mation of the secondary alcohol **6c** would be consistent with a transition state, as in **10**, again resembling a structure leading to the more stable carbenium ion **12a**. In this situation, however, the more stable carbenium ion site is the primary carbon, because the positive charge can be stabilized by carbon-silicon σ-bond hyperconjugation (**12b**).[19]

Experimental Section

General Procedures. All steps in the preparation, transfer, and main reactions of the organometallic reagents studied here were conducted under an atmosphere of anhydrous and oxygen-free argon. All solvents and apparatus were likewise freed of traces of dissolved or adsorbed moisture and oxygen and then maintained under argon. Methods and techniques for working under anhydrous and anaerobic conditions and for conducting standard chromatographic and spectrometric analyses have been described previously.[20]

Starting Materials and Products. Diisobutylaluminum hydride and triisobutylaluminum were obtained as neat reagents from Texas Alkyls Inc., Deer Park, TX. Diisobutylaluminum *sec*-butoxide was generated in situ by the **cautious** treatment of $i\text{-}Bu_2AlH$ in heptane with 1 equiv of *sec*-butyl alcohol.

1,2-Epoxydecane and styrene oxide were commercially available and (epoxyethyl)triphenylsilane was prepared from the epoxidation of triphenylvinylsilane with *m*-chloroperbenzoic acid.[21]

The reaction products 1-decanol, 2-decanol, 1-phenyl-1-ethanol, and 2-phenyl-1-ethanol were purchased, while the 1-(triphenylsilyl)-1-ethanol and 2-(triphenylsilyl)-1-ethanol were synthesized by known procedures.[22]

General Reduction Procedure. On a 1.0–10.0-mmol scale, the epoxide was dissolved in 10–50 mL of the solvent and then added slowly to 1.1 equiv of the aluminum hydride source, which was contained in a like volume of solvent and, in certain cases, was previously complexed with an equivalent of a Lewis base (R_3N or R_2AlOR'). The reaction mixture was allowed to stir at the given temperature for the stated reaction period (Table I).

If necessary, the reaction mixture was cooled to 25 °C and then **slowly and cautiously** treated with water (**gas evolution**!). Thereupon, dilute, aqueous HCl was added to give two clear layers. The separated organic layer was dried over anhydrous $MgSO_4$ and then the volatiles were removed in vacuo. The residue was analyzed by gas chromatography and separated by flash column chromatography.

Reductive Dehalogenation of 2-Chloro-1-(triphenylsilyl)-1-ethanol (8). A solution of 203 mg (0.61 mmol) of **8**, which was prepared from **5c** and $MeAlCl_2$,[16] and 120 mg (0.59 mmol) of tri-*n*-butyltin hydride in 15 mL of anhydrous toluene was heated at reflux for 8 h. The solvent was removed in vacuo and the residue subjected to flash chromatography on silica gel with 5% ethyl acetate in hexane. The isolated 1-(triphenylsilyl)-1-ethanol (**7c**) was obtained pure in 81% yield and was identified by comparison of its mp and its IR, ^1H NMR, and ^{13}C NMR spectral properties with those of an authentic sample.[18]

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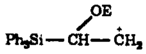
[19] Any electrophilic attack on **5c**, such as where E = $MeAlCl_2$, is known to favor formation of the carbenium ion β to silicon



$Ph_3Si-\overset{OE}{CH}-\overset{+}{CH_2}$

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The Gas-Phase Basicity of Hydroxamic Acid Derivatives

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Introduction

One can understand at first sight, already from the name "hydroxamic acids" that the basic properties of these compounds (**1**) have been less investigated.[1] The crystallized hydrochloride of benzohydroxamic acid (**2**) was prepared,[2] and p*K* values in sulfuric acid have been reported for several substituted protonated benzohydroxamic acids.[3] As far as the site of protonation is concerned, several kinetic studies[3-5] have assumed that it is the carbonyl oxygen (see Scheme I, formula **1a** or **1b** with possible hydrogen bonds) rather than the nitrogen atom (**1c**), but without any proof, simply from an analogy with amides. The actual structure of the cation was seldom examined in contrast to the rather extensive discussion of the structure of the anion[1,6-8] and of the neutral molecule.[1,9,10] To our knowledge only the salt **2** was investigated by IR in dioxan[11] and by XPS in crystal,[12] in either case in favor of the structures **1a,b**. In a recent theoretical study[8] of formohydroxamic acid the structure **3a** was found slightly more stable than **3b** but distinctly more than **3c**. *N*-Alkyl-substituted hydroxamic acids seem to be more basic, and two forms of the cation (**1b** and **1c**; **1a** not considered) were claimed.[13] In aminohydroxamic acids the amino group is protonated first.[14]

In this paper we report the gas-phase basicities of acetohydroxamic acid (**4**) and of its *N*-methyl (**5**) and *O*-methyl (**6**) derivatives (Table I). In addition to the general interest—placing these compounds into the basicity scale[15]—we also hoped to get some information concerning the structure of the cation, particularly from a comparison with isosteric amides **7–9**.

Results and Discussion

The gas-phase basicities are collected in the table. The first conclusion emerges that hydroxamic "acids" are also relatively strong bases. In the whole scale[15] of the gas-phase acidity of organic acids (range of ~100 kcal), hydroxamic acids are placed relatively near the strongest acids, viz. at 27% of the whole range. But even in the scale of organic bases[15] (~110 kcal) they fall in the vicinity of strong bases (at 35% of the whole range). Compared with amides hydroxamic acids are stronger acids (by 15 kcal) and weaker bases (by 7 kcal). In all cases the reason is evidently the electron-attracting inductive effect of the oxygen atom.[16] In the case of the acidity of hydroxamic acids this effect is corroborated by a change of the mesomeric structure of the anion: the substitution by an oxygen induces an electron attraction from N and renders the mesomerism within the O=C—N unit better balanced. The two effects seem to strengthen each other in an efficient way.[17] In water solution[1] the difference in acidity between hydroxamic acids and amides is leveled. In the case of basicity even the order is reversed. A comparison with carboxylic acids is less easy to interpret: hydroxamic

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Scheme I

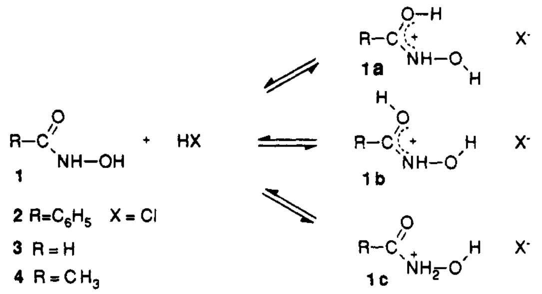

Table I. Gas-Phase Basicities of Hydroxamic Acid Derivatives and of Some Simple Amides (kcal mol^{-1})

entry	compound	GB[a]	experimental ΔG's[c]
4	$CH_3CONHOH$	197.3 (0.2)	diisopropyl ether, −1.09; tetrahydrothiophene, +0.55
5	$CH_3CON(CH_3)OH$	200.9 (0.3)	pyrimidine, −2.42; pyrrole, +0.32
6	$CH_3CONHOCH_3$	201.3 (0.1)	dimethylformamide, −1.84; pyrrole, +0.95
7	$CH_3CONHCH_3$	204.5 (0.4)	cyclopropylamine, −0.22; 2-fluoropyridine, +1.3; methylamine, −0.64
8	$CH_3CON(CH_3)_2$	208.4[b]	
9	$CH_3CONHC_2H_5$	206.2 (0.1)	cyclopropylamine, −0.61; methylamine, +0.77

[a] This work, unless otherwise stated. The uncertainties in parentheses are based on comparison of separate experiments with various reference compounds and are estimates of the reliability of the relative gas-phase basicities. absolute values may be uncertain by ±2 kcal, see ref 15. [b] Reference 15. [c] Gibbs energies of proton transfer to the indicated reference base, measured at 338 K. A positive value corresponds to a compound which is a stronger base than the reference.

acids are both stronger acids[6] and bases in the gas phase. Part of this effect may be due to the greater polarizability of the larger molecule.

The question of the site of protonation cannot be answered in a quite straightforward way from our results. Note that the similar problem of the site of deprotonation of 4 was investigated,[6] exploiting the compounds 5 and 6 as models, each containing only one of the two acidic H atoms. Similar model compounds are not possible for the protonation. We may only attempt to evaluate the substituent effects in more detail by referring always to alkyl-substituted amides with the same number of heavy atoms (Table I). In this way the polarizability effects are practically eliminated. The difference in basicity between 4 and 7 or between 5 and 8 is equal to 7.5 kcal but is reduced to 5 kcal in the case of the pair 6 and 9. For this reason we attribute the effect of 2.5 kcal to the hydrogen bond in 4 and 5, stabilizing the neutral species. The remaining 5 kcal are attributed to the electron-attracting effect of the oxygen atom, while the polarizability effect, due simply to the presence of an additional atom, is assumed to be equal as in amides, say 6 kcal. The whole picture is compatible with the assumption that all the compounds of the table are protonated at the same place, viz. on the carbonyl oxygen atom. If a protonation on the nitrogen should also take place, one could expect a strengthened basicity of the compound 5 which has the most basic nitrogen atom. By the same token, however, referring to the inductive effect of the next atom, one can predict that an N-protonation is not to be expected: when it has not been observed on amides, it is still less probable with hydroxamic acids.

In conclusion, the acid–base behavior of hydroxamic acids and their functional derivatives in the gas phase is consistent with understanding their structure as N-substituted amides with an adjoining electron-attracting substituent. The name "acid" seems to be obsolete.

Experimental Section

The compounds 4–6 were described previously;[6] compounds 7 and 9 as well as all reference compounds were commercial products.

Proton-transfer equilibria were monitored by Fourier transform ion cyclotron resonance (FT-ICR) as described in detail in a previous article.[18]

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Synthesis of Optically Quadratic Nonlinear Phenylpyridylacetylenes

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The nonlinear optical properties of organic compounds have been extensively studied in the last decade. Compounds with noncentrosymmetric crystal packing exhibit the quadratic optical phenomenon that is needed for second harmonic generation (SHG) by laser diodes as well as for theoretical treatment of molecular interactions.[1] The molecular framework that typically brings about SHG is a π-conjugated intramolecular donor–acceptor charge-

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