kcal. This would set $E_2 \simeq$ 71-76 kcal and log $A_2 \simeq$ 16-17. These values seem too high, but recognizing the trend we have assumed for reaction 2 the compromise value of A_2 equals $10^{15.6}$ s^{-1}. With use of the above high-pressure A factors and the 1158 K rate constants, RRKM fall-off calculations were performed with the results shown in Table IV. The calculated Arrhenius parameters for the shock tube are lower than those observed but still lie within the error limits of the experimental data. As expected, the calculated Arrhenius parameters for the stirred-flow conditions are higher than those observed, and the rate constants are factors of 5-6 times lower. Thus the rate constant calculations for the ES primary processes are consistent with a chain component to the stirred-flow reaction as previously argued.

It is quite possible that the chain reaction decomposition of ES under stirred-flow conditions is not initiated by any of the four primary processes considered here but rather is due to the acetylene moiety reactivity. Thus we found, while conducting control experiments, that acetylene reacts at rates within a factor of 2 of those of ES when passed through the stirred-flow reaction under reaction conditions ($k_{HC\equiv CH} \simeq 10^{6.6} \times e^{-29000\,cal/RT}$ s^{-1}). The reaction is probably initiated by carbene formation (HC≡CH → CH$_2$=C:); this kind of reaction has been observed at our reaction temperatures.[19] Initiation of the ES stirred-flow reaction in this manner would explain why acetylene was not an effective quenching agent under stirred-flow conditions but was effective under shock-tube conditions. Thus if reaction 1 were the initiation reaction in the stirred-flow pyrolysis, acetylene would have to act as a quenching agent. Since it did not, some other initiation process is suggested.

Conclusion

It is evident that the ES decomposition is a complex reaction. At low temperatures, as encountered in static and stirred-flow systems, wall catalysis is indicated. At moderate temperatures chain reactions which cannot be completely quenched contribute significantly to the overall reaction. The homogeneous gas-phase dissociation reactions at moderate temperatures, while in practice eclipsed by chain reactions of indeterminant nature, should proceed mainly through silirane and silirene intermediates and produce acetylene, ethylene and vinylsilylene (reactions 1-3). At shock tube reaction temperatures, H$_2$ elimination (reaction 4) as well as reactions 1-3 are the initiation processes. The shock-tube reaction has a small chain component which decreases in importance with increasing temperature. It can be quenched by standard silylene trapping agents.

Appendix I. RRKM Calculations

Calculations used RRKM theory[22] and the Beyer–Swinehart algorithm[23] for calculating state densities and sums (Table V). Collision efficiency estimates were obtained from equations developed by Troe.[24]

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Analysis of Stereochemical Properties of Molecular Orbitals of (Trimethylsilyl)acetylenes by Penning Ionization Electron Spectroscopy

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The Penning ionization electron spectra (PIES) resulting from thermal collision of He* (2^3S) metastable atoms and He I ultraviolet photoelectron spectra (UPS) were measured for (trimethylsilyl)acetylene and bis(trimethylsilyl)acetylene. Comparison of the relative intensities of the observed bands in PIES provided information of the stereochemical properties of the individual molecular orbitals of these compounds. The π(C≡C) orbitals of the monosilylacetylene showed a large activity of PIES, whereas the activity of the corresponding orbitals of the disilylacetylene was relatively low. This finding can be explained in terms of the effective steric shielding of the orbital by the two trimethylsilyl groups.

Introduction

In the framework of one-electron approximation, molecular orbital calculations yield orbital energies and orbital wave functions of molecules. The squares of wave functions give spatial electron distributions of molecular orbitals. From chemical point of view, the knowledge of both energies and electron distributions of individual molecular orbitals is very important. In most cases, where Koopmans' theorem[1] can be applied, orbital energies are related to observed ionization potentials obtained by photoelectron

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Table I. IP Values, Assignments, and Relative Band Intensities [I(PIES) and I(UPS)] for (Trimethylsilyl)acetylene

band	IP$_{obsd}$/eV	IP$_{calcd}$/eV	assignt	rel band intensity	
				I(PIES)	I(UPS)
1	10.18	10.48	7e [π(C≡C)]	5.5	2.3
2	11.10	11.87	6e [σ(Si—C$_{Me}$), π(Si—C$_{Ac}$)]	1.8	1.4
3	12.15	13.35	12a$_1$ [σ(Si—C$_{Ac}$)]	0.3	0.7
4–7	12.6–15.3	14.34	1a$_2$ [σ(C$_{Me}$—H)]	6.0^a	6.0^a
		14.70	5e [σ(C$_{Me}$—H)]		
		15.28	4e [σ(C$_{Me}$—H)]		
		15.73	11a$_1$ [σ(C$_{Me}$—H)]		
8	16.17	18.26	10a$_1$[Si(3s), σ(C$_{Ac}$—H), σ(C≡C)]	1.5	0.6

^{a} The integrated intensity for bands 4–7 due to six σ(C$_{Me}$-H) orbitals is taken to be 6.0.

Table II. IP Values, Assignments, and Relative Band Intensities [I(PIES) and I(UPS)] for Bis(trimethylsilyl)acetylene

band	IP$_{obsd}$/eV	IP$_{calcd}$/eV	assignt	rel band intensity	
				I(PIES)	I(UPS)
1	9.63	10.16	7e' [π(C≡C)]	2.5	2.6
2	10.57	11.56	6e'' [σ(Si–C$_{Me}$)]	3.9	4.8
3	11.26	12.03	6e' [σ(Si—C$_{Me}$), π(Si—C$_{Ac}$)]		
4	11.48	12.88	10a$_1$' [σ(C≡C)]		
5	12.45	13.82	9a$_1$'' [σ(Si—C$_{Ac}$)]	0.8	1.3
6–13	12.7–15.6	14.34	1a$_2$'' [σ(C$_{Me}$—H)]	12.0^a	12.0^a
		14.35	1a$_2$' [σ(C$_{Me}$—H)]		
		14.68	5e'' [σ(C$_{Me}$—H)]		
		14.72	5e' [σ(C$_{Me}$—H)]		
		15.27	4e'' [σ(C$_{Me}$—H)]		
		15.30	4e' [σ(C$_{Me}$—H)]		
		15.69	9a$_1$' [σ(C$_{Me}$—H)]		
		15.80	8a$_1$'' [σ(C$_{Me}$—H)]		
14	16.18	18.19	8a$_1$' [Si(3s), σ(C≡C)]	0.7	0.4

^{a} The integrated intensity for bands 6–13 due to 12 σ(C$_{Me}$-H) orbitals is taken to be 12.0.

spectroscopy.[2–4] On the other hand, it is very difficult to provide direct experimental information on spatial electron distributions of molecular orbitals from photoelectron spectroscopic studies.

Recent studies of Penning ionization electron spectroscopy of molecules have revealed that Penning ionization (A* + M → A + M$^+$ + e$^-$) can be considered as an electrophilic reaction of an excited atom (A*) with a molecule (M) yielding an ionic state of the molecule (M$^+$) together with an ejected electron in a continuum state (e$^-$).[5] The excited atom attacks a molecular orbital from which an electron is extracted into the vacant orbital of the atom. Analysis of the kinetic energy distribution of the ejected electrons provides a Penning ionization electron spectrum (PIES).[6] Band intensities of PIES reflect the relative yields of various ionic states (M$^+$) which are directly connected with the relative activities of the relevant molecular orbitals toward the electrophilic attack by the metastable atoms; an outer orbital exposed to the outside of the van der Waals surface interacts with the metastable atom more effectively to yield larger intensities of PIES compared to an inner orbital having small electron densities in the outside. Such an effect may be summarized as stereoelectronic effect of molecular orbitals on Penning ionization.[5] This characteristic of PIES has been successfully applied to (1) the assignments of bands in He I UV photoelectron spectra (UPS) of various organic molecules[7] and

(2) the study of spatial electron distributions of individual molecular orbitals.[8]

The electronic structure of silylacetylenes has been the subject of extensive investigations and discussed from the viewpoint of σ–π and d$_\pi$–p$_\pi$ interactions.[9–12] However, to our knowledge, little information has so far been available on the stereochemical properties of the molecular orbitals of these compounds. In order to obtain such information, the activity of molecular orbitals in Penning ionization is studied for (trimethylsilyl)acetylene and bis(trimethylsilyl)acetylene in this paper.

Experimental Section

(Trimethylsilyl)acetylene and bis(trimethylsilyl)acetylene were prepared according to literatures.[13] Purity was checked by the absence of spurious absorptions in IR spectra and signals in NMR spectra.

He* (2^{3}S, 19.82 eV) Penning ionization electron spectra (PIES) and He I UV photoelectron spectra (UPS) were measured by
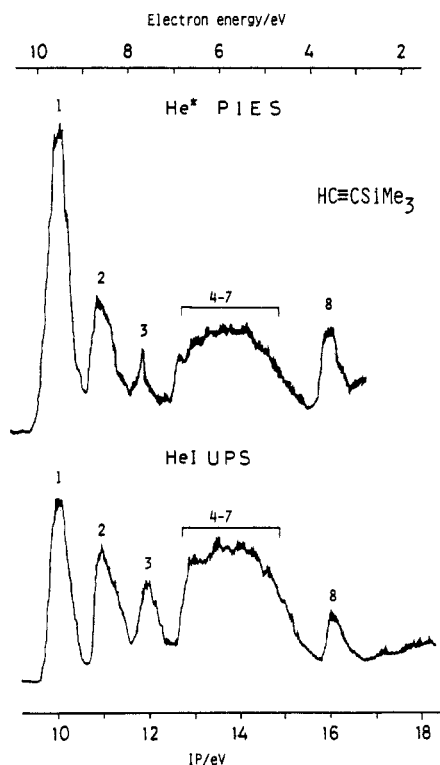
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Figure 1. Transmission-corrected He* (2³S) PIES (upper) and He I UPS (lower) for (trimethylsilyl)acetylene.

Figure 2. Transmission-corrected He* (2³S) PIES (upper) and He I UPS (lower) for bis(trimethylsilyl)acetylene.

means of the electron spectrometer described elsewhere.[5,8b] The metastable atoms were produced by impact of 60-eV electrons to the beams of thermal helium atoms. A water-cooled helium discharge lamp was used to quench the 2^1S metastable atoms from the mixture of 2^1S and 2^3S atoms. The He I resonance photons (21.22 eV) were produced by dc discharge in pure helium gas. The electron spectra were obtained at an ejection angle of 90° with respect to the metastable atom beam or the photon beam by means of a hemispherical type analyzer with electron lens systems and scanning electrodes. The energy dependence of the transmission efficiency of the electron spectrometer was determined as described in a previous paper.[5]
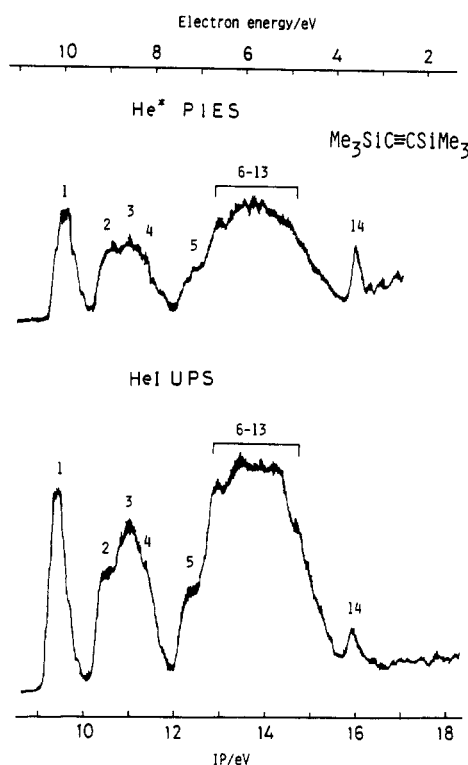
Calculations

Molecular orbital calculations were made by the ab initio method with a 4-31G basis set for carbon and hydrogen atoms and with a 3-21G basis set for silicon atoms.[14,15] The calculated ionization potentials (IP) which were taken to be the negative of the SCF orbital energies (Koopmans' theorem[1]) are listed in Tables I and II, together with the observed IP.

Results and Discussion

In Figures 1 and 2 He* (2³S) PIES and He I UPS of (trimethylsilyl)acetylene and bis(trimethylsilyl)acetylene are shown. The observed bands are assigned to relevant molecular orbitals from which electrons are ejected upon ionization (Tables I and II).

Although the band positions in the PIES correspond to those in the UPS, the relative intensities are considerably different. For (trimethylsilyl)acetylene, band 1 which is assigned to the $\pi(C\equiv C)$ orbitals is considerably enhanced in the PIES with respect to bands 4-7, arising from the ionization from the C-H σ orbitals [$\sigma(C_{Me}-H)$] of the

methyl groups (Figure 1 and Table I). The observed trend can be explained in terms of the selection rule for PIES; the outer orbital is more active than the inner orbital.[5] In the present case, the $\pi(C\equiv C)$ orbitals which are exposed outside the van der Waals surface should be reactive toward the attack by the metastable atom to give an enhanced band in the PIES. This interpretation is reasonable, since the possibility of the electron transfer from a target molecule to the metastable atom is governed by spatial overlap of the inner-shell vacant orbital of the metastable atom with the relevant molecular orbitals.[5] On the other hand, band 3 for the monosilylacetylene which can be assigned as the Si—C≡ σ orbital [$\sigma(Si-C_{Ac})$] is weakened in the PIES. It is now clear that the $\sigma(Si-C_{Ac})$ orbital, localized mostly on the Si-C skeleton, is shielded by the $\pi(C\equiv C)$ orbital and other orbitals (e.g., the σ-($C_{Me}-H$) orbitals) to show a low activity in the Penning ionization.

The PIES of the monosilylacetylene also shows that band 8 at about 3.5 eV (IP = 16.17 eV in the UPS) is fairly enhanced with respect to the bands attributed to the σ-($C_{Me}-H$) orbitals. This band was previously assigned by Heilbronner and co-workers[10] to $\sigma(Si-C_{Me})$ (Si-C σ orbitals of the methyl groups) and $\sigma(Si-C_{Ac})$ (axially symmetric Si-C σ orbital) orbitals on the basis of symmetry considerations and of semiquantitative correlation diagrams using basis orbital parameters derived from the UPS of the acetylenes. Alternatively, we assign this band to the ionization from the orbital having the Si(3s) and $\sigma(C_{Ac}-H)$ characters as well as the $\sigma(Si-C_{Ac})$ character based on the results of the ab initio MO calculations (Table I). This assignment is supported by the following observations. (i) In the spectra of tetramethylsilane and hexamethyldisilane, the band which are related to the orbitals having the Si(3s) character occur in nearly the same IP region at ca. 15.7 eV.[16] (ii) For acetylene the $\sigma(C_{Ac}-H)$ orbital shows a

(14) Kosugi, N. Program GSCF2, Program Library: The Computer Center, the University of Tokyo: Tokyo, Japan, 1981.

(15) Geometrical parameters used for the calculations of the mono- and disilylacetylenes were as follows. Bond lengths (Å): 1.20 (C≡C), 1.825 (Si—C_{Ac}), 1.05 (C_{Ac}—H), 1.875 (Si—C_{Me}), 1.115 (C_{Me}—H). Bond angles (deg): 107.5 (C_{Me}-Si-C_{Me}), 109.5 (H-C_{Me}-H) (Zeil, W.; Haase, J.; Dakkouri, M. *Discuss. Faraday Soc.* **1969**, *47*, 149).

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relatively large activity in PIES, and this is ascribed to the distribution of the orbital spreading out without nodes in the molecular plane.[5] The enhancement of band 8 suggests that this band is related to the orbital having the $\sigma(C_{Ac}-H)$ character.

An interesting point worth mentioning can be seen in the reactivities of the $\pi(C\equiv C)$ orbitals of the mono- and disilylacetylenes toward the electrophilic attack by the metastable helium atom. In the UPS the band arising from the ionization of the $\pi(C\equiv C)$ orbitals appears at 9.63 eV for bis(trimethylsilyl)acetylene and 10.18 eV for (trimethylsilyl)acetylene, respectively (Table II). Thus substitution of a trimethylsilyl group for the acetylenic hydrogen on the monosilylacetylene decreases the IP by 0.6 eV (Tables I and II). In the context of Koopmans' theorem,[1] this difference reflects that the $\pi(C\equiv C)$ orbitals is destabilized by the inductive and/or hyperconjugative effect of the second trimethylsilyl group. Thus, on the basis of this consideration only, a conclusion could be drawn reasonably that the orbital would be more reactive toward the electrophile compared to that of the monosilylacetylene. However, as is seen in Figure 2 and Table 2, this expectation turned out not to be the case in the PIES. Instead, the $\pi(C\equiv C)$ of the disilyl derivative is found to be less reactive toward the metastable atom. This observation leads us to conclude that the steric effects of the two trimethylsilyl groups, which shield the orbital from the impact of the metastable atom, overcome the electronic activation.

Although the Penning ionization process is the gas-phase electron-transfer reaction, it is of considerable interest to compare the observed PIES activities of the $\pi(C\equiv C)$ orbitals in these silylacetylenes with chemical reactivities toward electrophilic attack in solution. From the arguments previously advanced, it is expected that the reactivity of the $\pi(C\equiv C)$ bonds toward electrophilic reagents should be retarded by steric shielding as the number of the silyl groups increases. This expectation is found to apply well in the case of the 1,3-dipolar cycloaddition of diazoalkanes to the acetylene derivatives in which bis-(trimethylsilyl)acetylene has been found to be much less reactive than (trimethylsilyl)acetylene.[17] Thus, Penning ionization electron spectroscopy has its important application in the study of organosilicon compounds, since it provides useful information on the stereochemical environment of a particular molecular orbital which will take part into chemical reactions.

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Cis–Trans Isomerization of Alkyl-Substituted Allylic Ion Pairs. 1. Isomerization of (Neopentylallyl)lithium, -sodium, and -potassium in Tetrahydrofuran

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(Neopentylallyl)lithium, -sodium, and -potassium have been prepared by established methods under conditions where the trans configuration is, as far as possible, produced. Their isomerization rates to the thermodynamically more stable cis form have been measured as a function of temperature. Fairly large differences in rates were observed in the order Li > Na > K. Both preexponential factors and activation energies increased in the reversed order. Isomerization barriers parallel those for terminal methylene group rotation. The implications of these observations are discussed.

Rotation about the $\alpha\beta$ and $\beta\gamma$ bonds in alkyl-substituted allyl ion pairs (R–CH$_\gamma$–CX$_\beta$–CH$_{2\alpha}$⁻M⁺; I) is of interest on theoretical grounds and for the interpretation of reaction mechanisms. $\alpha\beta$-Rotational barriers are relatively easily obtained from coalescence temperatures of the proton NMR signals of the α-methylene group and are available for a number of allylic derivatives of the alkyl metals.[1] Generally, CH$_2$ rotation of the lithium derivatives is observable at considerably lower temperatures than with those of potassium, and in both compounds when the temperature is raised, it is the trans isomer whose methylene group begins to rotate first. A little qualitative information is available on the ease of rotation around the β–γ bond (cis–trans isomerization). The earliest indications that allylic lithium compounds are quite labile in

solution were made by Seyferth and Jula.[2] Transmetalation of *trans*-crotyltrimethyltin with *n*-butyllithium in ether/hexane at room temperature produced a 60/40 mixture of *trans*- and *cis*-crotyltrimethylsilane on quenching with trimethylchlorosilane. Identical results were obtained starting from *cis*-crotyltrimethyltin. Lithium compounds again appear to have lower rotation barriers although no quantitative data are available for the derivatives of the other alkali metals. Ia (R = neopentyl, X = CH$_3$, M = Li) undergoes trans to cis isomerization at –40 °C in tetrahydrofuran (THF) with a half-life of ~40 min.[3] In heptane the trans form is more stable, but a similar lifetime is observable at 0 °C for the cis to trans isomerization.[4] Thompson and Ford[1] have indicated that

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