

Rate Coefficients for Intramolecular Homolytic Substitution of Oxyacyl Radicals at Sulfur

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It is predicted on the basis of *ab initio* and density functional calculations that intramolecular homolytic substitution of oxyacyl radicals at the sulfur atom in ω -alkylthio-substituted radicals do not involve hypervalent intermediates. With *tert*-butyl as the leaving radical, free energy barriers ΔG^\ddagger (G3(MP2)-RAD) for these reactions range from 45.8 kJ mol⁻¹ for the formation of the five-membered cyclic thiocarbonate (**8**) to 56.7 kJ mol⁻¹ for the formation of the six-membered thiocarbonate (**9**). Rate coefficients in the order of 10⁴–10⁶ s⁻¹ and 10¹–10⁴ s⁻¹ for the formation of **8** and **9**, respectively, at 353.15 K in the gas phase are predicted at the G3(MP2)-RAD level of theory.

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Introduction

The *Dark Ages* of free radical chemistry are now truly behind us with radical reactions now at the forefront of modern synthetic methodology.^[1,2] Contributions by many researchers over several decades provided many, but not all, of the fundamental rate data required for the design of successful free radical strategies.^[1,2] In his 1981 review,^[3] Beckwith alluded to six key radical reaction types. This list included bond homolysis, combination, electron transfer, β -scission, homolytic addition and homolytic substitution. Of these six key classes, homolytic addition chemistry has enjoyed considerable popularity following the general availability of vital kinetic data,^[4] and the onset of molecular modelling techniques that provided unparalleled insight into the *exo/endo* paradox associated with the cyclisation of the 5-hexenyl radical.^[5,6]

Intramolecular homolytic substitution is one of the more recent additions to the chemists' heterocycle-forming synthetic armoury,^[7–9] and this can be attributed, again, to the rise in available kinetic data associated with this chemistry.^[10] Considering that radical reactions are mostly under kinetic control; the nature of the heteroatom as well as the leaving radical need to be well understood for homolytic substitution to occur in preference to fast alternative pathways such as hydrogen transfer involving the attacking radical. Homolytic substitution at the sulfur atom has been used in several synthetically useful applications, some examples of which are depicted in Scheme 1.^[11–13] Malmström and coworkers showed that when treated with tributyltin hydride, aryl bromide **1** reacts to afford the dihydrobenzothiophene **2** (after deprotection), presumably through a process involving intramolecular homolytic

substitution of aryl radical **3** at sulfur (example 1).^[11] Similarly, bromide **4** is transformed into the cyclic sulfoxide with inversion of stereochemistry (example 2),^[12] while **5** reacts under similar conditions to form the cyclic sulfinate (example 3).^[13]

Recently we have been interested in the chemistry of acyl and oxyacyl radicals because they often involve multiorbital interactions during key bond-forming reactions that are not available to ordinary alkyl and aryl radicals.^[14–17] For example, acyl radicals have been shown to masquerade as electrophiles in their reactions with imines and this phenomenon has been exploited by Ryu and coworkers in the construction of lactams (Scheme 2), as well as thiolactones.^[15,18,19] Oxyacyl radicals also exhibit interesting properties;^[20,21] however, there are many fewer examples in the literature of synthetic chemistry involving these radicals.^[10]

Of relevance to the discussion in this paper is the single known example of intramolecular homolytic substitution chemistry involving an oxyacyl radical; we showed some time ago that a novel cyclic selenocarbonate can be prepared through oxyacyl radical attack at a selenium atom (Scheme 3).^[22] The lack of reports of this chemistry in the literature can be ascribed to the paucity in kinetic data for reactions involving oxyacyl radicals; indeed even existing fundamental hydrogen transfer rate constants are at best estimates.^[23]

With the advent of modern computing infrastructure and methods, it is now possible to calculate kinetic data for radical reactions that are within experimental error; indeed we have published several examples involving both homolytic addition and substitution chemistry.^[24–26] These outcomes provide confidence in our ability to predict rate data for radical reactions for

which limited data exist and in this manner provide information important for the design of synthetic methodology based on this chemistry.^[27,28] With that in mind, we now report the results of our computational study into ring-closure chemistry involving oxyacyl radicals and sulfur; ω -alkylthio-substituted oxyacyl radicals are predicted to cyclise without the involvement of any hypervalent intermediate and with rate coefficients of 10^1 – 10^6 s⁻¹ (353.15 K) that are dependent on ring size and leaving radical.

Computational Procedures

The following methodology is based on computational procedures that have successfully reproduced experiment in previous studies of radical cyclisation kinetics, as well as a broad range of other radical processes.^[27] Standard *ab initio* molecular orbital theory calculations were performed in *Gaussian 09*^[29] and *Molpro 2009.1*.^[30] Geometries of all species were optimised at the UB3LYP/6–31G(d) level of theory. Frequency calculations were also performed at this level and scaled by their appropriate scaling factors.^[31] Improved energies were then obtained using

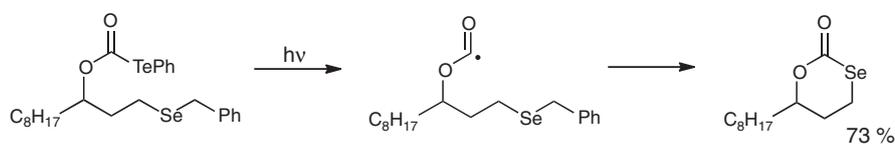
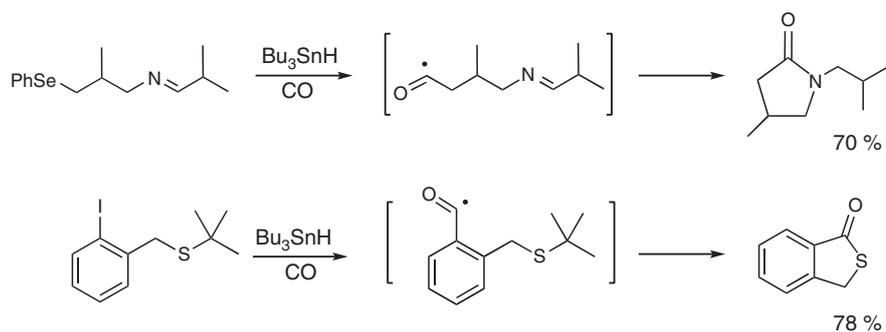
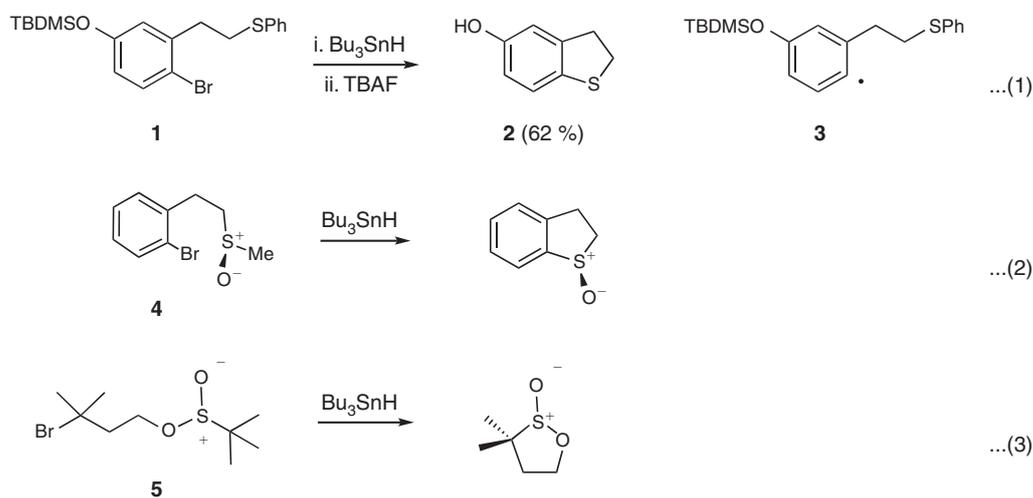
G3(MP2)-RAD, a high-level composite method that approximates (U)RCCSD(T) calculations with a large triple zeta basis set via additivity corrections at the R(O)MP2 level of theory.^[32]

Having obtained the geometries, frequencies and total electronic energies of each reactant, product and transition structure; gas-phase rate coefficients (k) were calculated via the standard transition state theory Eqn 1, while the corresponding equilibrium constants (K) were calculated using Eqn 2.^[33]

$$k(T) = \kappa(T) \frac{k_B T}{h} (c^\circ)^{1-m} e^{\frac{-\Delta G^\ddagger}{RT}} \quad (1)$$

$$k(T) = (c^\circ)^{\Delta n} e^{\frac{-\Delta G}{RT}} \quad (2)$$

In this equation, $\kappa(T)$ is the tunnelling correction factor, T is the absolute temperature, R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), k_B is the Boltzmann constant ($1.380658 \times 10^{-23} \text{ J molecule}^{-1} \text{ K}^{-1}$), h is the Planck's constant ($6.6260755 \times 10^{-34} \text{ Js}$), $c^\circ (=P/RT)$ is the standard unit of concentration (mol L^{-1}) and m is the molecularity of the



reaction, ΔG^\ddagger is the Gibb's free energy of activation and ΔG is the Gibb's free energy of reaction. The tunnelling coefficient $\kappa(T)$ corrects for quantum effects in motion along the reaction path and can be assumed to be unity in the cyclisation reactions studied, due to the large masses of the reacting groups.

Enthalpies (H), entropies (S) and Gibb's free energies (G) were initially calculated using the optimised geometries and frequencies in conjunction with the standard textbook formulae, based on the statistical thermodynamics of an ideal gas under the harmonic oscillator and rigid-rotor approximation. As described previously for the analogous reaction at selenium, we tested the accuracy of these results, for a subset of the reactions, using improved values in which all low frequency torsional modes were treated as hindered internal rotations using the standard 1D-torsional eigenvalue summation (TES) method, applied at a 60° resolution. A full description of this method has been reported previously.^[24,34] This study showed that for intramolecular homolytic substitution at selenium, the harmonic

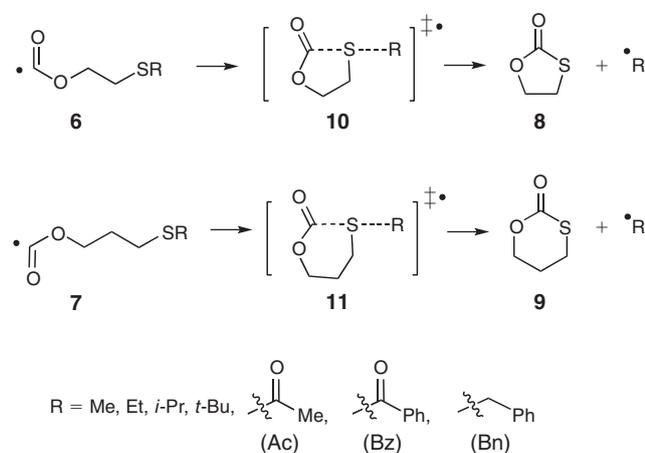
oscillator approximation slightly overestimates the rate coefficients (by a factor of 2–6 for the studied reactions).^[24] As this error was relatively small and systematic, it is reasonable to assume that it is not likely to influence the main conclusions of this study. Therefore, we have opted to use the more economical harmonic oscillator approximation for this work.

Results and Discussion

Rate (k , s^{-1}) and equilibrium (K , mol L^{-1}) constants and associated thermodynamic parameters were calculated for the intramolecular homolytic substitution reactions of the ω -alkylthio-substituted oxyacyl radicals (**6**, **7**; R = Me, Et, *i*-Pr, *t*-Bu, Bn, Ac, Bz) to give the cyclic thiocarbonates (**8**, **9**) as depicted in Scheme 4. Calculated kinetic and thermodynamic parameters at 353.15 K are provided in Table 1, Arrhenius plots for the reactions of **6** are given in Fig. 1, and similar plots for **7** can be found as Fig. S1 in the Supplementary Material together with results at other temperatures.

The optimised transition structures (**10**, **11**) for each cyclisation reaction are provided in Figs 2 and 3, along with the associated Mulliken charges on the leaving group and sulfur atom; complete geometries for all species are provided in the Supplementary Material.

Consistent with previous studies of ring closures at sulfur and selenium,^[26,27,35,36] the reactions in this study are also calculated to be concerted and to proceed through transition states with nearly collinear geometries; transition states **10**, **11** exhibit angles between attacking and leaving radicals that lie in the range of 160 – 175° (Figs 2 and 3). In all the transition states there is a significant elongation of the bond between sulfur and the leaving group with respect to the corresponding starting radical. For example, for formation of the 5-membered thiocarbonate **8**, when R = Me, the transition state separation of 2.12 \AA is to be compared with the analogous distance in the starting material (1.83 \AA), and this represents a 16% bond elongation. Similar elongations of 14 (Et), 12 (*i*-Pr) and 11% (*t*-Bu) are also



Scheme 4.

Table 1. Calculated changes in enthalpy (ΔH , kJ mol^{-1}), entropy (ΔS , $\text{J mol}^{-1} \text{K}^{-1}$), and free energy (ΔG , kJ mol^{-1}) of activation and reaction, and corresponding rate (k , s^{-1}), Arrhenius frequency factor (A , s^{-1}), activation energy (E_a , kJ mol^{-1}), and equilibrium constant (K , mol L^{-1}) data for the cyclisation reactions of radicals **6** and **7** at $253.15 \text{ K}^{\text{A}}$

R	ΔH [kJ mol^{-1}]	ΔH^\ddagger [kJ mol^{-1}]	ΔG [kJ mol^{-1}]	ΔG^\ddagger [kJ mol^{-1}]	ΔS [$\text{J mol}^{-1} \text{K}^{-1}$]	ΔS^\ddagger [$\text{J mol}^{-1} \text{K}^{-1}$]	K [kJ mol^{-1}]	k [s^{-1}]	Log(A)	E_a [kJ mol^{-1}]
Radical 6										
Me	−4.6	47.5	−47.0	57.8	120.0	−29.4	3.1E+05	2.1E+04	11.8	50.4
Et	−3.7	43.4	−56.9	46.4	150.7	−8.6	8.9E+06	1.0E+06	12.9	46.3
<i>i</i> -Pr	−2.0	40.2	−52.5	48.5	142.9	−23.7	2.0E+06	4.9E+05	12.1	43.1
<i>t</i> -Bu	−2.3	39.1	−57.7	45.8	156.8	−19.0	1.2E+07	1.3E+06	12.3	42.0
Ac	8.0	44.9	−39.1	50.4	133.3	−15.6	2.1E+04	2.6E+05	12.5	47.8
Bz	12.1	45.6	−36.3	52.1	136.9	−18.3	8.0E+03	1.5E+05	12.3	48.5
Bn	−42.2	44.5	−88.8	46.6	132.1	−5.9	1.3E+14	9.5E+05	13.0	47.4
Radical 7										
Me	13.5	66.8	−29.4	76.6	121.3	−27.9	7.6E+02	3.4E+01	11.8	69.7
Et	13.9	64.6	−33.5	73.9	134.5	−26.2	3.1E+03	8.6E+01	11.9	67.6
<i>i</i> -Pr	14.4	59.9	−36.2	68.5	143.3	−24.6	7.9E+03	5.3E+02	12.0	62.8
<i>t</i> -Bu	10.8	51.5	−44.6	56.7	156.9	−14.6	1.4E+05	3.1E+04	12.5	54.4
Ac	22.6	63.2	−27.6	64.5	142.0	−3.7	4.1E+02	2.1E+04	13.1	66.1
Bz	26.7	62.6	−23.2	67.9	141.2	−15.1	9.3E+01	6.6E+02	12.5	65.5
Bn	−24.8	58.2	−71.3	60.7	131.5	−7.1	1.1E+11	7.8E+03	12.9	61.1

^ACalculated at the G3(MP2)-RAD//B3-LYP/6–31G(d) level of theory using the standard formulae for the statistical thermodynamics of an ideal gas under the harmonic oscillator and rigid rotor approximation. Arrhenius parameters are based on an Arrhenius fit to the calculated data over the temperature range 298.15–398.15 K.

observed. As such, whilst all transition states appear ‘late’, those reactions with comparatively lower barriers tend to be slightly ‘earlier’ in accordance with the Hammond postulate.

Rate coefficients for the cyclisation of ω -alkylthio substituted oxyacyl radicals are leaving group dependent with values of 10^4 – 10^6 s $^{-1}$, for 5-membered cyclic thiocarbonate formation at 353.15 K. The corresponding rate coefficients for 6-membered cyclic thiocarbonate formation are slower, covering a range of 10^1 – 10^4 s $^{-1}$ – the difference primarily arising from the activation energy term. A similar difference is observed between the

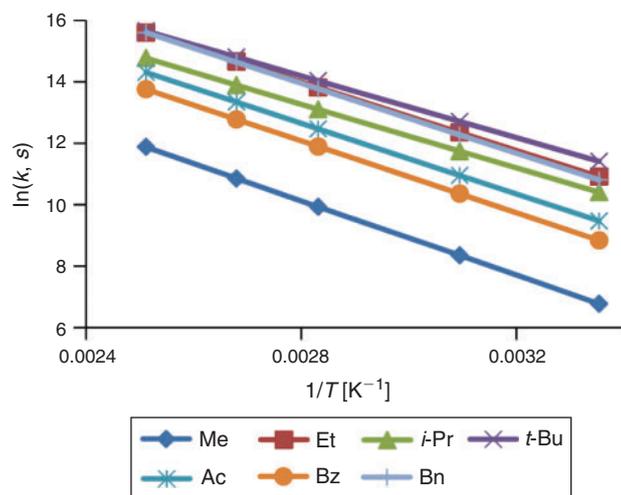


Fig. 1. Arrhenius plots for the cyclisation of oxyacyl radical (**6**) to form five-membered thiocarbonate (**8**) over the temperature range 298.15–398.15 K.

equilibrium constants for the formation of **8** and **9**. However, at any given temperature, it appears that the leaving group has a much greater effect upon the equilibrium constant, which extends over 11 orders of magnitude, unlike the rate coefficient, which spans only three. The kinetic preference for 5-membered thiocarbonate formation parallels previous studies of alkyl radical cyclisations at sulfur and selenium and is most likely due to reduced strain in the accompanying transition state.^[26,27,35,36]

Within a given series (**6** or **7**), the trend in the equilibrium constant appears to be governed by the strength of the breaking S–R bonds. The strength of the breaking bond can be understood using the corresponding CH₃S–R bond dissociation energies, which are dependent upon the stability of the leaving radical R•, as measured by its radical stabilisation energy (RSE), and the ability of R to stabilise the breaking S–R bond. Indeed, for both series of reactions there is a reasonable correlation between the reaction enthalpies and the corresponding CH₃S–R bond dissociation energies ($R^2 = 0.88$ and 0.95 for **6** and **7**, respectively). As such formation of **8** and **9** through loss of the resonance-stabilised benzyl-leaving radical is ~ 30 – 40 kJ mol $^{-1}$ more exoergic than reaction via loss of the less stabilised alkyl radicals (R = Me, Et, *i*-Pr, *t*-Bu), consistent with the large difference in their RSEs.^[37] On the other hand, reaction with acyl leaving radicals (R = Ac, Bz) is the least thermodynamically favourable due to the carbonyl group on the leaving radical stabilising the S–R bond by resonance.

For formation of the 5-membered cyclic thiocarbonate **8**, all reactions are calculated to be exothermic, with the exception of the loss of the acyl type (R = Ac, Bz) radical leaving groups. Additionally all reactions are strongly exoergic due to an increase in translational and rotational entropy across the

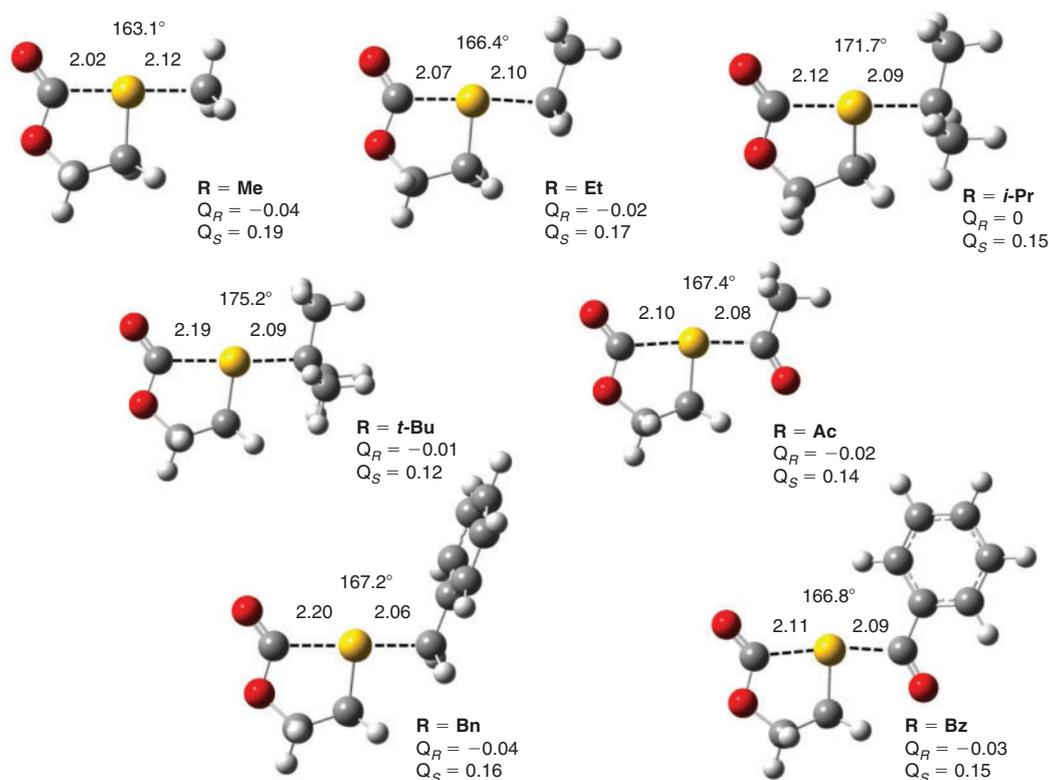


Fig. 2. UB3-LYP/6–31G(d) optimised transition structures (**10**) for the formation of the five-membered cyclic thiocarbonates (**8**) showing the key geometric features and the total charge on the leaving group (Q_R) and sulfur atom (Q_S).

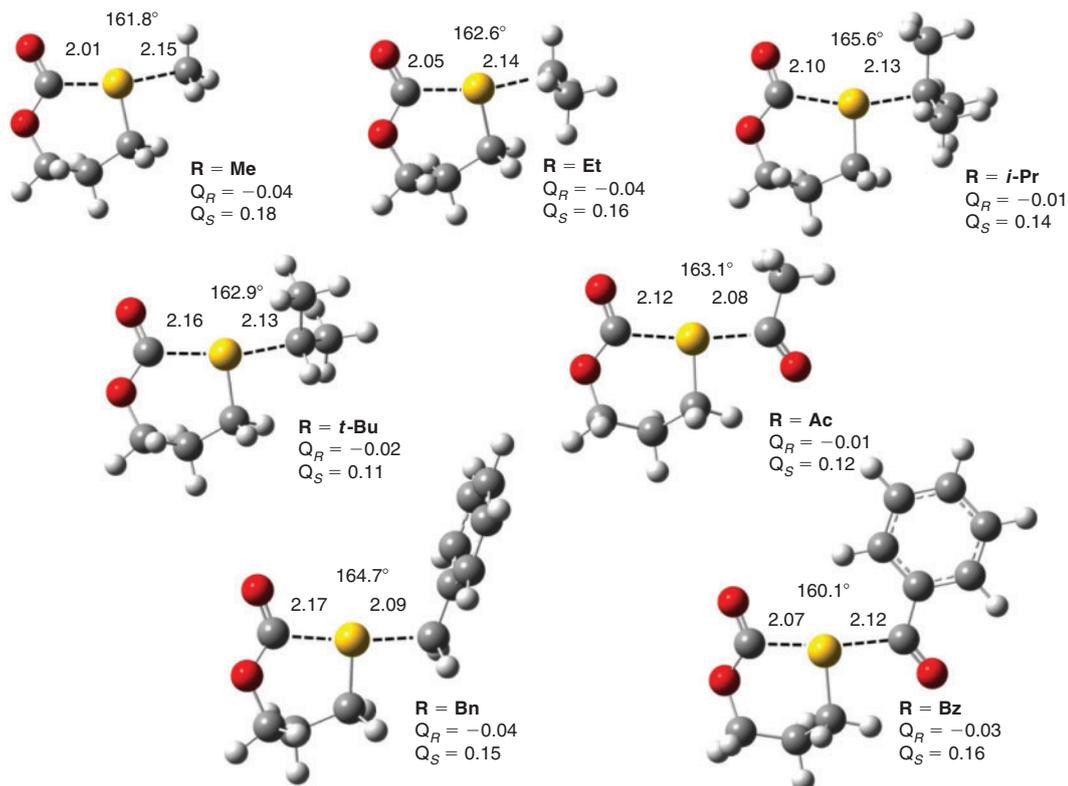


Fig. 3. UB3-LYP/6-31G(d) optimised transition structures (**11**) for the formation of the six-membered cyclic thiocarbonates (**9**) showing the key geometric features and the total charge on the leaving group (Q_R) and the sulfur atom (Q_S).

considered temperature range. In comparison, all reactions forming the 6-membered cyclic thiocarbonate **9** are endothermic, with the exception of the loss of a benzyl radical leaving group. However, all are strongly exoergic, due to an increase in translational and rotational entropy, across the considered temperature range.

The effect of the nature of the leaving radical (R) on the kinetics of these reactions is considerably smaller than their effect on the equilibrium constant, spanning just three orders of magnitude as the leaving group is varied instead of nearly eleven observed for the corresponding equilibrium constants (with the exception of loss of acetyl radical to form **9**). The trends with respect to the leaving group are very similar in both series, though as noted above, the rate coefficients for the six-membered cyclisations are systematically slower. Within a series, the differences in rate coefficients arise primarily in the reaction barriers; the frequency factors for all studied reactions fall in the relatively small range of 10^{11} – 10^{13} s $^{-1}$.

It is instructive to compare these calculations with those for the analogous cyclisation of ω -alkylseleno-substituted oxyacyl radicals.^[27] The cyclisation of ω -alkylthio-substituted oxyacyl radicals are thermodynamically more favourable than the analogous reaction at selenium by ~ 3 – 10 kJ mol $^{-1}$, presumably due to decreased strain of the product. However, not unexpectedly, formation of the cyclic thiocarbonates is less kinetically favourable than the analogous reaction for the formation of the cyclic selenocarbonate by ~ 2 – 4 orders of magnitude, mirroring previous kinetic studies involving alkyl and aryl radical reactions at sulfur and selenium.^[10,24,38,39] These (kinetic) observations are most likely the result of more favourable orbital overlap in the selenium-containing transition states over their sulfur-containing counterparts (**10**, **11**) in this study.^[8]

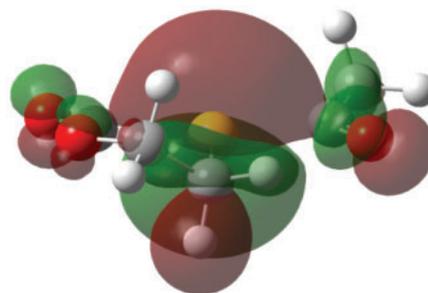
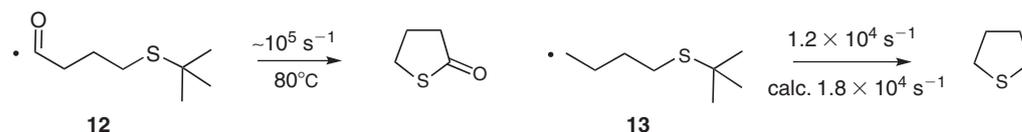


Fig. 4. B3-LYP/6-31G(d) singly-occupied molecular orbital (SOMO) for transition state **10**.

For the simple alkyl radical series, R = Me, Et, *i*-Pr, *t*-Bu, the calculated rate constants largely follow the thermodynamic trend, with the least favourable leaving group R = Me having the slowest rate coefficient and the most favourable leaving group R = *t*-Bu having the fastest. However, this trend breaks down when one considers the loss of benzyl and acyl-type radicals.

Compared with the simple alkyl radical series, R = Bn is considerably slower than would be expected on the basis of its reaction enthalpy. This suggests that the aromatic ring of the benzyl group is less able to stabilise the developing benzyl radical in the transition state (**10**, **11**; R = Bn) when compared with the hyperconjugation afforded by the methyl groups in the developing tert-butyl radical (**10**, **11**; R = *t*-Bu). Similar trends were observed in our previous selenocarbonate study^[27]; inspection of the transition state geometries (Fig. 2 and Fig. 3) reveals considerable distortion at the leaving carbon in both



Scheme 5.

cases. For the development of 5-membered thiocarbonate (**10**), when R = Bn the average deviation from planarity at the developing singly occupied molecular orbital (SOMO) within the leaving group is 15.5° , while the similar angle for R = *t*-Bu is 12.6° . However, it has been well established that these angles in the free benzyl and tert-butyl radicals are 0 and 10° respectively.^[40] We conclude, therefore, as was noted for the analogous selenium containing reactions, the transition states containing the benzyl radical leaving group are less stable than expected on the basis of product radical stability because of the distortion of the benzyl moiety.^[27] This is consistent with the ‘earlier’ nature of the transition states (**10**, **11**, R = Bn) as evidenced by the shorter S–C_{Bn} separations apparent in Figs. 2 and 3.

With acyl leaving radicals (R = Ac, Bz) the reactions are the least thermodynamically favourable being $10\text{--}20 \text{ kJ mol}^{-1}$ less exoergic than for the corresponding reaction involving the loss of simple alkyl radicals. Not surprisingly, as was observed previously,^[27] the carbonyl functional group of the leaving acyl radical is able to stabilise the S–R bond through resonance, thus increasing the stability of the starting radical over the product. This effect is not available for reactions involving the loss of the other radical leaving groups.

The stabilising contribution of the carbonyl group has the opposite effect on the reaction kinetics; acyl groups are able to stabilise the transition states by resonance resulting in a lowering of the activation barrier. Fig. 4 depicts the singly-occupied molecular orbital (SOMO) of transition state **10** (R = Ac). From this image, it is clear that there is significant overlap of the sulfur lone pair across both carbonyls of the transition state, and this provides significant transition state stabilisation.

It is always instructive to make comparisons between calculated and available experimental data. While no experimentally derived rate data exist for oxyacyl radical cyclisation reactions at higher heteroatoms, rate data do exist for the 4-(*tert*-butylthio)butanoyl radical (**12**), which was reported to ring close with a rate constant of around 10^5 s^{-1} (80°)^[19] about an order of magnitude faster than the analogous alkyl radical (**13**) (Scheme 5).^[39] Given that oxyacyl radicals are intrinsically more reactive than acyl radicals,^[41] our prediction that they ring-close about two orders of magnitude more rapidly than their alkyl counterpart (for a given leaving group) is plausible and also consistent with observations made for the analogous selenium series.^[27] It is noteworthy that similar calculations to those reported in this work were able to reproduce the rate constant for the cyclisation of **13**, providing further confidence in our current predictions.^[26]

Conclusions

G3(MP2)-RAD calculations have been used to explore the potential energy surfaces for several intramolecular homolytic substitution reactions of oxyacyl radicals at sulfur to form five- and six-membered thiocarbonates (**8**, **9**). These reactions are predicted to proceed via ‘smooth’ transition states and without the involvement of hypervalent intermediates. We have shown

that the transition states may be stabilised in different ways by hyperconjugation or resonance.

When compared with the analogous reaction at selenium, ring closure at sulfur shows that as expected, formation of cyclic thiocarbonates (**8**, **9**) are thermodynamically more favourable than the analogous reaction at selenium by $\sim 3\text{--}10 \text{ kJ mol}^{-1}$, but kinetically less favourable by $\sim 2\text{--}6$ orders of magnitude.

Comparisons between calculated rate coefficients and available experimental data for related systems provide confidence that the calculated values of *k* are reliable. In the absence of any experimentally determined rate data for oxyacyl radical cyclisations at high heteroatoms, this work provides, for the first time, rate coefficients and Arrhenius data useful for the synthetic practitioner interested in exploiting the potential wealth of chemistry associated with oxyacyl radicals.

Supplementary Material

Kinetic and thermodynamic parameters at all studied temperatures, a comparison of rate coefficients calculated using the harmonic oscillator approximation and hindered rotor model, and complete optimised geometries and corresponding total energies are available on the Journal’s website.

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