observed in these systems suggest that the S_0 and S_1 states of methoxy-substituted benzenes and toluenes may be quite different, much more so than has been observed for alkyl-substituted benzenes.

Acknowledgment. We thank J. Campbell for obtaining the NMR spectra, J. Paine for helpful discussions, and R. Ferguson, A. Kassman, A.C. Lilly, and B. LaRoy for their support and encouragement. This work was supported in part by ONR.

Registry No. 4, 100-66-3; **5**, 104-93-8; **6**, 100-84-5; **9**, 578-58-5; **12**, 1515-95-3; **13**, 91-16-7; **15**, 151-10-0; **16**, 150-78-7.

Supplementary Material Available: Experimental procedures for the preparation of 1-methoxy-3-(methyl-d_3)benzene[29] (**7**), 1-(methoxy-d_3)-3-methylbenzene[30] (**8**), 1-methoxy-2-(methyl-d_3)benzene (**10**), 1-(methoxy-d_3)-2-methylbenzene (**11**), and 1,2-di(methoxy-d_3)benzene[31] (**14**) (3 pages). Ordering information is given on any current masthead page.

The Gas-Phase Acidities of the Alkanes

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Abstract: The gas-phase acidities of 15 simple alkanes have been determined in a flowing afterglow-selected ion flow tube (FA-SIFT) by a kinetic method in which alkyltrimethylsilanes are allowed to react with hydroxide ions to produce a mixture of trimethylsiloxide ions by loss of alkane and alkyldimethylsiloxide ions by loss of methane. The reaction is proposed to proceed by addition of hydroxide ion to the silane to form a pentacoordinate siliconate ion intermediate which decomposes through two transition states, one in which negative charge is placed on a methyl group and the other in which negative charge is placed on the alkyl group. The ratio of siloxide ions produced is proposed to be correlated to the relative basicity of the methyl and alkyl anions. The method is calibrated by making use of the known acidities of methane ($\Delta H^\circ_{\text{acid}} = 416.6$ kcal/mol) and benzene ($\Delta H^\circ_{\text{acid}} = 400.7$ kcal/mol). In general, methyl substitution is found to stabilize alkyl anions in the gas phase except that the ethyl anion is found to be more basic than the methyl anion. By combining the gas-phase acidities with the bond dissociation energies, the electron affinities (EA) of the corresponding alkyl radicals can be calculated. Many simple alkyl radicals are found to have negative EA's. The results for the alkyl groups studied are as follows, where the first number is the $\Delta H^\circ_{\text{acid}}$ (kcal/mol) of the corresponding alkane and the second number (in parentheses) is the EA (kcal/mol) of the alkyl radical: ethyl 420.1 (−6.4), isopropyl 419.4 (−9.5), cyclobutyl 417.4 (−7.5), cyclopentyl 416.1 (−7.0), *sec*-butyl 415.7 (−5.8), *n*-propyl 415.6 (−1.9), *tert*-butyl 413.1 (−5.9), isobutyl 412.9 (0.8), 3-butenyl 412.0 (1.7), cyclopropyl 411.5 (8.4), cyclopropylmethyl 410.5 (3.2), 1-methylcyclopropyl 409.2 (8.0), neopentyl 408.9 (4.8), vinyl 407.5 (16.1), and 2-propenyl 405.8 (15.8).

With the single exception of methane, the gas-phase acidities of the alkanes have not been determined,[1] and little more is known about their acidities in solution.[2] The problem is an experimental one; with few exceptions[3-5] alkyl anions have not been detected in the gas phase so that it has not been possible to apply the usual methods for determining their basicity. Yet such a determination would be of great fundamental interest, for it could, in principle, reveal a great deal about the electronic structures of simple anions. The problem is especially intriguing because theoretical calculations are, to some extent, at variance with experimental analogies. For example, replacement of a hydrogen atom in water by a methyl group to produce methanol results in a 10-kcal/mol *increase* in acidity.[6] Yet a number of high-level ab initio calculations[7] and a few investigations on carbanion salts in solution[2] indicate that the analogous substitution in the alkane series, from methane to ethane, will result in an acidity decrease.

$$H_2O \rightarrow HO^- + H^+ \qquad \Delta H^\circ_{\text{acid}} = 391 \text{ kcal/mol} \tag{1}$$

$$CH_3OH \rightarrow CH_3O^- + H^+ \qquad \Delta H^\circ_{\text{acid}} = 381 \text{ kcal/mol} \tag{2}$$

$$CH_4 \rightarrow CH_3^- + H^+ \qquad \Delta H^\circ_{\text{acid}} = 417 \text{ kcal/mol} \tag{3}$$

$$CH_3CH_3 \rightarrow CH_3CH_2^- + H^+ \qquad \Delta H^\circ_{\text{acid}} = \text{unknown} \tag{4}$$

In view of the failure of the standard methods for determining the acidity of these extremely weak acids, we were led to search for an alternative method which might prove useful as a general tool for investigating substituent effects on the acidity of alkanes. We reported preliminary results of our investigations in an earlier paper.[8] In the meantime we have made substantial instrumental improvements which greatly increase the accuracy of our results. In addition, we have extended our method to a much greater number of compounds so that a better analysis of substitution patterns can emerge.

Our method for determining the gas-phase acidities of the alkanes is a kinetic one based on a linear free energy relationship and grew out of our studies of the gas-phase anion chemistry of silanes.[9] We first used trimethylsilyl derivatives of organic

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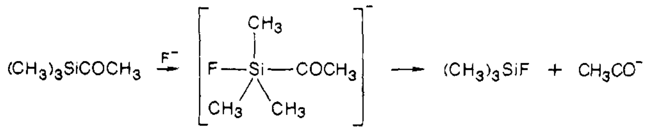
compounds as precursors for the generation of specific anions in the gas phase, anions which might not arise from proton abstraction reactions of the parent, nonsilylated compound. For example, the acetyl anion results from the reaction of acetyltrimethylsilane with fluoride ion.[10] We picture this reaction as proceeding through a pentacoordinate silicon anion (I) as shown in eq 5. Addition of fluoride ion to the silane to form this intermediate is highly exothermic. In the absence of solvent to remove this exothermicity, I will either revert to reactants or expel a carbanion by cleavage of a carbon–silicon bond. In this case the acetyl anion is formed exclusively since it is much less basic than the methyl anion. The reaction is driven by the formation of the extremely strong silicon–fluorine bond.

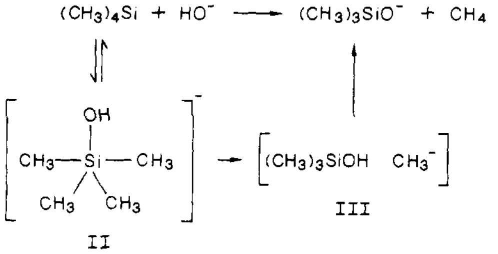


I

(5)

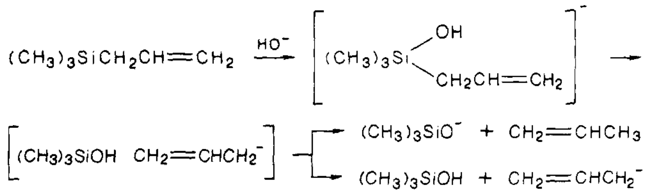
While the fluoride reaction can be used to generate moderately basic anions like acetyl and allyl, it fails for the formation of alkyl anions since insufficient energy is generated by silicon–fluorine bond formation to compensate for the greater basicity and smaller electron binding energy of the alkyl anions as compared to fluoride ion. Indeed, at 0.5 Torr of helium pressure, reaction of tetramethylsilane leads not to the production of CH_3^-, but rather to the formation of the pentacoordinate adduct, $(CH_3)_4SiF^-$, which transfers its excess energy to the helium bath gas.[11]

In contrast, reaction of tetramethylsilane with hydroxide ion forms trimethylsiloxide ion at every collision. By analogy with the fluoride reactions, we believe that this conversion occurs as shown in eq 6. Exothermic addition of hydroxide ion forms the pentacoordinate siliconate anion (II) which can revert to reactants or expel a methyl anion. While II does not contain sufficient energy to eject CH_3^-, it can form the ion–dipole complex III, in which a methyl anion is "solvated" by the trimethylsilanol molecule. Within this complex CH_3^- reacts rapidly and irreversibly with the hydroxyl hydrogen to form methane and the siloxide ion.



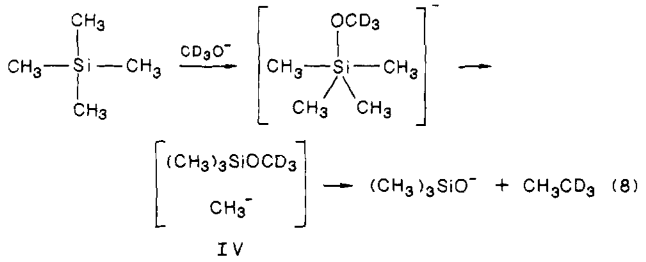
(6)

There are several experimental observations which lend credence to the mechanism postulated. For example, reaction of allyltrimethylsilane with hydroxide ion produces a mixture of trimethylsiloxide ion, by loss of propylene, and allyl anion, by loss of trimethylsilanol. In this case some of the relatively stable carbanion can escape from the complex before reaction with the hydroxyl hydrogen, as shown in eq 7.



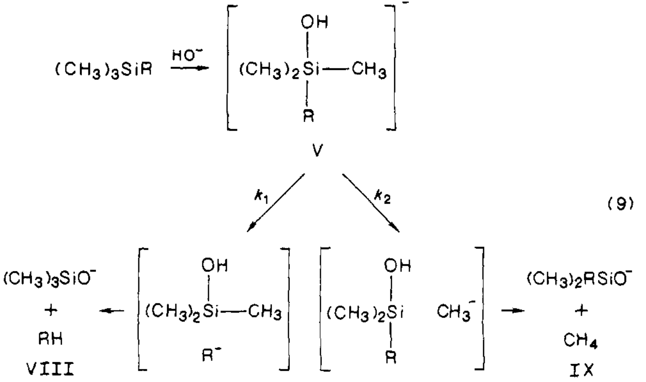
(7)

In a related experiment, Bowie and co-workers[12] allowed tetramethylsilane to react with CD_3O^- in an ion cyclotron resonance spectrometer and found undeuterated trimethylsiloxide ion among the product ions. The production of this ion is most reasonably accounted for by formation of a silane ether–methide ion complex (IV) in which the carbanion induces an S_N2 reaction on the methyl ether (eq 8). Indeed, even in the reaction of tetramethylsilane with fluoride ion there is some formation of an anion, $(CH_3)_2F$-$SiCH_2^-$, resulting from addition of F^- and loss of CH_4, again implicating a methyl anion intermediate which, in this case, abstracts a proton from one of the methyl groups.[11]



(8)

If an alkyltrimethylsilane is allowed to react with hydroxide ion in the gas phase, two siloxide ions are produced, one resulting from loss of methane and the other from loss of the alkane. The formation of these two ions is easily accounted for by the mechanism given above; the initially formed siliconate ion (V) can expel an alkyl or a methyl anion, either of which can rapidly react with the hydroxylic hydrogen to form the hydrocarbon and the siloxide ion (eq 9). We proposed[8] that the relative amounts of the two siloxide ions formed as the products of this reaction, (VIII and IX), reflect the ease of formation of the two ion–dipole complexes VI and VII, and that this in turn will be dominated by the relative ease of formation of the two carbanions, R^- and CH_3^-, taking into consideration, of course, the need for a statistical correction because of the presence of three methyl groups and only a single alkyl group. Our method of determining alkane acidities is then basically a simple one. A series of alkyltrimethylsilanes was prepared and each silane allowed to react with hydroxide ion in the gas phase using a flowing afterglow-selected ion flow tube. The relative amount of the two siloxide ions produced was determined. A linear free energy relationship between the logarithm of the siloxide ion ratio and the acidity of the corresponding alkanes was assumed, and the slope of the correlation was determined from the results for the cleavage reaction of phenyltrimethylsilane, since the acidities of both benzene and methane are accurately known.[1]



The key to the assumed correlation is that loss of RH and CH_4 depends upon the relative ease of forming R^- and CH_3^- in the transition state which is related to the enthalpy difference, $\Delta\Delta H$, of forming complexes VI and VII. This difference will, in turn, depend upon the sum of the differences in the R–Si and CH_3–Si bond strengths and the electron affinities of R and CH_3 as:

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[10] DePuy, C. H.; Bierbaum, V. M.; Damrauer, R.; Soderquist, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 3385.

[11] DePuy, C. H.; Bierbaum, V. M.; Flippin, L. A.; Grabowski, J. J.; King, G. K.; Schmitt, R. J.; Sullivan, S. A. *J. Am. Chem. Soc.* **1980**, *102*, 5012. A general treatment of both the computational and experimental aspects of siliconate formation has recently been published. Damrauer, R.; Burggraf, L. W.; Davis, L. P.; Gordon, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 6601.

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$$\Delta\Delta H = [\mathrm{BDE}(\mathrm{R{-}Si}) - \mathrm{BDE}(\mathrm{CH_3{-}Si})] - [\mathrm{EA}(\mathrm{R}) - \mathrm{EA}(\mathrm{CH_3})] \tag{10}$$

Analogously the difference in acidity between RH and CH_4 depends upon the differences in the R–H and CH_3–H bond strengths and the same electron affinities as:

$$\Delta\Delta H = [\mathrm{BDE}(\mathrm{R{-}H}) - \mathrm{BDE}(\mathrm{CH_3{-}H})] - [\mathrm{EA}(\mathrm{R}) - \mathrm{EA}(\mathrm{CH_3})] \tag{11}$$

where BDE is the bond dissociation energy and EA is the electron affinity of the radical. In order for there to be a correlation between these two processes the carbon–silicon bond dissociation energies must vary in approximately the same way as do the carbon–hydrogen bond dissociation energies. While carbon–silicon bond dissociation energies are not known for most alkyl groups, several carbon–tin BDE's are known and do correlate with carbon–hydrogen BDE's,[13] and it seems reasonable to suppose that bonds to silicon will also do so. With this assumption we can write, with respect to the two pathways in eq 9

$$\ln\,[k_1/k_2] = -\beta[\Delta H^\circ_{\mathrm{acid}}(\mathrm{RH}) - \Delta H^\circ_{\mathrm{acid}}(\mathrm{CH_4})] \tag{12}$$

where the constant β measures the sensitivity of the cleavage reaction toward the acidity difference between RH and CH_4.[14,15]

Experimental Section

All experiments were carried out with a tandem flowing afterglow-selected ion flow tube instrument (FA-SIFT) which has been described in detail previously.[16] In the source flow tube, hydroxide ions were formed by dissociative electron attachment to H_2O entrained in a stream of helium (~0.4 Torr pressure). The hydroxide ions as well as their H_2O solvated cluster ions were extracted through a small orifice into a vacuum chamber equipped with a quadrupole mass filter which was tuned to allow for the passage of m/z 17 ions. The mass-selected hydroxide ions were then injected into a stream of helium in a second flow tube and allowed to react with the appropriate alkylsilane. In this way, the reactions could be studied in the absence of other ions and precursor gas. At the end of the second flow tube, the ions were sampled through a small orifice, analyzed with a quadrupole mass filter, and detected with an electron multiplier.

The reactions were studied at 298 K with a helium buffer gas pressure of 0.5 Torr and flow of 250 STP $cm^3\ s^{-1}$. Branching ratios were derived in the following way. For each silane, the ratio of product siloxide ion intensities was determined as a function of ion–neutral reaction distance; silanes were introduced to the flow tube through a manifold of inlets located between 9 and 48 cm from the detection orifice. The observed ratios were extrapolated to zero effective reaction distance to eliminate the effects of differential diffusion losses of the ions and possible secondary reaction paths. The observed ratios exhibit little dependence on the concentration of the silane, indicating negligible contributions from secondary reactions. There is, however, a significant dependence of the ion ratios (up to 70% variation) on the reaction distance, indicating that the product ions have different diffusive losses and, therefore, different diffusion coefficients. This is reasonable since the ion products vary substantially in mass and size. Therefore, extrapolation to zero reaction distance is essential in extracting accurate product ratios. In addition, all the ratios were statistically corrected to account for the unsymmetrical substitution pattern of the silanes, which included three methyl groups and one unique alkyl group.

A series of fluorophenyl anions ($C_6H_4F^-$, $C_6H_3F_2^-$, $C_6H_2F_3^-$, and $C_6HF_4^-$) was employed to determine the mass discrimination of the detection system.[17] These ions were generated by reaction of injected hydroxide ion with the parent fluorobenzenes added immediately downstream of the SIFT injector. In this way the mass selection and injection system remained tuned to HO^- for all experiments and the mass discrimination measurements could be accomplished readily. For each fluorophenyl ion, both the ion current on the detection orifice plate and the ion count rate at the electron multiplier were monitored. The ratio of these values was determined for each ion and plotted versus mass. The correction to the measured count rate of a siloxide ion of particular mass was then interpolated from this graph. These corrections were generally small but amounted to a factor of 2 in some instances. The mass discrimination data were taken both before and after the branching ratio data to average any changes which occur and to check for consistency. The reported ratios include all three corrections and are the average of usually two or three series of measurements. The ratios are readily reproducible to within ±10%.

Table I. Branching Ratios for the Reaction of $R(CH_3)_3Si + HO^-$

R	$(CH_3)_3SiO^-/R(CH_3)_2SiO^-$ [a] observed[b]	$(CH_3)_3SiO^-/R(CH_3)_2SiO^-$ [a] corrected[c]	N[d]
ethyl	0.52 ± 0.02	0.46 ± 0.02	3
isopropyl	0.70	0.54	1
cyclobutyl	1.28	0.84	1
methyl	(1.00)	(1.00)	–
cyclopentyl	2.06 ± 0.04	1.11 ± 0.02	3
sec-butyl	1.89 ± 0.14	1.21 ± 0.09	3
n-propyl	1.65 ± 0.16	1.26 ± 0.15	3
tert-butyl	3.36 ± 0.03	2.16 ± 0.02	2
isobutyl	3.56 ± 0.23	2.29 ± 0.14	3
3-butenyl	4.25 ± 0.03	2.80 ± 0.03	2
cyclopropyl	3.96 ± 0.05	3.10 ± 0.03	2
cyclopropylmethyl	5.86 ± 0.32	3.86 ± 0.19	3
1-methylcyclopropyl	8.03 ± 0.44	5.09 ± 0.26	3
neopentyl	10.5 ± 0.5	5.48 ± 0.22	3
vinyl	8.27 ± 0.98	7.43 ± 0.81	3
hydrogen	8.44 ± 0.27	9.45 ± 0.30	2
2-propenyl	13.8 ± 0.37	10.8 ± 0.4	2
phenyl	71.9 ± 4.1	33.9 ± 1.9	3
allyl	>100	>80	1

[a] Branching ratios are corrected for statistics as outlined in the Experimental Section. The estimated errors are listed as standard deviations in the case of three or more measurements and absolute differences in the case of two measurements. [b] Derived from extrapolations to zero effective reaction distance. [c] Corrected for mass discrimination. [d] Number of independent measurements.

The necessary alkylsilanes were either obtained commercially or prepared by literature procedures. All reagents were purified as necessary before use. The fluorobenzenes were of reagent grade and used without further purification. The helium (99.995%) was purified by passage through a liquid nitrogen cooled molecular sieve trap before entering the flow tube.

Results

In Table I we report the results we have obtained for the cleavage reactions of 18 silanes with hydroxide ion in our FA-SIFT. Comparing the observed and corrected ratios, it is obvious that correcting for mass discrimination is important, especially with the heavier ions such as phenyldimethylsiloxide. The corrected siloxide ion ratios obtained in this study are in good agreement with those reported earlier[8] with the single exception of that for trimethylsilane.[18] In our earlier work we used hydrogen and methane as anchor points on the acidity scale because no other reliable acidities in this region were available. In this work, we have chosen to use benzene as one of the reference points in place of hydrogen. We believe this choice is appropriate since we are determining acidities of carbon–hydrogen bonds including several involving sp^2 carbons.[19] The measured siloxide ratios were then used to determine the gas-phase acidities of the other alkanes.

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(13) Neumann, W. P. *The Organic Chemistry of Tin*; Wiley: London, 1970.

(14) The ease of silane cleavage with base in solution correlates with the basicity of the carbanion being expelled; see: Eaborn, C.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1975**, 937.

(15) This method of determining the relative basicities of ions is similar, in principle, to the method of Cooks and co-workers in which cluster ions are given internal energy by collisions in a mass spectrometer: Wright, L. G.; McLuckey, S. A.; Cooks, R. G.; Wood, K. V. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *42*, 115.

(16) Van Doren, J. M.; Barlow, S. E.; DePuy, C. H.; Bierbaum, V. M. *Int. J. Mass Spectrom. Ion Proc.* **1987**, *81*, 85.

(17) Van Doren, J. M. Ph.D. Thesis, University of Colorado at Boulder, 1987.

(18) In the earlier work (ref 8), we reported a ratio, $(CH_3)_3SiO^-/(CH_3)_2SiHO^-$, of 20:1 for the reaction of $(CH_3)_3SiH$ with HO^-. This ratio was obtained in two completely independent experiments several months apart. With our present sample of trimethylsilane under the same reaction conditions, we obtain, reproducibly, a ratio of 9.45:1. We can only attribute the difference to an impurity in the trimethylsilane used in one of the experiments. All other ratios were duplicated within experimental error in our most recent experiments.

(19) If we use a ratio of 9.45 for the cleavage of trimethylsilane (see ref 18), then the calculated acidity of H_2 is 406.4 kcal/mol, 6.0 kcal/mol larger than the experimental value (400.4). If we use the previous value of 20, the calculated value is 403 kcal/mol, 1.6 kcal/mol larger than the experimental value.

Table II. Thermodynamic Data Derived from the Silane Cleavage Branching Ratios[a]

R	exptl ΔH°_{acid} (RH)[b]	EA ($R^\bullet$)[c]	BDE (R–H)[d]	calcd ΔH°_{acid} (RH)[e]
ethyl	420.1	−6.4	100.1	422.2
isopropyl	419.4	−9.5	96.3	422.5
cyclobutyl	417.4	−7.5	96.3	421.2
methyl	(416.6)	1.8	104.8	(416.6)
cyclopentyl	416.1	−7.0	95.5	
sec-butyl	415.7	−5.8	96.3	421.9
n-propyl	415.6	−1.9	100.1	419.3
tert-butyl	413.1	−5.9	93.6	421.9
isobutyl	412.9	0.8	100.1	
3-butenyl	412.0	1.7	100.1	
cyclopropyl	411.5	8.4	106.3	412.6
cyclopropylmethyl	410.5	3.2	100.1	413.9
1-methylcyclopropyl	409.2	8.0	103.6	
neopentyl	408.9	4.8	100.1	
vinyl	407.5	16.1[f]	110.0	406.9
2-propenyl	405.8	15.8	108.0	
phenyl	(400.7)	23.8	110.9	

[a] All values in kcal mol^{-1}. Parentheses denote reference values. [b] Derived from the correlation in eq 12. The errors in the relative acidities are ±1 kcal mol^{-1} or less given the validity of the method. The ΔH°_{acid} value obtained for methoxymethyl (407.5 kcal mol^{-1}) was similar to that found in the previous communication; see ref 8. [c] Electron affinities derived from the thermodynamic cycle in eq 13. [d] Bond dissociation energies taken from ref 27. For those compounds not found in this reference, standard values for primary (100.1), secondary (96.3), and tertiary (93.6) groups are assumed. Values for vinyl and cyclopropyl were taken from ref 28. Values for 1-methylcyclopropyl and 2-propenyl were estimated by analogy to similar systems. For methyl, see ref 1. [e] Theoretical values taken from ref 7b. [f] The EA of the vinyl anion has recently been measured and is 15.4 kcal/mol: Ellison, G. B., personal communication.

The siloxide ratios can easily be reproduced to within 10% or less, and the largest measured ratio before statistical correction is 20 (allyl gives a ratio greater than 30, but this value was not used in the acidity determinations). Therefore the relative acidities can be determined with great experimental precision, especially since we are spanning an acidity range of about 20 kcal/mol with a ladder of 17 steps. Relative to each other, and given the validity of the method, the errors in the acidities are ±1 kcal/mol or less. The acidities of benzene and methane are both known to within 1 kcal/mol. Therefore the method is capable of distinguishing small differences in acidity accurately.

As a check for internal consistency we measured the siloxide ion ratios for cleavage of triethylmethylsilane, diethyldimethylsilane, and ethyltrimethylsilane. After appropriate statistical corrections the ratios were 0.46, 0.43, and 0.51 respectively, for an average value of 0.47 ± 0.04, which is within our 10% error limits. Even using the extreme values of 0.43 and 0.51 leads to less than a 1-kcal/mol difference in the calculated acidity of ethane.

Discussion

The acidities listed in Table II are derived from eq 12 using a correlation ($\beta = 0.221$) based on the known acidities of methane, $\Delta H^\circ_{acid} = 416.6 \pm 0.8$ kcal/mol, and of benzene, $\Delta H^\circ_{acid} = 400.7 \pm 0.5$ kcal/mol. The other acidities in the table are assigned from the siloxide ratios. Let us first examine the results to see if the calculated acidities show trends which make intuitive sense. There are several checks we can make which show that they do. For example, while the acidity of ethylene has not been determined exactly, it is known to be only slightly less acidic than ammonia and has been estimated as 408 kcal/mol,[20] in agreement with the value we derive. For cyclopropane we would expect, on the basis of its hybridization and chemical reactivity in solution, that its acidity should lie between those of ethylene and the saturated alkanes. At a predicted value of $\Delta H^\circ_{acid} = 411.5$ kcal/mol, we find it to lie almost halfway between methane and ethylene. We would also expect that the introduction of an electronegative group into a nonconjugating position of an alkane would increase its acidity. Indeed we find that the methyl group in methylcyclopropane is more acidic ($\Delta H^\circ_{acid} = 410.5$ kcal/mol) than the corresponding methyl groups in isobutane ($\Delta H^\circ_{acid} = 412.9$ kcal/mol) and that the methyl group in 1-butene ($\Delta H^\circ_{acid} = 412.0$ kcal/mol) is more acidic than the methyl groups in propane ($\Delta H^\circ_{acid} = 415.6$ kcal/mol).

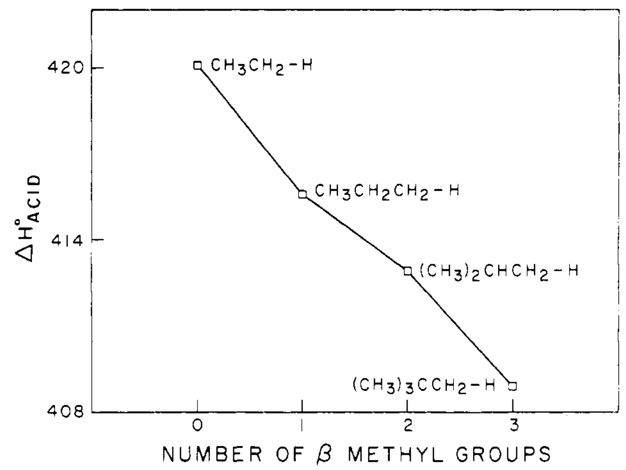

Figure 1. Effects of β-methyl substitution on alkane acidity.

Further evidence for the intermediacy of carbanions in these cleavage reactions is found if we examine the effect of β-methyl substitution on the acidity of a methyl group. In the alcohol series Brauman and Blair[6] have shown that the acidity of the hydroxyl group increases with the number of β-methyls along the series methyl alcohol ($\Delta H^\circ_{acid} = 380.6$ kcal/mol), ethyl alcohol ($\Delta H^\circ_{acid} = 377.4$ kcal/mol), isopropyl alcohol ($\Delta H^\circ_{acid} = 375.4$ kcal/mol), and *tert*-butyl alcohol ($\Delta H^\circ_{acid} = 374.6$ kcal/mol).[1] Each β-methyl group increases the acidity of the OH group by an average of 2 kcal/mol. A parallel but somewhat larger effect is observed on CH_2–H acidity along the corresponding alkane series ethane ($\Delta H^\circ_{acid} = 420.1$ kcal/mol), propane ($\Delta H^\circ_{acid} = 415.6$ kcal/mol), isobutane ($\Delta H^\circ_{acid} = 412.9$ kcal/mol), and neopentane ($\Delta H^\circ_{acid} = 408.9$ kcal/mol). In this series each β-methyl group increases the acidity of the methyl group by an average of 4 kcal/mol. This slightly larger effect is reasonable since the much more strongly basic carbanions would be expected to make greater demands on the methyl groups, which are postulated to stabilize anions by polarization. A similar stabilizing effect of a β-methyl group, but on a secondary anion, is seen in the greater acidity of the 2-position in butane ($\Delta H^\circ_{acid} = 415.7$ kcal/mol) than that of the corresponding 2-position of propane ($\Delta H^\circ_{acid} = 419.4$ kcal/mol).

The effects of α-methyl substitution on carbanion stability are less consistent and so harder to interpret. In general an α-methyl group decreases the basicity of a carbanion, and so increases the acidity of the corresponding alkane, although to a lesser extent than does a β-methyl group. For example, acidity increases in forming a primary carbanion from ethane ($\Delta H^\circ_{acid} = 420.1$ kcal/mol), a secondary anion from propane ($\Delta H^\circ_{acid} = 419.4$ kcal/mol), and a tertiary anion from isobutane ($\Delta H^\circ_{acid} = 413.1$ kcal/mol). Substitution of a methyl group on the cyclopropyl anion increases its stability slightly, so that cyclopropane ($\Delta H^\circ_{acid} = 411.5$ kcal/mol) is a slightly weaker acid than methylcyclopropane ($\Delta H^\circ_{acid} = 409.2$ kcal/mol), and a similar acid strengthening effect is seen upon substituting a methyl group into ethylene. The exception is found in the introduction of the first methyl group; ethane is found to be 3.5 kcal/mol less acidic than methane. The differing effects of α- and β-methyl substitution are shown graphically in Figures 1 and 2. For β-substitution there is a monotonic increase in acidity with the number of methyl groups (Figure 1). For α-substitution there is an initial decrease in acidity for the first methyl, followed by a small increase for the second, and a larger increase for the third (Figure 2). One might postulate that *tert*-butyltrimethylsilane contains some ground-state strain which is relieved in the cleavage; such strain

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(20) Grabowski, J. J. Ph.D. Thesis, University of Colorado at Boulder, 1983.

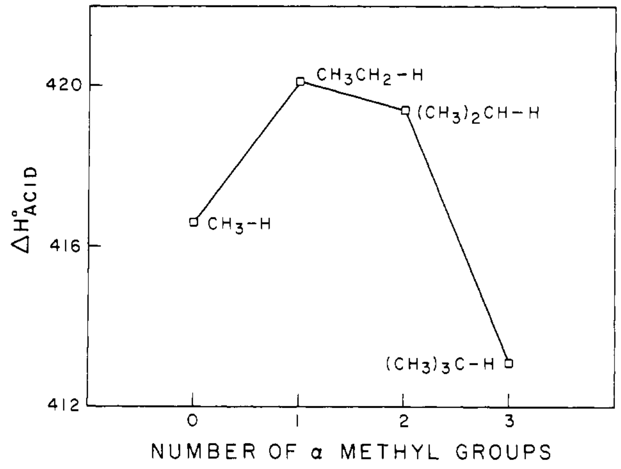


Figure 2. Effects of α-methyl substitution on alkane acidity.

would have the effect of increasing the apparent acidity of isobutane. Eaborn et al.[14] noted that certain tertiary carbanions deviate from the line in their silane cleavage reactions in solution, and postulated a ground-state steric effect to account for the deviations. On the other hand, no evidence for steric strain in *tert*-butylsilanes was found by force-field calculations,[21] nor do we see any evidence for it in the cleavage reactions of our other tertiary silanes. To account for the nonlinear relationship in Figure 2, we postulate that a methyl group substituted onto a carbanion has two competing effects: an acid-weakening effect which quickly saturates as the number of methyl groups increases, and an acid-strengthening polarization effect, analogous to that of β-methyl substitution, which continues to increase with each additional methyl. Upon introduction of the first methyl group, the acid-weakening effect predominates, for the second methyl group the two effects approximately cancel, and for the third methyl group the stabilizing effect predominates. It should also be pointed out that while replacement of a hydrogen atom in water by a methyl group leads to a large increase in acidity, a similar replacement in ammonia to form methylamine has no effect on the N-H acidity ($\Delta H^\circ_{acid}(NH_3) = 403.6$ kcal/mol, $\Delta H^\circ_{acid}(CH_3NH_2) = 403.3$ kcal/mol).[1] If we extrapolate along the series from oxygen to nitrogen to carbon, we are not surprised to find ethane to be less acidic than methane.

The relative positions of the cyclic compounds on the acidity scale are also consistent with previous knowledge and the discussion given above. For example, Streitwieser et al.[22] found that while cyclopropane undergoes hydrogen–deuterium exchange in solution much more rapidly than do noncyclic alkanes, cyclobutane does not, a fact consistent with our finding that cyclobutane shows no enhanced gas-phase acidity while cyclopropane does. The slightly greater acidity of cyclopentane than that of cyclobutane can reasonably be ascribed to a greater degree of β-substitution in the former anion.

The gas-phase acidity of an alkane is related to the electron affinity (EA) of the corresponding alkyl radical by a thermodynamic cycle involving its carbon–hydrogen bond dissociation energy (BDE) and the ionization potential (IP) of the hydrogen atom. This relationship is shown for methane in eq 13. Indeed the acidity of methane has not been measured directly but rather calculated from its BDE and the EA of the methyl radical.[3] The gas-phase acidities determined in the present work can be combined with known bond dissociation energies in the reverse of this cycle to calculate electron affinities for the corresponding alkyl radicals. These values are included in Table II. As can be seen, the EA's of many of the simple alkyl radicals are predicted to be negative, indicating that the anions are unstable with respect to loss of an electron and formation of the radical (electron detachment). The electron in the methyl anion is known experimentally to be bound by only 1.8 kcal/mol.[3] Replacement of one of its hydrogen atoms by a methyl group stabilizes the radical but destabilizes the anion, so that it is not surprising that the ethyl anion is unbound. A similar effect prevails for most alkanes. It is only in the case of neopentane, where the three β-methyl groups stabilize the anion but not the radical, that a stable anion results upon deprotonation. These negative EA's account for the fact that most alkyl anions cannot be produced as discrete species in the gas phase. Recently Squires and co-workers[4,5] have developed a method for the generation of gas-phase anions in which carboxylate ions lose CO_2 by collision-induced dissociation (CID) as shown in eq 14.

$$\begin{array}{llll} CH_4 & \longrightarrow CH_3^\bullet + H^\bullet & \text{BDE} = 105 \text{ kcal/mol} & \\ CH_3^\bullet + e^- & \longrightarrow CH_3^- & -\text{EA} = -2 \text{ kcal/mol} & (13) \\ H^\bullet & \longrightarrow H^+ + e^- & \text{IP} = 314 \text{ kcal/mol} & \\ \hline CH_4 & \longrightarrow CH_3^- + H^+ & \Delta H^\circ_{acid} = 417 \text{ kcal/mol} & \end{array}$$

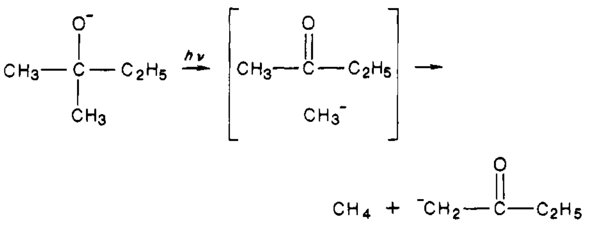
$$\text{R-COO}^- \xrightarrow{\text{CID}} R^- + CO_2 \qquad (14)$$

The methyl anion, the neopentyl anion, and the cyclopropyl anion have all been generated by this method; we predict all of these anions to be bound. Alkyl anions which we predict to be unbound cannot be formed in this way. Thus there is good agreement between Squires' experiments and ours.

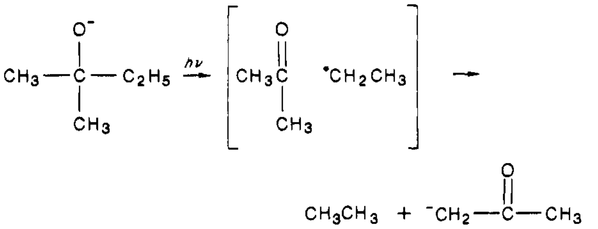
In a sense, then, the gas-phase acidity of many alkanes is only a hypothetical quantity since their ionization would lead not to a proton and a carbanion, but rather to a proton, a radical, and an electron (eq 15). We might well ask then if alkyl carbanions

$$CH_3CH_3 \rightarrow CH_3CH_2^\bullet + H^+ + e^- \qquad (15)$$

are reasonable intermediates in our siloxide cleavage reactions. Brauman and co-workers[23] have observed an analogous photochemically induced cleavage reaction of alkoxide ions in an ion cyclotron resonance spectrometer. He has proposed two mechanisms for these cleavages, depending upon whether or not the alkyl anion formed within the intermediate ion–dipole complex is bound or unbound. For example, in the photochemical cleavage of the *tert*-pentoxide ion, methane is presumed to be formed by way of a methyl anion as in eq 16, since it is known to be a bound species, but ethane loss is presumed to proceed through an ethyl radical, as in eq 17, with the electron loosely bound either to the



$$CH_3C(O^-)(CH_3)C_2H_5 \xrightarrow{h\nu} \left[CH_3C(=O)C_2H_5 \; CH_3^- \right] \longrightarrow CH_4 + {}^-CH_2C(=O)C_2H_5 \qquad (16)$$



$$CH_3C(O^-)(CH_3)C_2H_5 \xrightarrow{h\nu} \left[CH_3C(=O)CH_3 \; {}^\bullet CH_2CH_3 \right]^- \longrightarrow CH_3CH_3 + {}^-CH_2C(=O)CH_3 \qquad (17)$$

ketone or to the complex as a whole. He has suggested that silane

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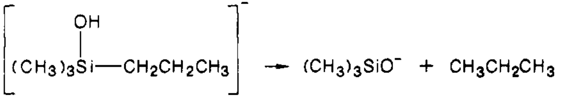
(21) Ouellette, R. J.; Baron, D.; Stolfo, J.; Rosenblum, A.; Weber, P. *Tetrahedron* **1972**, *28*, 2163. We have carried out MM2 force field calculations on *tert*-butyltrimethylsilane using the recently published parameters that have been extended to silicon (Frierson, M. R.; Imam, M. R.; Zalkow, V. B.; Allinger, N. L. *J. Org. Chem.* **1988**, *53*, 5248). We found that *tert*-butyltrimethylsilane is strain free.

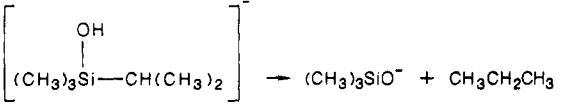
(22) Streitwieser, A., Jr.; Caldwell, R. A.; Young, W. R. *J. Am. Chem. Soc.* **1969**, *91*, 529.

(23) Tumas, W.; Foster, R. F.; Brauman, J. I. *J. Am. Chem. Soc.* **1988**, *110*, 2714.

cleavages occur by the same two mechanisms, an anion mechanism for bound anions and a free radical mechanism for those anions which are unbound. This was a plausible hypothesis based on the results in our preliminary communication,[8] since at that time we (and the Brauman group) had studied only three alkyl groups whose anions are predicted to be unbound, namely, the ethyl, isopropyl, and *tert*-butyl groups, and the ease of loss of these three groups is in the order of their expected radical stability. However, the results for the much larger number of alkyl groups reported in this paper cannot be interpreted in this way. For example, consider the loss of propane from *n*-propyltrimethylsilane (eq 18) and from isopropyltrimethylsilane (eq 19). In the former case



$$\left[(CH_3)_3\overset{OH}{Si}—CH_2CH_2CH_3\right]^- \rightarrow (CH_3)_3SiO^- + CH_3CH_2CH_3 \quad (18)$$

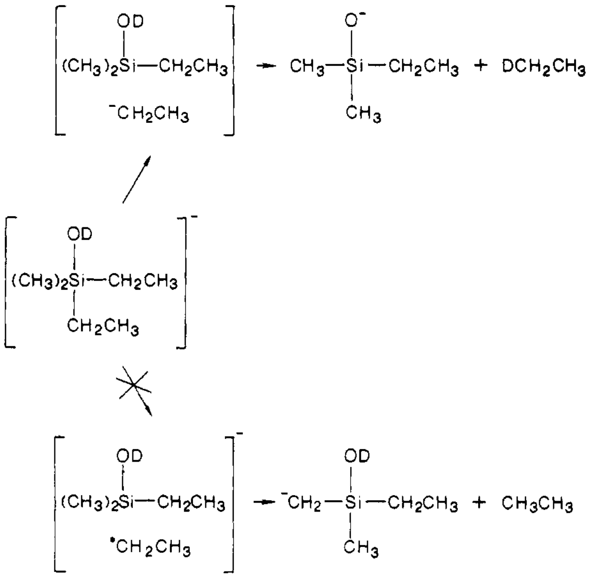


$$\left[(CH_3)_3\overset{OH}{Si}—CH(CH_3)_2\right]^- \rightarrow (CH_3)_3SiO^- + CH_3CH_2CH_3 \quad (19)$$

a primary radical would have to be postulated as an intermediate and in the latter case a secondary radical, yet the *n*-propyl group is lost more easily than the isopropyl group.

Similarly isobutane is lost more readily by cleavage of a bond between silicon and a primary carbon atom in isobutyltrimethylsilane than it is by cleavage of a bond to a tertiary carbon atom in *tert*-butyltrimethylsilane. If a radical intermediate were involved, one would expect the primary group to be lost less rather than more readily in both cases. We therefore prefer the hypothesis that a carbanionic intermediate is involved in our silane cleavages and in the alkoxide cleavages as well.

In a further attempt to find evidence for the intermediacy of alkyl radicals, we allowed diethyldimethylsilane to react with DO^- and examined the product ions for the presence of deuterium. The predicted results based on the two possible mechanisms are shown in eq 20. If a carbanion intermediate is formed, it would be



$$\left[(CH_3)_2\overset{OD}{\underset{CH_2CH_3}{Si}}—CH_2CH_3\right]^- \quad (20)$$

$$\left[(CH_3)_2\overset{OD}{Si}—CH_2CH_3 \;\; {}^-CH_2CH_3\right] \rightarrow CH_3—\overset{O^-}{\underset{CH_3}{Si}}—CH_2CH_3 + DCH_2CH_3$$

$$\left[(CH_3)_2\overset{OD}{Si}—CH_2CH_3 \;\; {}^\bullet CH_2CH_3\right]^- \rightarrow {}^-CH_2—\overset{OD}{\underset{CH_3}{Si}}—CH_2CH_3 + CH_3CH_3$$

expected to abstract a deuteron from the alcohol group forming a siloxide ion which does not contain deuterium. As confirmation, the diethylmethylsiloxide ion produced by loss of methane in this compound is free of deuterium, and it is indisputably formed by way of the methyl anion. The ethyldimethylsiloxide ion produced by loss of ethane can be postulated to proceed through the intermediacy of either the ethyl anion or the ethyl radical. If the ethyl anion is an intermediate, it would also abstract the deuteron from the oxygen and lead to a deuterium-free siloxide ion. However, if ethane loss proceeds by way of an ethyl radical, the radical might be expected to abstract a hydrogen atom from one of the alkyl groups rather than from the oxygen, since radicals usually attack C–H bonds more readily than O–H bonds, which are generally stronger.[24] Only a deuterium-free siloxide product ion is actually observed, so that both methane and ethane loss proceed by abstraction of deuterium from the OD bond, in best accord with the carbanionic hypothesis.

It should be emphasized, however, as Brauman and co-workers[23] have also pointed out, that we are generating not a free carbanion but rather one within an ion–dipole complex in which it may be said to be "solvated" by a trialkylsilanol molecule. Ion–dipole complex energies are typically of the order of 15–20 kcal/mol, which may be sufficiently large to inhibit electron detachment. Two ab initio molecular orbital calculations have been carried out on the cleavage reaction of tetramethylsilane with hydroxide ion,[25,26] and they both indicate that carbon–silicon bond breaking and carbon–hydrogen bond making occur together in the transition state, but that both bonds are long and the methyl group has a great deal of negative charge. We believe that substituents influence the stability of this transition state in the same way they would influence the stability of the free anions. It is not uncommon in chemistry to extrapolate into regions of inherent instability in order to gain an insight into molecular properties of species which do not otherwise exist.

Schleyer et al.[7b] have published the most extensive list of calculated gas-phase acidities of alkanes, and the agreement between their theoretical values and our calculated ones is quite good. We have included their calculated values in Table II. We plan to extend our method to the determination of the acidities of other alkanes and also to measure the gas-phase acidities of alkanes substituted with heteroatoms.

Acknowledgment. We gratefully acknowledge support of this research by the National Science Foundation under Grants CHE-8503505 (to C.H.D. and V.M.B.) and CHE-8615808 (to R.D.). We thank Drs. Jane M. Van Doren and Steven R. Kass for their valuable contributions to many aspects of this work.

Registry No. Ethyltrimethylsilane, 3439-38-1; isopropyltrimethylsilane, 3429-52-5; 3-butenyltrimethylsilane, 763-13-3; tetramethylsilane, 75-76-3; cyclopentyltrimethylsilane, 14579-05-6; *sec*-butyltrimethylsilane, 4215-90-1; trimethylpropylsilane, 3510-70-1; *tert*-butyltrimethylsilane, 5037-65-0; isobutyltrimethylsilane, 1118-09-8; 3-butenyltrimethylsilane, 76-31-33; cyclopropyltrimethylsilane, 930-40-5; (cyclopropylmethyl)trimethylsilane, 931-82-8; (1-methylcyclopropyl)trimethylsilane, 79237-38-0; neopentyltrimethylsilane, 106865-89-8; trimethylvinylsilane, 754-05-2; trimethylphenylsilane, 768-32-1; trimethylsilane, 993-07-7; allyltrimethylsilane, 762-72-1; ethane, 74-84-0; cyclobutane, 287-23-0; methane, 74-82-8; cyclopentane, 287-92-3; butane, 106-97-8; propane, 74-98-6; isobutane, 75-28-5; 1-butene, 106-98-9; cyclopropane, 75-19-4; methylcyclopropane, 594-11-6; neopentane, 463-82-1; ethene, 74-85-1; propene, 115-07-1; benzene, 71-43-2; ethyl, 2025-56-1; 1-methylethyl, 2025-55-0; cyclobutyl, 4548-06-5; methyl, 2229-07-4; cyclopentyl, 3889-74-5; *sec*-butyl, 2348-55-2; propyl, 2143-61-5; *tert*-butyl, 1605-73-8; isobutyl, 4630-45-9; 3-butenyl, 2154-62-3; cyclopropyl, 2417-82-5; cyclopropylmethyl, 65338-31-0; 1-methylcyclopropyl, 2154-76-9; neopentyl, 3744-21-6; vinyl, 2669-89-8; 2-propenyl, 1981-80-2; phenyl, 2396-01-2.

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(24) Since the relative bond strengths of the C–H and O–H bonds in the silanol are unknown, this argument is not conclusive.

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