23.2	9.1	76.0
			*d*3	∞	1.895	2.389	2.594	76.8	33.7	24.0
	Br	Br	*d*1	1.601	1.651	1.634	1.524	15.4	10.4	−29.3
			*d*2	1.909	2.151	2.03	2.757	33.2	18.3	75.7
			*d*3	∞	2.151	2.406	2.757	66.8	43.7	24.3
	Cl	Br	*d*1	1.601	—	1.617	1.524	—	5.2	−29.3
			*d*2	1.909	—	1.971	2.84	—	9.8	78.8
			*d*3	∞	—	2.507	2.518	—	27.7	27.2
	Br	Cl	*d*1	1.603	—	1.617	1.524	—	4.6	−30.1
			*d*2	1.737	—	2.507	2.518	—	72.3	72.8
			*d*3	∞	—	1.971	2.84	—	90.2	21.2
CH_3	Cl	Cl	*d*1	1.609	1.708	1.605	—	28.1	8.3	—
			*d*2	1.759	1.904	1.807	—	21.5	7.7	—
			*d*3	∞	1.904	2.43	—	78.5	32.7	—
	Br	Br	*d*1	1.607	1.653	1.636	—	14.2	9.2	—
			*d*2	1.937	2.181	2.057	—	33.4	18.1	—
			*d*3	∞	2.181	2.441	—	66.6	43.2	—
	Cl	Br	*d*1	1.607	—	1.619	—	—	3.9	—
			*d*2	1.937	—	1.993	—	—	8.9	—
			*d*3	∞	—	2.558	—	—	26.4	—
	Br	Cl	*d*1	1.609	—	1.619	—	—	3.3	—
			*d*2	1.759	—	2.558	—	—	73.6	—
			*d*3	∞	—	1.993	—	—	91.1	—

increase in $\Delta E^{(2)}_{\sigma-\sigma^*}$ upon adduct formation in the TS, that is, $\delta\Delta E^{(2)}_{\sigma-\sigma^*} = \Delta E^{(2)}_{\sigma-\sigma^*}(T^-) - \Delta E^{(2)}_{\sigma-\sigma^*}(R)$ is smaller. The initial state σ–σ* charge transfer is greater for the thiocarbonyl due to much lower $\pi^*_{C=S}$ levels compared to the corresponding $\pi^*_{C=O}$ in the carbonyl compounds.[1]

On the other hand, correlation energies for the π-adducts are known to be overestimated in the MP2 calculations.[14] This trend seems to lower the chloride exchange barriers for the carbonyl transfers too much so that the MP2 energies become lower than those for the thiocarbonyl transfers, which are restored to the correct relative level in the G2(+) results. The overestimation of the correlation energy in the MP2-level chloride exchange barrier for the carbonyl transfer may result from a large difference in the $S_N\pi$ TS structure between carbonyl and thiocarbonyl transfers; for the former, the percentage bond formation and cleavage, $\%\Delta n^{\neq}$, are 61 and 39% (Table 4), whereas for the latter the corresponding values are 34 and 9%, so that the TS is more balanced in the carbonyl transfer than the much earlier TS structure in the thiocarbonyl transfer.

Reference to Table 4 reveals that the degree of bond formation at the TS is greater for the bromide ($\%\Delta n^{\neq} = 44$ and 43% for R = H and CH_3) than for the chloride exchanges (34 and 33% for R = H and CH_3). This may seem to contradict our recent prediction that the lower the (intrinsic) barrier [*e.g.*, $\Delta E^{\neq} = -8.2$ *vs.* -4.4 kcal mol^{-1} for Cl^- and Br^- exchanges, respectively, with R = CH_3 at the G2(+) level] the greater is the degree of bond formation.[15] However, this prediction applies strictly to the intrinsic barriers $\Delta E^{\neq}_o$, that is, the barriers in the thermoneutral reactions[15] ($\Delta E^\circ = 0$), but the barriers noted above are not for the thermoneutral processes. In fact, the extent of bond formation in the TS found is in accord with that expected thermodynamically, since the presence of the intermediate T^- leads to an endothermic-type process. Thermodynamically, the TS is located later on the reaction coordinate as the reaction is more endothermic[16] ($\Delta E_{Int.} = -10.3$ *vs.* -4.3 kcal mol^{-1} with R = CH_3 for Cl^- and Br^- exchanges). The intermediate T^- is located in a truely thermoneutral position, and hence the prediction is borne out when we consider the $\%\Delta n^{\neq}$ values on going from the reactants to intermediate, $\%\Delta n^{\neq} = 77$ *vs.* 67% for Cl^- *vs.* Br^- (well depths $\Delta E^{\neq} - \Delta E_{Int.}$ are 2.6 and 0.2 kcal mol^{-1} with R = H at the MP2/6-311+G** level). In the carbonyl transfers the intermediates are practically nonexistent with $\Delta E^{\neq} \cong \Delta E_{Int.}$ ($\cong \Delta E^{\neq}_o$) so that the $\%\Delta n^{\neq}$ values are in accord with the prediction: 61 *vs.* 58% for Cl^- *vs.* Br^- for which the $\Delta E^{\neq}_o$ values are -7.9 and -6.8 kcal mol^{-1} with R = H at the MP2/6-311+G** level. Since the degree of bond breaking in the TS for the thiocarbonyl transfer is much smaller (Table 4), the deformation energies, $\Delta E^{\neq}_{def}$, are accordingly much smaller than for the carbonyl transfers (see ESI).

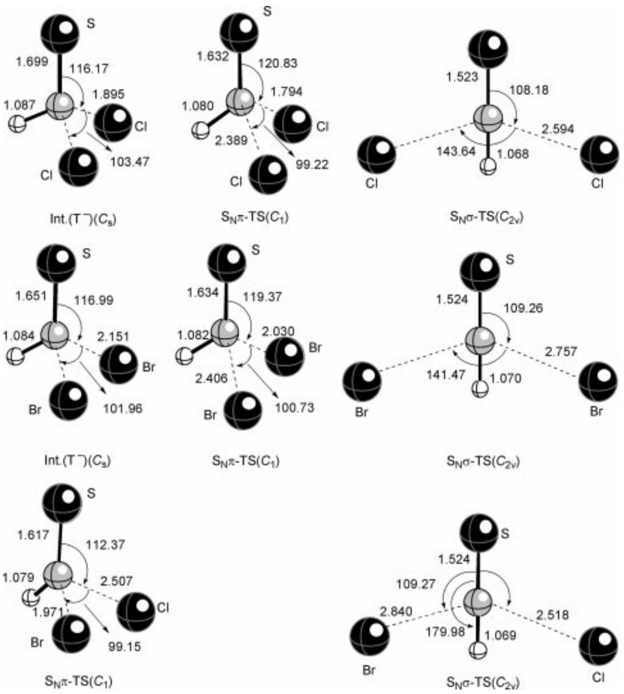


Fig. 1 The structures of the TS and intermediate with R = H.

The TS and intermediate structures are shown in Fig. 1 and 2. For the non-symmetric transfers, X ≠ Z, the relatively large endo- (or exo-) thermicity [$\delta\Delta G^\circ \simeq 11$ kcal mol^{-1} at the G2(+) level] leads to the single adduct corresponding to the tetrahedral TS (C_1) with no intermediate formation. The reaction barriers are largely controlled by the thermodynamic driving force, ΔG°.[16] The $S_N\sigma$ pathways have rather higher activation barriers, by *ca.* 17 kcal mol^{-1}, than the $S_N\pi$ paths so that the gas-phase reactions of the thiocarbonyl transfers should proceed through an out-of-plane π-attack pathway. An important difference between the carbonyl and thiocarbonyl transfers is that the stretching of the C=S bond (9–10% for X = Z) upon adduct (TS) formation is much greater than that of the C=O bond (1–3%) due to the much lower $\pi^*_{C=S}$ (0.05–0.06 a.u.) than $\pi^*_{C=O}$ (0.16–0.17 a.u.) level (see ESI). As a result, polarization of $C^{\delta+}$—$S^{\delta-}$ is much stronger (see ESI) than $C^{\delta+}$—$O^{\delta-}$ in the TS, which leads to somewhat greater electrostatic repulsion between the three atoms, $X^{\delta-}$, $Y^{\delta-}$ and $Z^{\delta-}$, as shown in Table 3. The stronger electrostatic repulsion $\Sigma\Delta E_{es}$ coupled with the lower proximate σ–σ* charge transfer energies $\delta\Delta E^{(2)}_{\sigma-\sigma^*}$ in the $S_N\pi$ TS (Table 3) for the thiocarbonyl than carbonyl transfers constitutes the major factor behind the higher activation barriers for the thiocarbonyl than carbonyl transfers, despite the lower deformation energies (ΔE_{def}, see ESI) involved in the thiocarbonyl TSs due to shorter stretching of the C–Z bonds. The greater tendency for stable intermediate formation in the thiocarbonyl transfers is a con-

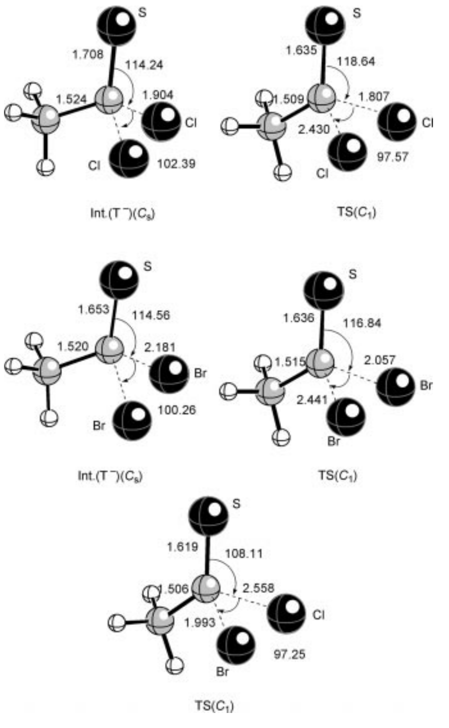


Fig. 2 The structures of the TS and intermediate with R = CH_3.

sequence of the greater energy gap, $\Delta\varepsilon = \varepsilon_{\sigma^*} - \varepsilon_{\pi^*}$ (see ESI), as has been noted above.[1,3,4]

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