Hydrogen Donor Abilities of Germanium Hydrides

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Summary: Rate constants for the reaction of primary alkyl radicals with a variety of germanium hydrides have been measured by using the one-carbon ring expansion of cyclopentanones as a timing device. The radical-trapping abilities of these germanes and other common group 14 hydrides are compared.

Introduction

Free radicals are of considerable importance in the development of organic chemistry, and many radical-based strategies employ group 14 hydrides.[1] The majority of such chain processes have been carried out by using Bu_3SnH or $(TMS)_3SiH$, which are the most widely used reagents under reduction conditions.[1,2] One of the propagation steps of these radical-chain reactions is the hydrogen transfer from the reducing agent to a radical (eq 1).[3] To modulate the hydrogen donor abilities of

$$R^\bullet + X_3MH \longrightarrow RH + X_3M^\bullet \qquad (1)$$

silicon hydrides, a significant number of compounds have been introduced as reducing agents based on their rate constants with primary alkyl radicals.[3,4]

In the germanium hydride series only the rate constants of a variety of carbon-centered radicals with tributylgermanium hydride have been reported. Table 1 shows the kinetic data that were mainly obtained by competition methods from Ingold's laboratory.[5−9] Activation parameters were also obtained for the 5-hexenyl and 1-methyl-5-hexenyl radicals.[5,7] To our knowledge, there are not any data available on the reactivity of other substituted germanium hydrides, with the exception of our preliminary results on the reaction of $(Me_3Si)_3GeH$ with 5-hexenyl radical, for which we reported a value of 3.1×10^6 M^{-1} s^{-1} at 25 °C.[10] Herein, we describe our kinetic studies on the hydrogen donor abilities of a variety of substituted germanium hydrides toward primary alkyl radicals.

Table 1. Rate Constants for the Reaction of Carbon−Centered Radicals with Bu_3GeH at ca. 30 °C

radical	k, $M^{-1}s^{-1}$	ref
$CH_3^\bullet$	5×10^5	5
$CH_2{=}CH(CH_2)_4CH_2^\bullet$	1.0×10^5	5
$Me_3SiCH_2CH_2CH_2^\bullet$	1.0×10^5	6
$Me_3SiCH_2CH_2^\bullet$	8.8×10^4	6
$Me_3SiCH_2^\bullet$	6.3×10^5	6
$CH_2{=}CH(CH_2)_4\dot{C}HMe$	2.2×10^4	7
$C_6H_5^\bullet$	2.6×10^{8} [a]	8
$Me_2C{=}CH^\bullet$	3.5×10^{7} [a]	8
c-$C_3H_5^\bullet$	1.3×10^{7} [a]	8
n-$C_7F_{15}^\bullet$	1.5×10^7	9

[a] The value probably refers to the reaction mixture of phenyl or 2,2-dimethyl vinyl or cyclopropyl and its acyloxy radical percursor (see ref 3).

Results and Discussion

An indirect procedure for measuring the rate constant of eq 1 involves competition between this process and a unimolecular path of the radical (*free-radical clock* methodology[11]). In his review Newcomb summarized competition methods and calibrated unimolecular rearrangements of radicals for this purpose.[3] For example, the rate constants, k_H, of the primary alkyl radical $U^\bullet$ with a variety of germanium hydrides can be obtained (Scheme 1), providing that conditions can be found in which the radical $U^\bullet$ is partitioned between the two reaction channels (i.e., a reaction with the X_3GeH and a rearrangement to the $R^\bullet$ radical) and that the rate constant k_r has been previously determined.

This scenario can be achieved with the most popular example of 5-*exo* cyclization of the 5-hexenyl radical (eq 2)[12] and the recently calibrated one-carbon ring expan-

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Scheme 1

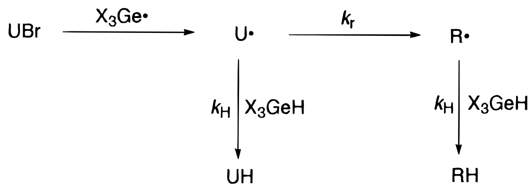
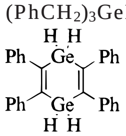
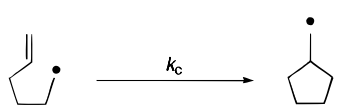


Table 2. Kinetic Data for the Hydrogen Atom Abstraction by Radicals 1 and 3 from a Variety of Germanes

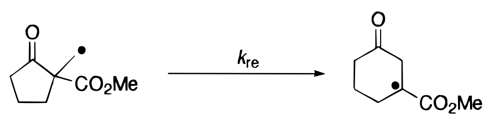
XH^a	radical clock	T, °C	k_H/k_c,[b,c] M^{-1}	k_H/k_{re},[b,c] M^{-1}	k_H, M^{-1} s^{-1}
Bu_3GeH	1 → 2	80	0.25[d]		3.8×10^5
	3 → 4	80		0.91 ± 0.22	3.8×10^5
$ArGeH_3$	3 → 4	80		6.7 ± 2.0	2.8×10^6
Ar_2GeH_2	3 → 4	80		5.1 ± 2.3	2.1×10^6
Ph_3GeH	3 → 4	80		9.1 ± 2.8	3.8×10^6
$PhCH_2(Et)GeH_2$	3 → 4	80		3.2 ± 0.5	1.3×10^6
$(PhCH_2)_3GeH$	3 → 4	80		7.1 ± 1.4	3.0×10^6
	3 → 4	80		44.8 ± 4.9	1.9×10^7
$(Me_3Si)_3GeH$	1 → 2	50	18.3 ± 3.2		1.5×10^7

[a] Ar = 2,4,6-trimethylphenyl. [b] Average of several different experiments (at least seven). [c] Errors correspond to one standard deviation. [d] Calculated from the Arrhenius expression given in ref 5.

sion of radical **3** (eq 3),[13] if the germanium hydride



1 **2** (2)



3 **4** (3)

concentration changes appreciably during the course of the reaction (bimolecular process under second-order conditions). Under these conditions eq 4 holds, where $[UH]_f$ is the direct reduction product, $[RH]_f$ the rearranged reaction product, and $[X_3GeH]_0$ the initial germanium hydride concentration.

$$\frac{[UH]_f}{[RH]_f} = \frac{1}{[RH]_f}\left\{[X_3GeH]_0 + \frac{k_r}{k_H}\right\}\left\{1 - e^{-(k_H/k_r)[RH]_f}\right\} - 1 \qquad (4)$$

The quantities of UH and RH were obtained by GC analysis, following the thermally initiated radical reaction, and by using an internal standard. The k_H/k_c and k_H/k_{re} ratios reported in Table 2 were obtained as the average of several different experiments (at least seven). Taking $k_c = 8.4 \times 10^5$ s^{-1} at 50 °C for reaction **1** → **2**[12] and $k_{re} = 4.2 \times 10^5$ s^{-1} at 80 °C for reaction **3** → **4**,[13] k_H values were calculated and are reported in Table 2.

The agreement between the rate constant obtained by Ingold's group and our group for the reaction of primary alkyl radical **1** and **3** with Bu_3GeH is gratifying. The rate constant for Ph_3GeH is 1 order of magnitude greater than Bu_3GeH, whereas the monosubstituted mesityl germane is about 1/4 slower, if the statistical number of hydrogens abstracted is taken into account. The second mesityl group has no activation, probably due to the twisting of the aryl group in the corresponding radical for steric hindrance and, therefore, to a lesser delocalization of the unpaired electron on the aromatic rings. Benzyl substitution, whether single or multiple, appreciably increases the rate constant about 2 times per substitution. This is probably due to a stabilizing interaction of the unpaired electron with the phenyl ring through space. The enhancement in the reactivity of 1,4-digermacyclohexa-2,5-diene is reshaped if taken into account the statistical number of hydrogens abstracted. However, the dienic substituent substantially increases the rate constant. Finally, the replacement of *n*-butyl groups in Bu_3GeH by Me_3Si groups produces about an 80-fold increase in the rate constant at 50 °C.

The rate constants increase along the series Bu_3GeH < Ph_3GeH < $(Me_3Si)_3GeH$ and are within 2 orders of magnitude. Since, the Ge−H bond dissociation energy in Bu_3GeH is 2.5 kcal mol^{-1} stronger than in Ph_3GeH,[14] this trend can be entirely attributed to more favorable thermodynamic factors along the series. However, polarized transition states may also play a role, since the rate constant of the $Me_3SiCH_2^\bullet$ radical with Bu_3GeH was found to be slightly faster than the corresponding value of the methyl radical.[6] In Table 3 are some representative data of the reaction of primary alkyl radicals with the most common group 14 hydrides. For a particular substituent the rate constant increases along the series R_3SiH < R_3GeH < R_3SnH, which is in good agreement with the available thermodynamic data of group 14 hydrides.[16] For a particular metal hydride, the rate constant increases along the substituent series alkyl < phenyl < Me_3Si. It is worth mentioning that although the replacement of alkyl groups in R_3SiH and R_3GeH by phenyl groups produces about a 10-fold increase in both rate constants, the replacement of alkyl groups by Me_3Si groups produces about a 400-fold and 80-fold increase in the rate constants for the silane and the germane, respectively, at 50 °C. The stability of the $(Me_3Si)_3Si^\bullet$ radical is due to through-space (hypercon-

Table 3. Comparison of Rate Constants (in M^{-1} s^{-1}) for the Reaction of Primary Alkyl Radicals with Various Group 14 Hydrides

R	R_3SiH^a	R_3GeH^b	R_3SnH
alkyl	3.4×10^3 at 80 °C	3.8×10^5 at 80 °C	6.4×10^6 at 80 °C[c]
phenyl	4.6×10^4 at 110 °C	3.8×10^6 at 80 °C	4.1×10^7 at 80 °C[d]
Me_3Si	7.2×10^5 at 50 °C	1.5×10^7 at 50 °C	

[a] From ref 4a. [b] This work. [c] From ref 12. [d] From ref 15.

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(16) Bond dissociation energies for Et_3Si-H, Bu_3Ge-H, and Bu_3Sn-H are 95.1, 88.6, and 78.6 kcal mol^{-1}, respectively.[15]

jugation) interaction between the bonding and/or antibonding Si−C *β*-bond.[17] The $(Me_3Si)_3Ge^{\bullet}$ radical is expected to be stabilized by similar interactions. This conjugative effect is also expected to be different in the two radicals due to the different sizes of the orbitals containing the unpaired electrons.

Experimental Section

Materials. The mesityl-substituted germanium hydrides were prepared by reacting an appropriate amount of mesMgBr with $GeCl_4$ followed by purification and reduction of the corresponding chloride with $LiAlH_4$.[18] Ph_3GeH,[19] $(PhCH_2)_3GeH$,[20] and $PhCH_2(Et)GeH_2$ [21] were synthesized following literature procedures starting from $GeCl_4$. 1,4-Digermacyclohexa-2,5-diene was prepared by reacting GeI_2 with diphenylacetylene followed by reduction of the tetraiodo derivative with $LiAlH_4$.[22] Bu_3GeH and $(Me_3Si)_3GeH$ were commercially available from Aldrich.

General Procedure for the Kinetic Experiments. Toluene or benzene containing a small amount of decane as an internal GC standard was used as solvent. Appropriate amounts of alkyl bromide (0.01 M), germanium hydride (0.02−0.07 M), and radical initiator (AIBN 10 mol %) were added, and the resulting solutions were degassed, sealed under argon in Pyrex ampules, and heated at the appropriate temperature for 5−20 min. The products of interest were identified by comparison of their retention times with authentic materials. For additional information on specific experimental conditions, see the tables in the Supporting Information.

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Supporting Information Available: Tables 4−11 giving a detailed product ratio of kinetics. This material is available free of charge via the Internet at http://pubs.acs.org.

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