



Rate Constants for the Reaction of Acyl Radicals with Bu_3SnH and $(\text{TMS})_3\text{SiH}$

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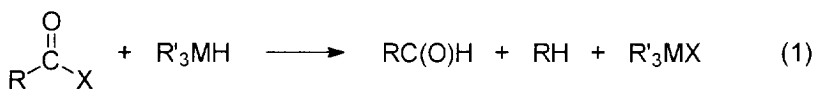
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Abstract: The rate constants for the hydrogen abstraction from Bu_3SnH and $(\text{TMS})_3\text{SiH}$ by acyl radicals have been measured by using competing decarbonylation reactions as timing devices.

Tri-*n*-butyltin hydride and tris(trimethylsilyl)silane are the most popular reagents employed in organic syntheses which utilise radical chain reactions to obtain the desired product.¹ For a synthetically useful radical chain reaction the intermediates must be disciplined. Thus, in planning a synthetic strategy one is faced with the problem of simultaneously occurring carbon-centered radicals which should be designed to carry out unique functions. Therefore, it is of considerable importance to know how rapidly different classes of carbon-centered radicals abstract hydrogen from different hydrides.² In 1981 and 1991, one of us with others determined rate constants and Arrhenius parameters for the reaction of some carbon-centered radicals with Bu_3SnH ³ and $(\text{TMS})_3\text{SiH}$,⁴ respectively. The numerous citations of the former article over the last decade indicate the importance of these widely used data in understanding and programming free-radical reactions.⁵ Recently, absolute rate constants for hydrogen transfer reactions of the perfluoro-*n*-heptyl radical with these hydrides have also been determined.⁶ In this study, we have used competing decarbonylation reactions as timing devices (free-radical clocks^{2,7}) to investigate the rates of primary, secondary and tertiary acyl radicals with the above common reducing agents.⁸

Acid chlorides and phenylseleno esters have been reported to undergo reductions to the corresponding aldehydes and alkanes in the presence of $(\text{TMS})_3\text{SiH}$ ⁹ or Bu_3SnH ¹⁰ and a free-radical initiator (eq 1).

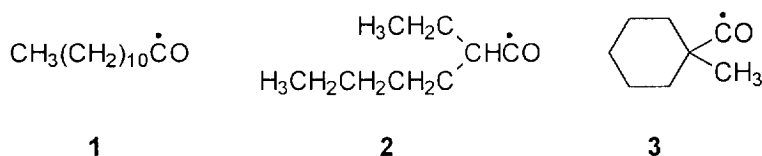


$\text{X}=\text{Cl}, \text{SePh}$

$\text{R}'_3\text{MH} = \text{Bu}_3\text{SnH}, (\text{TMS})_3\text{SiH}$

Thus, the acyl radicals **1-3** which are formed as intermediates in the reductions of the corresponding acid derivatives, either abstract hydrogens from the reducing agents or decarbonylate prior to the

hydrogen transfer. Therefore, a competition between the two processes allow for the determination of the rate constant for the hydrogen abstraction providing that the rate of decarbonylation is known.



We obtained by GC analysis the relative yields of RC(O)H and RH , under conditions in which hydrides were the only source of hydrogen and their concentrations did not change significantly during the experiment. Mean values of the k_d/k_{SiH} and k_d/k_{SnH} were obtained at different hydride concentrations according to $(k_d/k_{\text{MH}}) = ([\text{RH}]/[\text{RCHO}])[\text{R}'_3\text{MH}]$.^{11,12} The value of k_d/k_{SnH} for the primary acyl radical was calculated from the appropriate integrated rate equation.¹³ The data are summarized in table I.

Table I. Competitive Kinetic Data for the Reactions^a of Acyl Radicals with the Two Hydrides and Their Decarbonylation at 80°C

acyl radical	k_d/k_{SiH} , ^b M	k_d/k_{SnH} , ^b M	$k_{\text{SnH}}/k_{\text{SiH}}$
1	0.124 ± 0.026^c	$0.0097 \pm 0.0006^{d,e}$	12.78
2	4.075 ± 0.134^c	0.282 ± 0.022^d	14.45
3	98.73 ± 11.81^d	8.009 ± 0.260^d	12.32

^a*Tert*-butylbenzene together with the appropriate amount of hydride was employed as solvent. ^bErrors correspond to twice standard deviation. ^cAcid chloride as starting material. ^dPhenylseleno ester as starting material. ^eCalculated from the loss of starting material (see ref. 13).

As illustrated in table I, the three values obtained for $k_{\text{SnH}}/k_{\text{SiH}}$ are very close. Thus, at 80°C, acyl radicals abstract a hydrogen from Bu_3SnH about 13 times faster than $(\text{TMS})_3\text{SiH}$, this value being independent of the composition of the carbon substituent at the carbonyl moiety. Such a behaviour is in agreement with the fact that all $\text{R}\dot{\text{C}}\text{O}$ are σ -type radicals, and it is expected that they will exhibit very similar reactivities in their intermolecular reactions. On the other hand, the k_d/k_{SiH} and k_d/k_{SnH} increase approximately 30-fold on going from primary to secondary and on going from secondary to tertiary since the rates of decarbonylation of acyl radicals are highly dependent on the degree of stabilisation of the alkyl radical.¹⁴

Relative rate constants in Table I can be converted to absolute rate constants for hydrogen abstraction from the Bu_3SnH and $(\text{TMS})_3\text{SiH}$ via the absolute kinetic data for the decarbonylation reactions. Although kinetic data for such unimolecular processes are numerous,^{14,15} the choice is not an easy one. For example, the reported frequency factor for the endothermic decarbonylation scatters between 10^{11} and $4 \times 10^{14} \text{ s}^{-1}$.¹⁴ A value close to $10^{13.0} \text{ s}^{-1}$ is expected for a decomposition reaction.¹⁶ Furthermore, Fischer and coworkers have recently shown that the rate constant for the decarbonylation of

the pivaloyl radical decreases markedly with increasing solvent polarity,¹⁷ i.e. a 4-fold increase from acetonitrile ($1.9 \times 10^5 \text{ s}^{-1}$) to hexane ($8.3 \times 10^5 \text{ s}^{-1}$). With the due precaution, therefore, taking $k_d = 7.3 \times 10^5 \text{ s}^{-1}$ for the decarbonylation of tertiary acyl radicals in *tert*-butylbenzene as a solvent at 23°C ¹⁸ and assuming $\log(A/\text{s}^{-1}) = 13.0$ we first estimated $k_d = 1.0 \times 10^7 \text{ s}^{-1}$ at 80°C and then $k_{\text{SiH}} = 1.0 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ and $k_{\text{SnH}} = 1.3 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$, at 80°C . $(\text{TMS})_3\text{SiH}$ is 4-12 times and Bu_3SnH is 3-5 times less reactive with acyl radicals than with alkyl radicals at 80°C .^{3,4}

To our knowledge, the rate constant of the decarbonylation of primary alkyl substituted acyl radicals has been reported only in the gas phase¹⁹ whereas the decarbonylation of secondary alkyl substituted acyl radicals has previously been studied in tetraethoxysilane,²⁰ although in the latter the Arrhenius parameters are subject to large error due to uncertainties in the estimation procedure. Combination of the k_{SiH} and k_{SnH} with the kinetic data in Table I yields the rate constants (at 80°C) of $1.3 \times 10^4 \text{ s}^{-1}$ and $3.9 \times 10^5 \text{ s}^{-1}$ for the decarbonylation of primary and secondary alkyl substituted acyl radical, respectively, the former being a factor of 2 faster than the gas phase value¹⁹ and the latter a factor of 2.6 slower than the liquid phase value.²⁰

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11. Where k_d , k_{SiH} and k_{SnH} are the rate constants for decarbonylation, hydrogen abstraction from $(TMS)_3SiH$ and hydrogen abstraction from Bu_3SnH , respectively.
12. **General procedure for the kinetic measurements:** a solution of the acyl derivative, the appropriate hydride (in a ratio of ca. 1:20) and an internal GC standard, in *tert*-butylbenzene was degassed and sealed under argon in Pyrex ampules. The reaction mixture was photolysed at 80°C. Di-*tert*-butylperoxide was used as the radical initiator for the reactions with acyl chlorides. The products of the reactions were analysed by GC using a 30m x 0.53mm HP-5 column with temperature programming from 40 to 250°C using a HP Series II chromatograph. The products of interest were identified by comparison of their retention times with authentic materials.
13. Di-*tert*-butylperoxide together with an internal GC standard were added to a solution of a ca. 1:1 ratio of a known amount of tin hydride (from 0.1 to 0.15 M) and phenylseleno ester. The resulting solutions were degassed, sealed under argon in Pyrex ampules, and heated at 80°C for 3 to 4 hours. The k_d/k_{SnH} ratio was determined by using the following equation:

$$[RCHO]/[RH] = 1/[RH]\{[Bu_3SnH]_0 + k_d/k_{SnH}\}\{1 - e^{-k_{SnH}/k_d[RH]}\} - 1$$
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