Rate Constants and Arrhenius Functions for Hydrogen Atom Transfer from tert-Butyl Thiol to Primary Alkyl Radicals

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The radical clock method was used to determine rate constants for hydrogen atom transfer from t-BuSH to primary alkyl radicals over the temperature range -45 to 50 °C. Three clocks, cyclization of the 5-hexenyl radical (3a), ring opening of the cyclopropylcarbinyl radical (3b), and rearrangement of the 2,2-dimethyl-3-butenyl radical (3c), were used in THF, and 3a was used in toluene. Arrhenius functions for the two studies with 3a and the one with 3b were quite similar, and the Arrhenius function for 3c, when adjusted for direct comparison to reactions with simple primary radicals, was also similar. Combining the results from 3a and 3b in THF gave an Arrhenius function for hydrogen atom transfer from t-BuSH to primary radicals of log $(k/M^{-1} s^{-1}) = (8.37 \pm 0.08) - (2.00)$ ± 0.09 /2.3RT; the calculated rate constant at 25 °C is 8.0×10^6 M⁻¹ s⁻¹. This study ultimately relates the t-BuSH rate constants to those for hydrogen atom transfer to primary radicals from both Bu₃SnH and PhSH and serves to compare the latter two sets of kinetic data; it also demonstrates that the fast radical clock reactions of 3a and **3b** are calibrated against equivalent standards.

Thiols react rapidly with free radicals by S_{H}^{2} hydrogen atom transfer (eq 1). These reactions can be important in synthetic and mechanistic studies and are involved in radical trapping reactions in vivo as "radioprotectors" by water-soluble thiols like cysteamine, cysteine, and glutathione.¹ Reports of absolute rate constants for such re-

$$\mathbf{R}^{\bullet} + \mathbf{R}'\mathbf{S}\mathbf{H} \to \mathbf{R}\mathbf{H} + \mathbf{R}'\mathbf{S}^{\bullet} \tag{1}$$

actions are limited, and the results have not been consistent. Pulse radiolysis studies in alcohol solvents and water in the presence of water-soluble thiols gave rate constants for hydrogen abstraction at room temperature in the range of 3×10^7 to 5×10^8 M⁻¹ s⁻¹ for reactions with α -hydroxy carbon radicals and a number of undefined radicals formed by reaction of hydroxy with natural products such as nucleotides.¹ Reactions of simple alkyl radicals with thiols in organic solvents at 25 °C have been reported to occur with rate constants of about 3×10^4 to $2 \times 10^{6} \text{ M}^{-1} \text{ s}^{-1.2a,b}$ 1,4-Biradicals formed in Norrish type II cleavages, which react with RSH at the alkyl radical position like a simple alkyl radical, were found by laser flash studies to react with octanethiol at 22 °C with rate constants of 9×10^6 M⁻¹ s⁻¹ (for a tertiary center) and 1.13 \times 10⁷ M⁻¹ s⁻¹ (for a secondary center).^{2c} Our group reported that t-BuSH reacted with a primary radical in THF at 32 °C with a rate constant of $1.07 \times 10^7 M^{-1} s^{-1.3}$ Griller et al. recently reported⁴ a rate constant for the reaction of t-BuSH with a primary radical in isooctane at 25 $^{\circ}$ C of 2.3×10^5 M⁻¹ s⁻¹ with a caveat and the suggestion that the t-BuSH reactions should be calibrated against a reliable radical clock like 5-hexenyl.

In this paper, we have followed Griller's suggestion and used the "radical clock" method⁵ to measure the rate constants for reactions of *t*-BuSH with three free-radical clocks, the well-trusted 5-hexenyl cyclization, the cyclopropylcarbinyl ring opening, and the 2,2-dimethyl-3-butenyl rearrangement. The resulting rate constants and Arrhenius functions are quite consistent, and because of this consistency and the fact that the radical clocks were calibrated against different absolute basis reactions that are considered reliable, the values we obtained should also be reasonably accurate.





Results

We employed Barton's N-hydroxypyridine-2-thione esters (1 = R-PTOC where PTOC is (((2-thioxopyridiny))oxy)carbonyl)) as the free radical precursors. These compounds were developed by Barton's group as convenient radical sources for synthetic conversions,⁶ and we have previously shown that they are equally useful in kinetic studies.^{3,7} As Barton's group amply demonstrated,⁶ simple thiols like t-BuSH can serve as hydrogen atoms donors in reactions of 1 because the thiyl radical successfully adds to 1 in a radical chain propagation step with concomitant or subsequent cleavage of the N-O bond. N-Hydroxypyridine-2-thione ester precursors 2a-c (see Figure 1) for the 5-hexenyl radical (3a), the cyclopropylcarbinyl radical (3b), and the 2,2-dimethyl-3-butenyl radical (3c) were prepared from the corresponding acids by conventional methods.6

In radical chain reactions, precursors 2 gave radicals 3 that rearranged in first order processes (eq 2) to give the cyclopentylmethyl radical (4a) from 3a, the 3-butenyl radical (4b) from 3b, and the 1,1-dimethyl-3-butenyl radical (4c) from 3c. The rearrangement of 3c is somewhat more complex than the simple cyclization of **3a** to **4a** and ring opening of **3b** to **4b**; radical **3c** cyclizes to the (2,2dimethylcyclopropyl)methyl radical, which then partitions to 4c and back to 3c in about a 7:1 ratio.7b This does not complicate a kinetic analysis, however, because trapping of the intermediate cyclic radical by t-BuSH is too slow

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Table I. Arrhenius Functions for Radical Rearrangements and Hydrogen Atom Transfers from tert-Butyl Thiola

reaction	solvent	$\log A^b$	Eac	k _(25°C) ^d	note
3a → 4a		10.37 ± 0.32	6.85 ± 0.42	$2.2 \times 10^5 \text{ s}^{-1}$	е
$3b \rightarrow 4b$		13.00 ± 0.14	6.8 ± 0.2	$1.0 \times 10^8 \text{ s}^{-1}$	f
$3c \rightarrow 4c$		11.00 ± 0.14	5.88 ± 0.16	$4.8 \times 10^{6} \text{ s}^{-1}$	g
$3a + t$ -BuSH $\rightarrow 5a + t$ -BuS [•]	THF	8.38 ± 0.11	2.02 ± 0.13	$7.9 \times 10^{6} \text{ M}^{-1} \text{ s}^{-1}$, i
$3a + t$ -BuSH $\rightarrow 5a + t$ -BuS [•]	toluene	8.53 ± 0.25	2.28 ± 0.34	$7.2 \times 10^{6} \text{ M}^{-1} \text{ s}^{-1}$	j, k
$3\mathbf{b} + t$ -BuSH $\rightarrow 5\mathbf{b} + t$ -BuS'	THF	8.34 ± 0.09	1.96 ± 0.11	$8.0 \times 10^{6} \text{ M}^{-1} \text{ s}^{-1}$	ĥ, i
$3c + t$ -BuSH $\rightarrow 5c + t$ -BuS'	THF	7.66 ± 0.12	1.05 ± 0.15	$7.7 \times 10^{6} \text{ M}^{-1} \text{ s}^{-1}$	i, j
modified data for 3c ¹	THF	8.26 ± 0.12	2.05 ± 0.16		· •

^a Erros are 2σ . ^b For rearrangements, log (A/s⁻¹); for second-order reactions, log (A/M⁻¹ s⁻¹). ^c In kilocalories/mole. ^d Rate constant at 25 °C. ^cReference 9. ^fReference 7a. ^gReference 7b. ^hEleven kinetic measurements. ⁱTemperature range -44 (-45) to 50 °C. ^jNine kinetic measurements. ^kTemperature range -17 to 50 °C. ⁱResults from reactions of 3c scaled to reactions of Bu₃SnH with primary radicals; see text.



Figure 1. Precursors, radicals, and products.

to be important. Specifically, less than 1% yields of 1,1,2-trimethylcyclopropane were expected and found experimentally when 2c was allowed to react with PhSH under optimum conditions for trapping the cyclic radical,^{7b} and even lower yields are expected in the presence of t-BuSH.

reaction	rate constant	
$3 \rightarrow 4$	$k_{\rm r}$	(2)
$3 + t$ -BuSH $\rightarrow 5 + t$ -BuS*	$k_{\rm H}$	(3)

kн 4 + t-BuSH $\rightarrow 6 + t$ -BuS' (4)k...

$$4 \rightarrow 3 \qquad \qquad k_{-r} \qquad (5)$$

$$3 \text{ (or 4)} + 2 \rightarrow \text{R-S-pyr} + 3 \qquad k_{\text{T}} \qquad (6)$$

In the presence of t-BuSH, radicals 3 were trapped to give products 5 in second-order reactions (eq 3) that competed with the rearrangements. Radicals 4 also reacted with t-BuSH to give products 6 (eq 4). For the three rearrangements studied here, trapping of 4 by t-BuSH was much faster than the back rearrangement of 4 to 3 (eq 5); thus, the rearrangements were irreversible under our conditions. Alkyl radical trapping by the PTOC precursors (eq 6) to give alkyl pyridyl sulfides (R-S-pyr) was a potentially complicating side reaction. The rate constants $k_{\rm T}$ for two such "self-trapping" reactions of primary radicals have been determined,^{7c,d} and, consistent with these values, we observed less than 1% yields of R-S-pyr when t-BuSH concentrations were high (reactions of 2b and 2c). For reactions of 2a, however, low concentrations of t-BuSH were required, and R-S-pyr yields of 10% in the worst case (but more typically less than 5%) were obtained. For the kinetic analysis, we assumed that the self-trapping reactions had a negligible effect on the k_r/k_H values.

With t-BuSH present in excess, the rate constants for trapping 3 $(k_{\rm H})$ could be determined by eq 7, which results from a steady state treatment of 4, where k_r is the rate constant for rearrangement of 3, $[t-BuSH]_m$ is the average concentration of the thiol over the course of the reaction, and ([5]/[6]) is the ratio of the products formed. The rate constants for trapping of 4 $(k_{H'})$ do not appear in the rate expression because k_{-r} is much smaller than $(k_{H'}[RSH])$.

$$k_{\rm H} = k_{\rm r} [t - {\rm BuSH}]_{\rm m}^{-1}([5]/[6])$$
 (7)

In visible light initiated chain reactions, the three precursors 2 were allowed to react in the presence of t-BuSH in THF at temperatures ranging from -45 to 50 °C. Radical 3a was also generated in toluene in the presence of t-BuSH. Product yields were measured by GC, and rate constants for the trapping reactions were determined by eq 7.8 Arrhenius functions for the trapping reactions were then calculated. Table I contains the results from this work and the Arrhenius functions for the rearrangements of the radical clocks.

Discussion

Cyclization of the 5-hexenyl radical (3a) has been the most well trusted and most widely applied radical clock reaction. There is little doubt that this primary radical reacts in second-order reactions with rate constants that are essentially equal to those of other primary radicals because the functionality is so remote, and it is generally assumed that solvent effects on the cyclization reaction will be very small. The rate constants and Arrhenius function for the cyclization reaction were determined from the ratios of hexene and methylcyclopentane formed when 3a was produced in the presence of Bu₃SnH and the rate constants for reaction of primary radicals with Bu₃SnH.⁹ In turn, the basis rate constants for the reactions with Bu₃SnH were determined by laser flash studies conducted in the temperature range of -28 to 82 °C.⁹

The cyclization of **3a** is not an especially fast radical rearrangement, but it was fast enough to permit its use with t-BuSH at low concentrations. The derived Arrhenius parameters for the solvents THF and toluene are very similar as would be expected because, whereas these two solvents differ somewhat in polarity,¹⁰ neither the cyclization or 3a nor the hydrogen atom transfer reaction would be expected to occur with substantial charge polarization in their transition states. The larger error in the toluene studies resulted from difficulties in the product analyses.

As was the case with 3a, Arrhenius functions for the ring opening of the cyclopropylcarbinyl radical (3b) at warmer temperatures have been determined by allowing the ring

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opening to compete with trapping reactions (including hydrogen atom transfer from PhSH) that occur with known rate constants.^{7a,12} In this case, however, the necessary assumption that the trapping reaction will proceed with a rate constant equal to that for reaction of a simple primary radical is more questionable both because of a possible steric effect in the second-order trapping reaction of 3b and because of conjugation of the radical center of 3b with the cyclopropyl ring.^{13,14} The magnitude of the latter effect is especially difficult to anticipate. Experimentally, Walton recently found an activation energy for methylene rotation in 3b of about 2.7 kcal/mol and estimated a small stabilization energy in 3b of about 2.4 kcal/mol.¹³ From a correlation of rotational barriers to bond dissociation energies (BDE), Walton concluded that the BDE for the methyl hydrogen in methylcyclopropane is comparable to that of a tertiary hydrogen in an alkane.¹³ However, we have found that the rate constants for ring opening of 3b derived from competition against trapping by hydrogen atom transfer from thiophenol^{7a} are very similar to those found at comparable temperatures when the trapping reaction was coupling with a nitroxyl radical^{12d} or hydrogen atom transfer from R_3SnH .^{12a,b} Further, these PhSH derived values^{7a} were consistent with the kinetic results from low temperature ESR studies.¹⁵ Because of this consistency and because PhSH reacts with primary, secondary, and tertiary radicals with very similar rate constants,¹⁶ we conclude that 3b is a reasonable model for a primary alkyl radical in fast trapping reactions like those studied here. This conclusion is supported by the similarities in the Arrhenius functions for reactions of 3a, 3b, and 3c. However, it is entirely possible that **3b** will be a poor model for a primary radical in some reactions.

We have reported^{7a} a recommended Arrhenius function for ring opening of **3b** that is based on results from nitroxyl radical coupling,^{12d} thiophenol trapping,^{7a} and low-temperature ESR studies;¹⁵ however, for this work, we have used the Arrhenius function calculated only from thiophenol trapping because (1) the temperature range of those studies and the studies reported here are the same, (2) the basis rate constants for PhSH trapping of primary radicals appear to be very sound,¹⁶ and (3) we wished to make a direct comparison between data related to Bu₃SnH and PhSH trapping rate constants. The selection of the PhSH based rate constants for **3b** opening actually makes little difference in the analysis because rate constants calculated from the two functions in the temperature range we studied here are nearly the same.^{7a}

The agreement between the calculated Arrhenius functions for t-BuSH trapping of 3b and 3a (Table I) is striking. The virtual identity in the results reinforces one's trust in the derived values for the t-BuSH trapping reaction, and, at the same time, lends more credibility to the assumptions used in the initial determinations of the rate constants for ring opening of 3b.^{7a,12} Further, it should be emphasized that the rate constants of the basis reaction for the ring opening of 3b, i.e. the rate constants for reaction of thiophenol with a primary radical,¹⁶ were determined by laser flash studies and are completely unrelated to the tin hydride basis reactions used for measuring k_r for the cyclization of 3a.⁹ That the two independent approaches converge to give the same results for the kinetic values of *t*-BuSH trapping we have measured here interrelates and fortifies the entire set of fast radical rate constants now employed in indirect kinetic measurements.

The rate constants for the rearrangement of the 2,2dimethyl-3-butenyl radical (3c) were initially determined by competition against hydrogen atom transfer from Bu₃SnH.^{7b} It is known from laser flash studies that Bu₃SnH reacts somewhat faster with a neopentyl radical¹⁷ than with a simple primary radical,⁹ and, thus, the basis reaction used for the rearrangement of 3c was neopentyl trapping¹⁷ rather than primary radical trapping. Our group previously reported a rate constant for hydrogen atom transfer from t-BuSH to probe radical 3c at 32 °C of (1.07 $\pm 0.08) \times 10^7$ M⁻¹ s⁻¹ at the 95% confidence level,³ but this value must be adjusted by using the more recent rate constant for rearrangement of 3c.^{7b} The resulting value is $k_{\rm H} = (8.8 \pm 0.7) \times 10^6$ M⁻¹ s⁻¹ which agrees reasonably well with $k_{\rm H} = 8.2 \times 10^6$ M⁻¹ s⁻¹ at 32 °C calculated from the Arrhenius function in Table I.

Given that Bu₃SnH reacts faster with neopentyl radical than it does with primary radicals (by a factor of 1.3 at 25 °C),¹⁷ one might predict that the faster hydrogen atom transfers from t-BuSH to neopentyl and primary radicals would show a similar but attenuated effect; i.e. the reaction with 3c should be only slightly faster than that with 3a or 3b. The kinetic values we have found appear to be consistent with this prediction in that over the temperature range we studied the rate constants for reaction with the neopentyl type radical 3c are slightly greater than the averages for the primary radical studies. However, the Arrhenius function derived for reaction of t-BuSH with 3c appears to be inconsistent with those found for reactions with 3a and 3b. We would speculate that the differences in the Arrhenius functions for the t-BuSH trapping reactions reflect accumulated errors in the Arrhenius function for neopentyl trapping by Bu₃SnH¹⁷ and the Arrhenius function for the rearrangement of 3c.7b Thus, we would suggest that the Arrhenius function for trapping of **3c** by *t*-BuSH can be used to predict rate constants but should not be used to evaluate the entropic and enthalpic terms in the transition state of the reaction.

Since our main goal in this work was to study reactions of t-BuSH with primary radicals, we can use an alternative approach for evaluating the data from 3c trapping. Specifically, we can simply use the 3c radical as a vehicle for comparing the rates of reactions of t-BuSH directly with those for reactions of Bu₃SnH. We make the assumption that, to a first approximation, differences in the rates of reaction of a neopentyl and a primary radical with t-BuSH will be equal to the differences in the rates of reaction of these radicals with Bu₃SnH. Accordingly, the rate constants found for reaction of t-BuSH with 3c are then scaled to those for reaction of a normal primary radical by division by the rate constant for reaction of Bu₃SnH with neopentyl¹⁷ and multiplication by the rate constant for reaction of Bu₃SnH with a primary radical.⁹ As long as our assumption is reasonable, this procedure factors out

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Figure 2. Arrhenius function for reaction of *t*-BuSH with primary radicals.

a possible error in the original neopentyl rate constant,¹⁷ and it is equivalent to using a k_r for 3c based on reaction of Bu₃SnH with a simple primary radical. The resulting Arrhenius function is included in Table I. It predicts rate constants that are slightly low, probably reflecting the fact that the above assumption is not completely accurate, but the log A and E_a values are remarkably similar to those for reactions of 3a and 3b.

Combining the data for the 3a reactions in THF with the data for the 3b study gave an Arrhenius function for reaction of t-BuSH with primary radicals of

$$\log(k/M^{-1} \text{ s}^{-1}) = (8.37 \pm 0.08) - (2.00 \pm 0.09)/\theta (8)$$

where θ is 2.3RT kcal/mol and the errors are 2σ . This function is shown graphically in Figure 2 where it can be seen that the results from the two clocks are virtually indistinguishable. The calculated rate constant for reaction of a primary radical with t-BuSH at 25 °C is 8.0×10^{6} M⁻¹ s^{-1} . Inclusion of the data for **3a** in toluene has essentially no effect on eq 8 other than to increase the errors, and inclusion of the modified data for the 3c rearrangement would reduce both log A and E_a slightly and double the errors yet again. The function in eq 8 represents an equally weighted contribution of results based on two independently determined sets of primary rate data, Bu₃SnH and PhSH reactions with primary radicals, and, thus, we believe it is likely to be quite accurate. Because radical rate constants vary little with solvent changes, we recommend eq 8 for the calculation of rate constants for reaction of any primary radical with t-BuSH in organic media. Given that the hydrogen atom donors Bu₃SnH and PhSH react with secondary and tertiary radicals with almost the same rate constants as they react with primary radicals,^{9,16} eq 8 should also provide a reasonable estimation for the rate constants for reactions of secondary and tertiary radicals with *t*-BuSH.

The Arrhenius function of eq 8 can be compared to those for reactions of primary radicals with PhSH (log k = 9.3– $1.8/\theta$)¹⁶ and Bu₃SnH (log k = 9.1– $3.7/\theta$).⁹ As would be predicted based on the stability of the product radicals, the enthalpy of activation for t-BuSH is only slightly higher than that for PhSH but 1.7 kcal/mol lower than that for Bu₃SnH. However, the entropy of activation at 25 °C for t-BuSH of -22 eu is 3-4 eu more negative than those of both of the other hydrogen atom donors. This might reflect a minor steric effect of the tert-butyl group that does not have a counterpart in Bu₃SnH because of the long Sn-H and C-Sn bonds.

The literature contains reports of relative rate constants of radical reactions in competition with hydrogen atom

transfer from t-BuSH that can now be placed on an absolute scale. For example, the report by Griller et al.⁴ drew our attention to the fact that firm rate constants for the reactions of t-BuSH were not available. In that paper,⁴ the authors established a well-defined relative rate constant for an intermolecular hydrogen atom transfer to a primary radical center in competition with trapping by t-BuSH of 0.34 M at 25 °C and used this value along with a less reliable rate constant for the rearrangement extrapolated from lower temperature ESR data to calculate the rate constant for reaction with *t*-BuSH. As the authors note,⁴ a knowledge of the rate constant for hydrogen atom transfer from t-BuSH would have allowed a calculation of the rate constant for the rearrangement at 25 °C; the value for the first-order rearrangement at 25 °C can now be calculated as 2.7×10^6 s⁻¹.

In conclusion, the rate constants for hydrogen atom transfer from t-BuSH to primary radicals in the practical temperature range around room temperature are securely established in relation to the rate constants for reaction of Bu₃SnH and PhSH. This thiol provides an alternative basis reaction that can be used in the PTOC/thiol method⁷ or in other competition methods for measuring rate constants of both first-order radical rearrangements and second order radical reactions like halogen atom transfer from reactive organic halides.^{7c} Further, the cross-checks of the current study have provided yet another test of the accuracy of the kinetic values for the **3b** rearrangement;^{7a} the rate constants for ring opening of the cyclopropylcarbinyl radical ring opening should be considered to be as reliable as those for the 5-hexenyl cyclization.

Experimental Section

Materials. The preparation of the radical precursors 1-[(5-hexenylcarbonyl)oxy]-2(1*H*)-pyridinethione (**2a**), 1-[[(cyclopropylmethyl)carbonyl]oxy]-2(1*H*)-pyridinethione (**2b**), and 1-[[(2,2-dimethyl-3-butenyl)carbonyl]oxy]-2(1*H*)-pyridinethione (**2c**) have been reported.^{3,7a} Toluene and t-BuSH (Aldrich) were distilled before use. THF was distilled from potassium-benzophenone under nitrogen before use.

Method. The method used was similar to that previously reported for kinetic studies employing PhSH as the trapping agent.^{7a-c} Temperatures in the kinetic studies were considered to be accurate to ± 1 °C. The reaction samples contained 0.03–0.05 mmol of precursor 2 and a similar amount of a high-weight hydrocarbon for use as a GC standard in 1.0 mL of solvent. For studies with 2a, 0.07-0.14 mmol of t-BuSH was used. For studies with 2b, 0.9-2.8 mmol of t-BuSH was used. For studies with 2c, 0.5-1.8 mmol of t-BuSH was used. All reactions were run with stirring in tubes that were sealed under vacuum after flushing with nitrogen. After the reactions were complete (indicated by discharge of the initial yellow color), the tubes were cooled to -78°C before opening, and the reaction mixtures were promptly analyzed by GC on a 15-m DB-1 megabore column (J&W Scientific) or a 1/4 in. by 2 m AgNO₃ in ethylene glycol column.¹⁸ The hydrocarbon product identities were established by comparison to the GC retention times of authentic samples. Yields were determined by comparison to the internal standard using predetermined response factors. The yields of products (5b + 6b) and (5c + 6c) were in the range of 90-100%. Yields of (5a)+ 6a) generally were greater than 90%; at the lowest concentration of t-BuSH employed in the 2a studies, a 10% yield of alkyl pyridyl sulfides (from "self-trapping"7d) was observed.

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