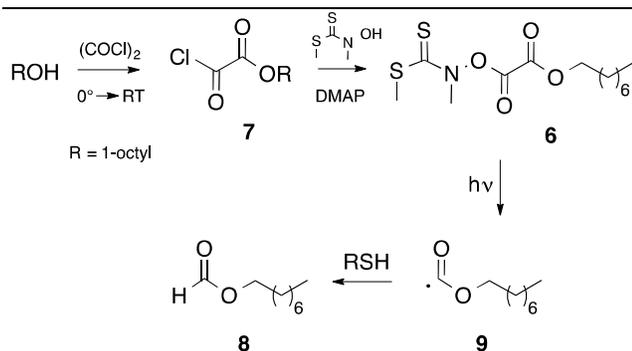




**N,S-Dimethyldithiocarbamyl Oxalates as Precursors for
Determining Kinetic Parameters for Oxyacyl Radicals**

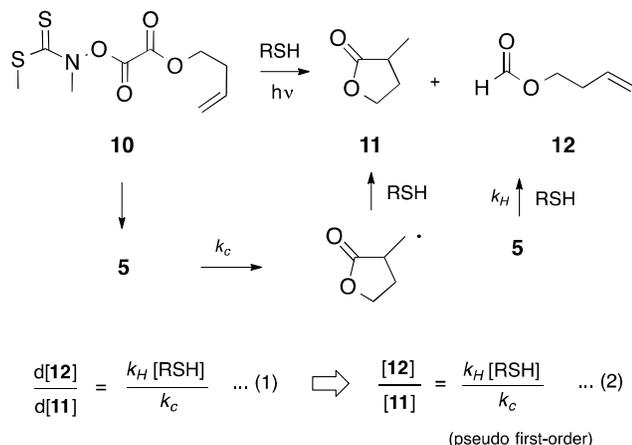
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Scheme 3.

overnight. Following removal of the solvent *in vacuo*, the residue, presumed to be the chloride **7** was dissolved in dichloromethane and further reacted with *N*-hydroxy-*N*,*S*-dimethylthiocarbamate³ and a catalytic amount of DMAP in dichloromethane to afford **6** in 94% yield (Scheme 3). The dithiocarbamate **6** was not stable to chromatography, however, in our hands, with the correct stoichiometry and careful workup, **6** could be isolated with excellent purity.[†]

When a solution of **6** and *tert*-dodecanethiol (RSH, 0.6 M), in benzene, was irradiated in a Rayonet photochemical reactor (350 nm) for one hour, we were delighted to observe the quantitative formation of 1-octyl formate (**8**) by GC analysis and direct comparison with an authentic standard; presumably **8** is formed from the intermediate oxyacyl radical **9**. This outcome demonstrates the synthetic utility of this novel radical precursor.



Scheme 4.

We next turned our attention to the cyclization of the 3-butenyloxyacyl radical **5**. The dithiocarbamyl precursor **10** was prepared in identical manner to **6** from 3-butanol and was isolated in 85% yield.[†] Given that the rate constant (k_H) for hydrogen transfer from tributyltin hydride to an oxyacyl radical **1** has been previously reported,⁷ initial experiments were carried out under photochemical conditions (Rayonet) in benzene using **10** and Bu₃SnH. Disappointingly, these experiments provided reaction mixtures that were difficult to analyse by GC because of broad overlapping signals that we ascribed to tin-based byproducts. Consequently, an alternative kinetic paradigm was required.

To our delight, when this reaction was repeated using *tert*-dodecanethiol as the source of hydrogen atom, GC analysis of the crude reaction mixture revealed cleanly the formation of methylbutyrolactone **11** and butenylformate **12** by comparison

Table 1. Relative rate data (21°C) for the ring closure of the butenyloxyacyl radical **5 in benzene. Reactions performed under pseudo first-order conditions in *tert*-dodecanethiol (RSH).**

[RSH] (M)	[12] / [11] ^a	k_H/k_c (M ⁻¹)	k_c^b (s ⁻¹)
0.43	0.27	0.63	1.1×10^7
0.75	0.41	0.55	1.2×10^7
1.20	0.64	0.53	1.3×10^7
2.00	1.09	0.55	1.3×10^7
2.50	1.46	0.58	1.2×10^7
3.00	1.76	0.59	1.2×10^7

^aAverage of three experiments. ^bSpot value calculated from equation 2 (see text).

with authentic samples (Scheme 4). When repeated with a ten-fold excess of thiol (pseudo first-order conditions) in benzene (21°C) at the concentrations listed in Table 1, ratios of [**12**]/[**11**] consistent with radical chemistry (Scheme 4) were observed (Table 1). The relative rate constant k_H/k_c is obtained by linear regression analysis of the data in Table 1 (Figure 1) and application of the integrated rate equation (eqn. 2).

Inspection of Figure 1 reveals excellent linearity ($R^2 = 0.996$) and confirms the validity of equation 2; a value of the relative rate constant (k_H/k_c) of 0.59 ± 0.02 is obtained. Determining a value for k_c requires knowledge of the rate constant for hydrogen atom transfer (k_H) from *tert*-dodecanethiol (RSH); unfortunately this rate constant has not been determined for oxyacyl radicals **1**.

It is well established that unlike acyl radicals, oxyacyl radicals are not stabilised by resonance, as evidenced by IR spectroscopy and computational studies.^{11,14} It is somewhat surprising therefore that the reported value of k_H for radicals **1** reacting with Bu₃SnH (1.1×10^6 M⁻¹s⁻¹, 80°C)⁷ is almost identical to that for acyl radicals (eg. **4**).¹⁵ On the basis of relative radical stabilities,¹⁴ we would expect **5** to react significantly faster with *tert*-dodecanethiol than its acyl counterpart (**4**). CCSD(T)/aug-cc-pVDZ calculations reported previously suggest that **5** is about 45 kJ mol⁻¹ less stable than **4**.¹⁴ Applying this same methodology to other radicals reveals that a primary alkyl radical (eg. ethyl) is about 55 kJ mol⁻¹ less stable than an acyl radical, while a vinylic radical (eg. ethylenyl) is calculated to be about 98 kJ mol⁻¹ less

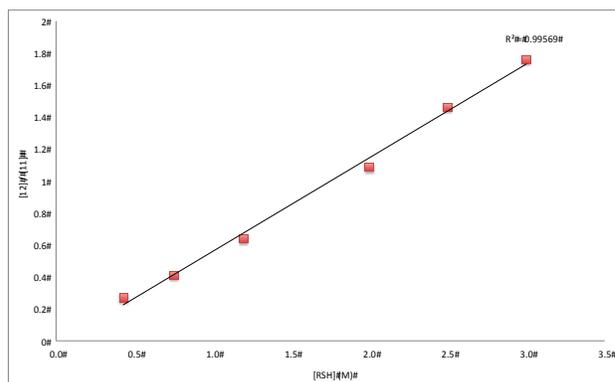


Figure 1. Dependence of [12]/[11] on *tert*-dodecanethiol concentration at 21°C for the cyclization of **5 in benzene.**

stable than **4** at CCSD(T)/aug-cc-pVDZ.⁸ These data, in turn, suggest that an oxyacyl radical such as **5** is more similar in reactivity to a primary alkyl radical than an acyl radical. Importantly, **5** would not be expected to react with a rate constant of an acyl radical (too slow), or a vinyl radical (too fast).

With this in mind, we suggest that **5** abstracts hydrogen atom from *tert*-dodecanethiol with a similar rate constant (k_H) to that of a primary alkyl radical, namely $6.8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ at 21°C.^{16¶} With this assumption, our value of k_H/k_c leads to:

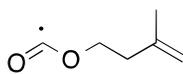
$$k_c = 1.2 \times 10^7 \text{ s}^{-1} (21^\circ\text{C}).$$

This value of k_c is in excellent agreement with our calculated (G3(MP2)-RAD) value of $1.5 \times 10^7 \text{ s}^{-1} (21^\circ\text{C})^4$ and significantly faster than the value reported previously.⁷

Not only are we delighted with the agreement between our calculated and experimental data, this study provides further validation of our computational methodology for determining rate data and also suggests that our assumption regarding k_H for oxyacyl radicals is approximately correct.

Alternatively, using our calculated value of k_c , we can determine a value for k_H of $7 \times 10^6 \text{ s}^{-1}$, slightly (but not significantly) higher than the value used earlier based on the experimental value for a primary alkyl radical (*vide supra*).

Finally, we are now in a position to revisit the the work of Bachi and Bosch and provide a more robust value for k_H for Bu_3SnH reduction of **1** by the application of equation 2. While



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the authors report data for the ring-closure of **5**, product ratios are reported in neat Bu_3SnH .⁵ Consequently, it is difficult to determine reliable reagent concentrations and, from them, to calculate rate constants. On the other hand, more robust data are provided for the cyclization of the related radical **13**. Using the reported product ratio and average value of $[\text{Bu}_3\text{SnH}]$,⁵ together with our value of k_c ($2.7 \times 10^7 \text{ s}^{-1}$, 80°C)⁴ for **13**, we suggest that $4.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ (80°C) is a more appropriate value for k_H when tributyltin hydride reacts with oxyacyl radicals **1**. This value for k_H is well aligned with that for a primary alkyl radical reacting with Bu_3SnH , namely $6.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ (80°C).¹⁸

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Notes and references

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†Electronic Supplementary Information (ESI): experimental details for the preparation of **6** and **10**. General protocol for kinetic experiments. ¹H

and ¹³C NMR spectra of compounds **6** and **10**. See DOI: 10.1039/b000000x/

⁵⁵ §This work.

¶This is k_H for a primary alkyl radical (5-hexenyl) reacting with *tert*-butylthiol (ref. 16). While many workers have assumed that *tert*-dodecanethiol reacts with the same rate constant as *tert*-butylthiol, we have recently verified, in independent work, that the two reagents react with primary alkyl radicals with rate constants (k_H) within experimental error of each other (ref. 17).

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