to tertiary amines, mostly substituted tribenzylamines. These are exothermic reactions with rate constants well below diffusion limits. For example, the rate constants for protonations of tribenzylamine and of *N,N*-dimethylbenzylamine are $1.8 \times 10^4\ M^{-1}\ s^{-1}$ and $4.2 \times 10^6\ M^{-1}\ s^{-1}$, respectively. Kreevoy suggests that the slow rates are the result of the necessity for removing a solvent molecule from the proton before reaction.

Bernasconi has found slow proton transfers in 50% (vol) aqueous dimethyl sulfoxide for the reactions of the morpholine adducts of activated ethylenes with bases.[15,16] Bernasconi's results bear a striking similarity to those of the present study. In both the reactions of 1,1-dinitro-2,2-diphenylethylene[15] and of benzylidenemalononitrile[16] with amines, the slow proton transfer is observed for reaction of morpholine but not for reaction of piperidine. The proton transfers from the morpholine adduct of 1,1-dinitro-2,2-diphenylethylene to tertiary amines is slower than to morpholine, while the transfer to an anion, *p*-nitrophenoxide ion, is faster than that to morpholine. Bernasconi suggests that steric effects are responsible for the slow proton transfers from the ammonium nitrogens.

The fact that the slow proton transfers in both Bernasconi's and the present work are observed for morpholine but not for piperidine reactions probably does not indicate a large difference in the proton transfer rate constants for the two amines. Most likely, as Bernasconi argues,[15] the different behaviors are due to slightly different balances of competing reaction rates for the two amines. In the present case of reactions with pyronin, the proton transfer from the piperidine adduct to piperidine would have to have a rate constant of less than $5 \times 10^6\ M^{-1}\ s^{-1}$ in order to cause observable behavior in the pseudo-first-order rate constants in the concentration range studied. This is only slightly larger than the value reported in Table III for the corresponding reaction of morpholine.

Equilibrium Constants for Alkoxide and Thiophenoxide Reactions. The equilibrium constant that we find for the addition of trifluoroethoxide ion to (*p*-(dimethylamino)phenyl)tropylium may be compared with the corresponding one for addition of hydroxide ion, $\log K = 6.65$.[13] The difference in values, 3.5 units, is only slightly greater than the difference in pK_a values of water (taken as 15.7) and trifluoroethanol, 3.3 units. The rate constant for reaction of trifluoroethoxide ion with the cation is 10 times greater than that for reaction of hydroxide ion. The conclusion, previously expected and now established, is that the greater kinetic reactivity of trifluoroethoxide than that of hydroxide ions cannot be due to a greater "carbon basicity" of the alkoxide ion.

The difference in pK_a's of thiophenol and carbomethoxymethanethiol in water, 1.5 units,[2,12] is very close to the difference of 1.4 units in the log K values for additions of the thiolates to (*p*-(dimethylamino)phenyl)tropylium ion.[17] Thiophenoxide ion, with a rate constant very near the diffusion limit, reacts 10 times faster than the alkanethiolate.[17] The greater kinetic reactivity of the thiophenoxide cannot be ascribed to greater equilibrium reactivity.

As long as the attaching atom of the nucleophile remains constant, the equilibrium reactivities of nucleophiles with cations closely parallel the basicities of the nucleophiles. Even this limited orderly behavior is not seen in the kinetics of reactions.

Acknowledgment. This work was supported by Grant GM-12832 from the National Institutes of Health, U.S. Public Health Service, and Grant CHE 7724701 from N.S.F.

Registry No. $CH_3OCH_2CH_2NH_2$, 109-85-3; $CF_3CH_2NH_2$, 753-90-2; *n*-PrS^-, 20733-14-6; *n*-PrSH, 107-03-9; $CH_3O_2CCH_2SH$, 2365-48-2; $CH_3O_2CCH_2S^-$, 64743-45-9; $C_6H_5S^-$, 13133-62-5; C_6H_5SH, 108-98-5; $CF_3CH_2O^-$, 24265-37-0; $HOCH_2CH_2S^-$, 57966-62-8; Me_2SO, 67-68-5; $DMAPTr^+$, 38054-74-9; CV^+, 7438-46-2; pyronin$\cdot BF_4^-$, 85338-00-7; malachite green, 569-64-2; *n*-butylamine, 109-73-9; piperidine, 110-89-4; morpholine, 110-91-8.

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[15] Bernasconi, C. F.; Carré, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 2698.

[16] Bernasconi, C. F.; Fox, J. P.; Fornarini, S. *J. Am. Chem. Soc.* **1980**, *102*, 2810.

[17] Ritchie, C. D.; Gandler, J. *J. Am. Chem. Soc.* **1979**, *101*, 7318.

[18] Ritchie, C. D.; Wright, D. J. *J. Am. Chem. Soc.* **1971**, *93*, 6574.

[19] Ritchie, C. D.; Virtanen, P. O. I. *J. Am. Chem. Soc.* **1972**, *94*, 4966.

[20] Ritchie, C. D.; Virtanen, P. O. I. *J. Am. Chem. Soc.*, **1972**, *94*, 1589.

Rate Constants and Arrhenius Parameters for the Reaction of a Primary Alkyl Radical with Tri-*n*-butylgermanium Hydride[1]

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Abstract: The rate constants for hydrogen atom abstraction from tri-*n*-butylgermanium hydride by the 5-hexenyl radical, k_5, have been measured in octane as solvent at temperatures varying from 233 to 393 K. Over this temperature range the data can be represented by $\log k_5\ (M^{-1}\ s^{-1}) = (8.44 \pm 0.47) - (4.70 \pm 0.62)/\theta$, where $\theta = 2.3RT$ kcal/mol. At ambient temperatures this germanium hydride is only about $^1/_{20}$ as reactive toward primary alkyl radicals as the corresponding tin hydride. This should make it a useful probe for slow alkyl radical rearrangements.

The free-radical chain reaction of tri-*n*-butyltin hydride with alkyl halides[4] has proved to be a particularly valuable method for studying the rearrangements of alkyl radicals.[5] As early as 1966 Walling et al.[6] showed that the reaction of 5-hexenyl bromide with the tin hydride could be represented by eq 1–4. By measuring the relative yields of hexene and methylcyclopentane at various tin hydride concentrations, Walling was able to calculate the rate constant ratio, k_2/k_3.[6,7] The absolute value of the rate constant for H atom abstraction from the tin hydride by a primary alkyl

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[1] Issued as N.R.C.C. No. 21212.

[2] N.R.C.C. Research Associate, 1982–1983.

[3] N.R.C.C. Visiting Scientist, 1982.

[4] Kuivila, H. G. *Acc. Chem. Res.* **1968**, *1*, 229–305.

[5] For reviews, see: Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. I, Essay 4. Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073–3100.

[6] Walling, C.; Cooley, J. H.; Ponaras, A. A.; Racah, E. J. *J. Am. Chem. Soc.* **1966**, *88*, 5361–5363.

[7] See also: Walling, C.; Cioffari, A. *J. Am. Chem. Soc.* **1972**, *94*, 6059–6064. Beckwith, A. L. J.; Moad, G. *J. Chem. Soc., Chem. Commun.* **1974**, 472–473. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1083–1092.

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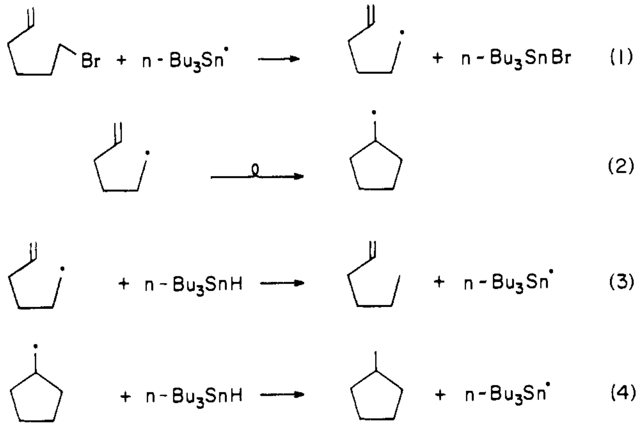


radical, i.e., k_3, was reported in 1968[8] and has subsequently been very accurately determined.[9] This has allowed the rate constant for reaction 2 and for other primary alkyl radical rearrangements to be calculated and compared.[5,10] However, the tin hydride method for measuring rate constants for radical rearrangements does have certain limitations. The relatively high value for k_3 (viz.[9] 2.2×10^6 M^{-1} s^{-1} at 296 K) renders the tin hydride method rather inaccurate for primary alkyl radical rearrangements which occur slowly ($k \leq$ ca. 10^3 s^{-1}) at ambient temperatures.

One suggested method for overcoming this difficulty has been to replace tributyltin hydride by the corresponding germanium compound, which should be a less reactive hydrogen donor.[12,13] However, absolute rate constants for H atom abstraction from n-Bu_3GeH have been measured only for the $CH_3\cdot$ and $CCl\cdot$ radicals.[12] In order to make n-Bu_3GeH a viable alternative to n-Bu_3SnH in quantitative studies of primary alkyl radical rearrangements, we now report the results of a detailed kinetic investigation of its reaction with the 5-hexenyl radical.

Experimental Section

n-Octane, containing a small amount of benzene as an internal VPC standard, was used as the solvent. It contained tri-*n*-butylgermanium hydride at a concentration of ca. 1 M or ca. 2 M and 5-hexenyl bromide at a concentration of ca. 0.1 M. A small quantity of di-*tert*-butyl peroxide was generally added to act as the free-radical chain initiator. Samples of this reaction mixture were degassed and sealed under vacuum in Pyrex or quartz tubes for thermolysis or photolysis, respectively. Each tube provided just one product sample for analysis. Reactions were initiated by the thermal decomposition of the peroxide at temperatures as low as 303 K and at all higher temperatures. Photolysis of the peroxide, or in some experiments of the reactants without added peroxide, was also employed to initiate the reaction at 273 K and was used, in addition, at 233 and 303 K. The consumption of 5-hexenyl bromide was varied from as low as 2% to as high as 43% but was generally kept in the range 5–25%. Reaction times varied from a few minutes to several weeks. Products were analyzed by VPC on a 24 ft × $^1/_8$ in. 20% Carbowax column operating at 60–200 °C. The hydrocarbon products of interest, 1-hexene, methylcyclotpentane, and cyclohexane, were identified by comparison of retention times with authentic material. The sum of the concentrations of these three hydrocarbons plus the 5-hexenyl bromide reactant remained constant to better than ±15% throughout the monitored course of reaction at each temperature.[14]

With the exception of tri-*n*-butylgermanium hydride (see Acknowledgment), the reactants and reference compounds were commerical materials, the purity of which was checked before use.

Table I. Kinetic Data for the Reaction of 5-Hexenyl Bromide with n-Bu_3GeH in n-Octane at Various Temperatures

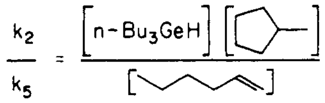
T, K	[n-Bu_3GeH],[a] M	k_2/k_5,[b] M
233[c]	0.96–1.92	0.806 ± 0.13
273[c]	0.96–1.92	1.25 ± 0.15
303[c]	0.96–1.92	2.82 ± 0.25
303[d]	0.96–1.92	2.90 ± 0.16
328[d]	0.96–1.96	3.45 ± 0.13
363[d]	1.00–1.96	4.24 ± 0.14
393[d]	0.96–1.96	4.81 ± 0.30

[a] Range of concentrations employed. [b] Errors correspond to one standard deviation. [c] Photoinitiation. [d] Thermal initiation.

Results

The two major hydrocarbon products were 1-hexene and methylcyclopentane, the relative concentrations of which varied in the expected manner at each temperature as the concentration of germanium hydride was changed but remained unchanged (within experimental error) during the course of a reaction.[14] Minor quantities of cyclohexane were also formed, its concentration relative to methylcyclopentane increasing with temperature (as expected[5-7]) from 1.7% (on the basis of methylcyclopentane) at 233 K to 3.7% at 393 K.[15]

Since the germane concentration remains essentially constant under our experimental conditions the following relation is obeyed:



where k_5 is the rate constant for the germane analogue of reaction 3. Mean values of the k_2/k_5 ratios obtained at different germane concentrations and varying extents of reaction at each temperature are summarized in Table I. The results of each individual experiment are recorded as supplementary material in Table II. Analysis of all experimental data yields the Arrhenius expression:

$$\log (k_2/k_5)\ (M) = (1.93 \pm 0.15) - (2.15 \pm 0.20)/\theta$$

where $\theta = 2.3RT$ kcal/mol and the errors correspond to 95% confidence limits.

Discussion

Combination of the Arrhenius expression for k_2/k_5 with that recently measured[9] for k_2 yields the relationship:

$$\log k_5\ (M^{-1}\ s^{-1}) = (8.44 \pm 0.47) - (4.70 \pm 0.62)/\theta$$

The comparable expression for hydrogen atom abstraction from tri-*n*-butyltin hydride by primary alkyl radicals is[9]

$$\log k_3\ (M^{-1}\ s^{-1}) = (9.07 \pm 0.24) - (3.69 \pm 0.32)/\theta$$

The difference between these two preexponential factors is just within our estimated error limits, while the difference between the activation energies is just outside those limits. A higher activation energy for the germane reaction is to be expected since Ge–H bonds are ca. 8–10 kcal/mol stronger than comparable Sn–H bonds.[12,16]

At room temperature (296 K) hydrogen abstraction from the germane ($k_5 = 9.3 \times 10^4$ M^{-1} s^{-1}) is considerably slower than that from the stannane ($k_3 = 2.2 \times 10^6$ M^{-1} s^{-1}). The value of k_5 at 296 K was also measured in benzene. The value obtained (7.8×10^4 M^{-1} s^{-1}) is equal within experimental error to the value in *n*-octane. Data from which this k_5 value was calculated are given in Table III as supplementary material.

The rate constant for reaction of the methyl radical with n-Bu_3GeH has been measured previously at room temperature by the rotating sector method.[12] However, the value obtained (viz.[12] 1.4×10^5 M^{-1} s^{-1}) was only about $^1/_{70}$ of the currently accepted rate constant for the $CH_3\cdot$ + n-Bu_3SnH reaction at this temperature (viz.[9] 1.0×10^7 M^{-1} s^{-1}). It would seem to be too low

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[8] Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 1055–1056, 7047–7055.

[9] Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739–7742.

[10] Radicals which undergo unimolecular rearrangements at known rates find wide use as "clocks" for measuring the rates of radical–molecule reactions.[11]

[11] Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317–323.

[12] Carlsson, D. J.; Ingold, K. U.; Bray, L. C. *Int. J. Chem. Kinet.* **1969**, *1*, 315–323.

[13] Kaplan, L. *Chem. Commun.* **1969**, 106–107; *React. Intermed. (Plenum)* **1981**, *2*, 251–314.

[14] The consumption of 1-hexene under standard reaction conditions with 1-hexane:n-Bu_3GeH (1:1, v/v) was checked and found to be ≤3%.

[15] Similar cyclohexane/methylcyclopentane ratios have been reported for the tin hydride reaction.[5-7]

[16] Jackson, R. A. *J. Organomet. Chem.* **1979**, *166*, 17–19.

3580 *J. Am. Chem. Soc.* **1983**, *105*, 3580-3583

by about a factor of 4. Indeed, a pair of competitive experiments involving the reaction of CH_3I with n-Bu_3SnH/n-Bu_3SnD and n-Bu_3SnD/n-Bu_3GeH showed that the tin hydride was 18 times more reactive than the germanium hydride at room temperature.[12] Since this difference in reactivity is similar to the factor of 24 (i.e., k_3/k_5) found for primary alkyl radicals we suggest that the $CH_3\cdot + n\text{-}Bu_3GeH$ reaction has a room-temperature rate constant of about 5×10^5 M^{-1} s^{-1}. Since n-Bu_3GeH has about $^1/_{20}$ the reactivity of the corresponding tin hydride toward methyl and primary alkyl radicals, it should prove useful as a probe for slow alkyl radical rearrangements.

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Registry No. Tri-*n*-butylgermanium hydride, 998-39-0; 5-hexenyl bromide, 2695-47-8; 5-hexenyl, 16183-00-9.

Supplementary Material Available: Two kinetic (Tables II and III) giving detailed kinetic data (3 pages). Ordering information is given on any current masthead page.

Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. 41. Diethoxyphosphonyl Radicals[1]

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Abstract: Rate constants for the abstraction of halogen atoms by diethoxyphosphonyl radicals from some organic halides have been determined by EPR spectroscopy using competitive methods. Some typical rate constants (M^{-1} s^{-1} units) at ambient temperatures in di-*tert*-butyl peroxide/diethyl phosphite (4:1, v/v) as solvent follow: *tert*-butyl chloride, 3.5×10^2; *n*-butyl bromide, 1.0×10^4; *tert*-butyl bromide, 3.0×10^5; benzyl bromide, 1.2×10^6. Diethoxyphosphonyl radicals are less reactive in halogen atom abstractions than triethylsilyl or tri-*n*-butyltin radicals.

Although dialkoxyphosphonyl radicals, $(R'O)_2\dot{P}O$, have long been recognized as intermediates in some reactions of dialkyl phosphites,[3] they were not identified by EPR spectroscopy in solution until 1972.[4] At that time, it was shown that the EPR spectrum due to the $(R'O)_2\dot{P}O$ radical could be replaced by that of an alkyl radical upon the addition of certain alkyl halides to the system.[4] This implies that diethoxyphosphonyl radicals, for example, can abstract halogen atoms fairly readily:

$$(EtO)_2\dot{P}O + RX \rightarrow (EtO)_2P(O)X + R\cdot \tag{1}$$

Advantage has occasionally been taken of reaction 1 to generate site-specific alkyl radicals for study by EPR spectroscopy.[5] However, for such purposes it has been far more common to employ either trialkylsilyl radicals[6,7] or trialkyltin radicals[7-9] as the halogen-abstracting agents:

$$R'_3Si\cdot + RX \rightarrow R'_3SiX + R\cdot \tag{2}$$

$$R'_3Sn\cdot + RX \rightarrow R'_3SnX + R\cdot \tag{3}$$

Since there are now quite extensive lists of absolute rate constants for reaction 2 for R′ = Et,[10] and for reaction 3 for R′ = *n*-Bu,[11] we decided to measure some absolute rate constants for reaction 1 since this would permit quantitative comparison of these three reactions. In the earlier kinetic studies,[10,11] the rate constants for reaction 2 were determined by laser flash photolysis and those for reaction 3 by the rotating sector technique. Neither procedure proved suitable for reaction 1. The laser flash photolytic technique relies on an essentially "instantaneous" generation of the radical in question. This could just be achieved for $Et_3Si\cdot$ radicals in a di-*tert*-butyl peroxide/triethylsilane mixture. However, relatively high silane concentrations were required since the rate constant for H-atom abstraction from the silane by *tert*-butoxyl radicals is only 5.7×10^6 M^{-1} s^{-1} at 300 K.[12] For diethyl phosphite the comparable reaction (4) can be estimated to have a rate constant

$$Me_3CO\cdot + (EtO)_2P(O)H \rightarrow Me_3COH + (EtO)_2\dot{P}O \tag{4}$$

of ca. 5×10^5 M^{-1} s^{-1} at room temperature,[13] which is much too slow for the "instantaneous" generation of diethoxyphosphonyl.[16] The rotating sector technique relies on the occurrence of a chain reaction of considerable chain length. Such a process does not occur between diethyl phosphite and alkyl halide at ambient temperatures.

For the above reasons values of k_1 were determined by kinetic EPR spectroscopy.[1,17,18] Competitive methods were employed,

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[1] Issued as N.R.C.C. No. 21211. Part 40: Sutcliffe, R.; Ingold, K. U. *J. Am. Chem. Soc.* **1982**, *104*, 6071-6076.

[2] N.R.C.C. Research Associate: (a) 1981-1982. (b) 1979-1981.

[3] Walling, C.; Pearson, M. S. *Top. Phosphorus Chem.* **1966**, *3*, 1-56. Cadogan, J. I. G. *Adv. Free-Radical Chem.* **1967**, *2*, 203-250.

[4] Davies, A. G.; Griller, D.; Roberts, B. P. *J. Am. Chem. Soc.* **1972**, *94*, 1782-1783.

[5] Chen, K. S.; Krusic, P. J.; Meakin, P.; Kochi, J. K. *J. Phys. Chem.* **1974**, *78*, 2014-2030.

[6] Hudson, A.; Jackson, R. A. *Chem. Commun.* **1969**, 1323-1324.

[7] Griller, D. *Magn. Reson. Rev.* **1979**, *5*, 1-23.

[8] Cooper, J.; Hudson, A.; Jackson, R. A. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1056-1060.

[9] Mendenhall, G. D.; Griller, D.; Lindsay, D.; Tidwell, T. T.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 2441-2447.

[10] Chatgilialoglu, C.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1982**, 104, 5123-5127.

[11] Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 7047-7055.

[12] Chatgilialoglu, C.; Scaiano, J. C.; Ingold, K. U. *Organometallics*, **1982**, *1*, 466-469.

[13] A value for k_4 of ca. 2×10^4 M^{-1} s^{-1} at 263 K has been reported,[14] which would correspond to ca. 5.5×10^4 M^{-1} s^{-1} at room temperature. However, this value was based on an estimated rate constant of 1×10^5 M^{-1} s^{-1} at 303 K for H-atom abstraction from cyclopentane by *tert*-butoxy radicals. The rate constant for this latter reaction has now been measured and found to be 8.8×10^5 M^{-1} s^{-1} at room temperature.[15]

[14] Brunton, G.; Ingold, K. U. *Org. Magn. Reson.* **1975**, *7*, 527-528.

[15] Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520-4527.

[16] The $(EtO)_2\dot{P}O$ radical can also be generated by reaction of *tert*-butoxyl with tetraethyl pyrophosphite,[4] but secondary reactions, including the formation of the *tert*-butyl radical,[4] can be a problem in this system.

[17] Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 193-200.

0002-7863/83/1505-3580$01.50/0 Published 1983 by the American Chemical Society