(23) The facile occurrence of the H-abstraction step, i.e., the second stage of reaction 7, which serves to "trap" the initially produced $C_6H_5\dot{C}HCH_3$ radical irreversibly and inhibit reversal of the first step, finds precedent in earlier studies on other low-spin cobalt(II) complexes, e.g., $[Co(CN)_5]^{3-}$ + $R\dot{C}HCH_3 \rightarrow [HCo(CN)_5]^{3-} + RCH{=}CH_2$. The competition between this process and the alternative combination reaction, $[Co(CN)_5]^{3-} + R\dot{C}HCH_3 \rightarrow [R(CH_3)CHCo(CN)_5]^{3-}$, is favored for secondary (i.e., $(CH_3)_2\dot{C}H$) relative to primary (e.g., $CH_3\dot{C}H_2$) radicals.[18]

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(26) One of the few transition metal-alkyl bond dissociation energies to have been directly determined, i.e., that of $CH_3Mn(CO)_5$ (~30 kcal/mol), also lies in this low range.[27] The "weakness" of transition metal-alkyl bonds thus appears to be fairly widespread.

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(28) On sabbatical leave from the University of Waterloo, Waterloo, Ontario, Canada.

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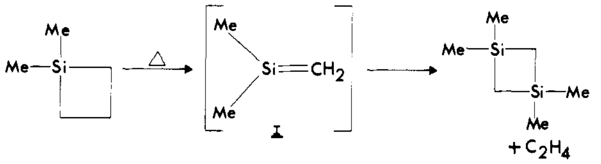
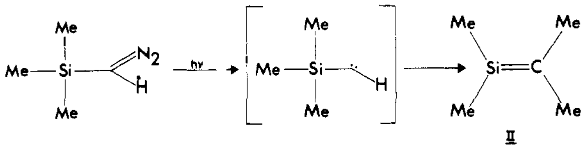
Heat of Formation of 1,1-Dimethylsilaethylene by Ion Cyclotron Resonance Spectroscopy

Sir:

Interest has time and again focused upon the generation and characterization of molecules containing formal carbon–silicon double bonds.[1,2] For example, the existence of 1,1-dimethylsilaethylene (I), as an intermediate in the pyrolysis reaction (1), has been suggested[2a] and the rate interpreted to yield a heat of formation of 12–29 kcal mol^{-1} for the species.[2d,3] Mass spectral evidence supporting the existence of I in the gas phase has only recently been advanced.[2w] The low-temperature matrix infrared spectra of both 1,1-dimethylsilaethylene (I)[5a,b] (obtained from the pyrolysis reaction 1) and 1,1,2-trimethylsilaethylene (II)[5c,d] (obtained upon photolysis of trimethylsiladiazomethane, reaction 2) have been recorded. Close parallels between the infrared spectrum of the silaethylene and that of trimethylethylene have been drawn[5b] and suggest the overall similarity of the geometrical structures of the two molecules. Although there exist no further experimental structural data to substantiate or contest such an interpretation, the best available molecular orbital calculations on parent silaethylene indicate a planar geometry with a barrier to rotation of 46 kcal mol^{-1},[6,7] which may be compared with the corresponding theoretical barrier of 64 kcal mol^{-1} for rotation in ethylene[6] (experimentally, the activation energy required for cis/trans isomerization of 1,2-dideuteroethylene is 65 kcal mol^{-1} [8]). These data provide some indication of the relative π-bond strengths of the two molecules.[9]



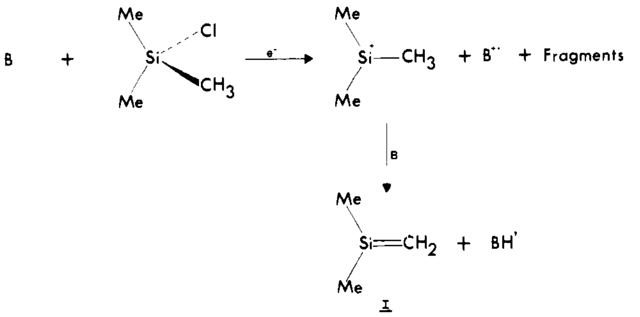
(1)



(2)

We describe in this communication a direct experimental determination of the heat of formation of 1,1-dimethylsilaethylene (I), and indirectly of its carbon–silicon π-bond strength, by ion cyclotron resonance (ICR) spectroscopy.[10]

Scheme I



Our experimental procedure is outlined in Scheme I.[11] Trimethylsilyl chloride, a base (B) of known strength and an inert buffer gas (Ar or Kr) are added to an ICR spectrometer in approximate ratio of 2:1:50–100 and total pressure on the order of 10^{-5} Torr. Electron impact results in the initial production of trimethylsilyl cation (via rapid halide loss from the radical cation of trimethylsilyl chloride) and, depending on base B, of $B^{+}\cdot$ and of fragment ions of B. If base B is sufficiently strong, it will be capable of proton abstraction from the trimethylsilyl cation, giving rise to an ion of mass corresponding to BH^+ and concurrently to the neutral molecule 1,1-dimethylsilaethylene. Therefore, by employing a series of abstracting bases of known and increasing strength, and by monitoring the onset of production of BH^+ (verified by standard double resonance techniques[10,11a] to arise from the trimethylsilyl cation), it is possible to determine an approximate enthalpy for deprotonation of the silicon-centered cation. Piperidine (enthalpy of proton transfer 21.9 kcal mol^{-1} greater than that of the ammonia standard)[12] was the strongest base considered which was not observed to abstract a proton from trimethylsilyl cation; the weaker bases, ethylmethylamine (19.4 kcal mol^{-1}) and trimethylamine (21.2 kcal mol^{-1}), did not result in proton abstraction. Isopropylethylamine ($\Delta H°$ of protonation 23.4 kcal mol^{-1} above NH_3) was the weakest base for which proton abstraction was observed; the stronger bases di-*n*-propylamine (23.9 kcal mol^{-1}) and diisopropylamine (26.0 kcal mol^{-1}) also lead to proton abstraction. These results were unaffected by further addition of buffer gas.

We conclude, therefore, that the proton affinity of 1,1-dimethylsilaethylene is >21.9 kcal mol^{-1} (relative to ammonia) but <23.4 kcal mol^{-1}. The average of these two relative values (22.7 kcal mol^{-1}), combined with the absolute enthalpy of protonation of ammonia (205 kcal mol^{-1})[13] and the heats of formation of trimethylsilyl cation (160 kcal mol^{-1})[14] and of H^+ (367.2 kcal mol^{-1}),[15] yields a value 20.5 kcal mol^{-1} for the heat of formation of 1,1-dimethylsilaethylene.

Three sources of error are easily identified. The first concerns the finite resolution of the gas-phase proton-affinity scale and the likelihood that slightly endothermic proton-transfer reactions as well as thermoneutral and exothermic processes will occur and will be detected. We suspect uncertainties on the order of ±1 kcal mol^{-1} in our measurement and interpretation of the threshold for proton abstraction from the trimethylsilyl cation due to these causes. Further uncertainty arises due to the requirement of an absolute basis for the proton-affinity scale. The absolute proton affinity of our standard, ammonia, is at present not completely certain, with estimates ranging from a low of 203 kcal mol^{-1} to a high of 207 kcal mol^{-1}.[13] Finally deduction of $\Delta H_f°$ for 1,1-dimethylsilaethylene requires a heat of formation for its precursor, the trimethylsilyl cation. The value that we have employed, 160 kcal mol^{-1},[14] derives from appearance potential measurements and is conceivably in error by as much as 2 kcal mol^{-1}.

Our experimental value for the heat of formation of 1,1-dimethylsilaethylene of 20.5 kcal mol^{-1} is consistent with the

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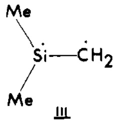
previously obtained estimates of 12-29 kcal mol^{-1}[2a,d,3] and 15.5 ± 5 kcal mol^{-1}.[22] Estimating the heat of formation of the related biradical (III) to be 54 kcal mol^{-1} (on the basis of an experimental value of −29.6 kcal mol^{-1} for the heat of formation of trimethylsilane[4b] and estimates of CH and SiH bond energies of 99[16] and 89[4b] kcal mol^{-1}, respectively), we arrive at a π-bond energy of $\simeq$34 kcal mol^{-1}. This is both significantly less than the π-bond energy associated with a C=C linkage (e.g., 60-65 kcal mol^{-1} in ethylene[8,9]) and the estimate of 46 kcal mol^{-1} obtained theoretically for parent silaethylene.[6] It is in somewhat better accord with the 30-42-kcal mol^{-1} range of values provided by Walsh[2d] on the basis of pyrolysis of 1,1-dimethyl-1-silacyclobutane and of trimethylsilane and of the estimate of 28 ± 8 kcal mol^{-1} suggested by Gusel'nikov and Nametkin[22] based on the analysis of their data.



III

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$$CH_3CH_3 \rightarrow CH_3CH_2\cdot + H\cdot \qquad \Delta H^\circ = 98 \text{ kcal mol}^{-1}$$

$$CH_3CH_2\cdot \rightarrow CH_2{=}CH_2 + H\cdot \qquad \Delta H^\circ = 38.5 \text{ kcal mol}^{-1}$$

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Coordination Chemistry of Copper(I) in the Gas Phase

Sir:

Coordination complexes comprise a large and important class of inorganic compounds. Comprehensive equilibrium studies on these species in solution have yielded extensive compilations of formation constants which, together with theoretical models, have provided insight into the covalent properties of metal centers as well as into the nature of specific metal–ligand interactions. Only recently, however, have a few of the corresponding complexes been studied in the gas phase by mass spectrometric methods.[1-5] These studies are of particular fundamental importance in that they yield the intrinsic properties of the metal center with various ligands in the absence of any solvation effects. Similar studies on organic molecules, for example, have in some instances drastically altered previously accepted principles such as in understanding the intrinsic effect of alkyl substitution on acid–base properties.[6] While such dramatic results may not be obtained with coordination complexes, it is evident that gas-phase studies are required for a complete understanding of the chemistry of these species.

Kebarle and co-workers, using variable-temperature-high-pressure mass spectrometry, have been on the forefront of this area.[7] Their studies have yielded accurate values of ΔH

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