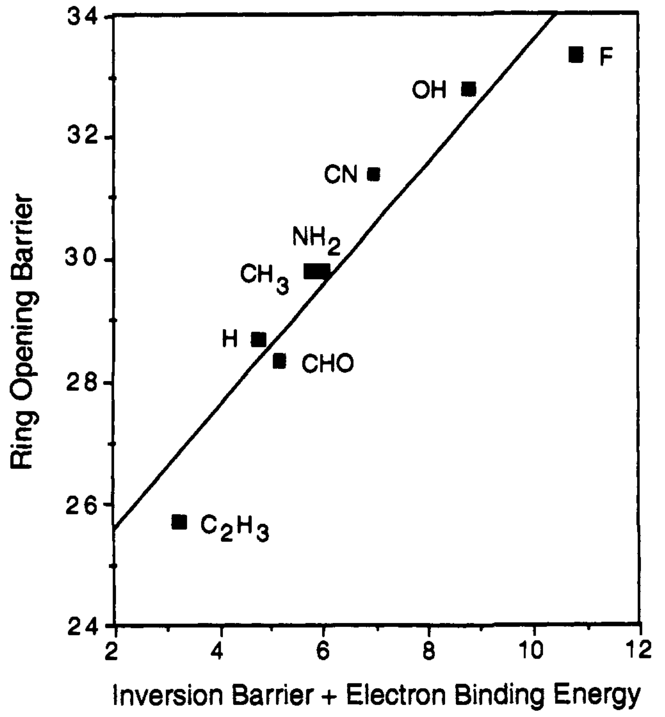

Figure 10. Calculated ring-opening barriers versus inversion barriers and electron binding energies, as reflected by the HOMO energies of the anions. The solid line is a least-squares fit of the data (y = 0.124(inversion barrier) − 0.101(HOMO energy) + 23.5, r = 0.955), where all of the values are at the MP2/6-31+G(d)//6-31+G(d) level and are in kcal mol^{-1}.

(proton affinity) makes relatively little difference. These results do account for the differences between the cyclopropyl anions and clearly indicate that there is a delicate balance of factors affecting the rearrangement rates. The plot shown in Figure 10 also indicates that those ions with low electron-binding energies (high HOMOs) and small inversion barriers will isomerize most readily. These two requirements are at odds with each other in that ions with small inversion barriers usually have large electron-binding energies and those with small binding energies typically have large epimerization barriers. These conflicting tendencies are well balanced in vinylcyclopropyl anion and, presumably, phenylcyclopropyl anion. In accord with expectations, the latter ion rearranges to 2-phenylallyl anion at 200 °C while the former isomerizes upon its formation.[47] The product, however, is not the expected 2-vinylallyl anion but rather the conjugate base of methylenecyclobutane. This ion arises from a competitive pathway which also is allowed by orbital symmetry.

We have shown that a variable temperature flowing afterglow device is a powerful instrument for studying unimolecular rearrangements. The structure of the substrate is an important factor influencing the activation energy and so is the presence of substituents. Cyclopropyl anions with small inversion barriers and small electron-binding energies rearrange most readily. Consequently, the bicyclobutyl anion, which is fairly rigid, is remarkably robust thermally. The conjugate bases of dimethyl 1,2-cyclopropanedicarboxylate, phenylcyclopropane, and cyclopropanecarboxaldehyde (**4a**, **1a**, and **2a**, respectively), on the other hand, rearrange anywhere from 75 to 250 °C. A wide variety of unimolecular rearrangements can be explored both qualitatively and quantitatively, and the results from such work will be reported in due course.

Acknowledgment. Support from the Minnesota Supercomputer Institute, the National Science Foundation (CHE-8907198), and the donors of the Petroleum Research Fund, as administered by the American Chemical Society, is all gratefully acknowledged.

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(47) Vinylcyclopropane reacts with OH$^-$ to give a rearranged product ion, whereas NH$_2^-$ reacts to afford vinylcyclopropyl anion. For further details, see ref 19.

The Photoelectron Spectrum of Thioformyl Cyanide

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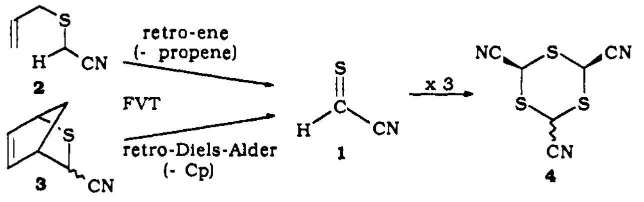
Abstract: Thioformyl cyanide, HCSCN, was generated, under flash vacuum thermolysis conditions, by retro-ene and retro-Diels–Alder cleavages of allylcyanomethyl sulfide and 3-cyano-2-thiabicyclo[2.2.1]hept-5-ene, respectively, and unambiguously characterized in the gas phase by photoelectron spectroscopy. Its unimolecular decomposition into carbon monosulfide and hydrogen cyanide was found to be strongly disfavored.

The formation of the reactive thioaldehyde thioformyl cyanide (**1**) has been demonstrated, in several reactions performed in the presence of 1,3-dienes, by the observation of the corresponding Diels–Alder adducts.[1] A kinetic investigation of the thermal retro-ene decomposition of allylcyanomethyl sulfide (**2**), leading to propene and 2,4,6-tricyano-*s*-trithiane, also involved the transient formation of **1**.[2] More recently, the flash vacuum thermolysis (FVT) of the same precursor **2** as well as the dehydrochlorination of cyanomethanesulfenyl chloride under vacuum gas solid reaction conditions allowed the first direct observation of compound **1** by millimeter wave spectroscopy.[3] The moments of inertia of **1**,

Scheme I



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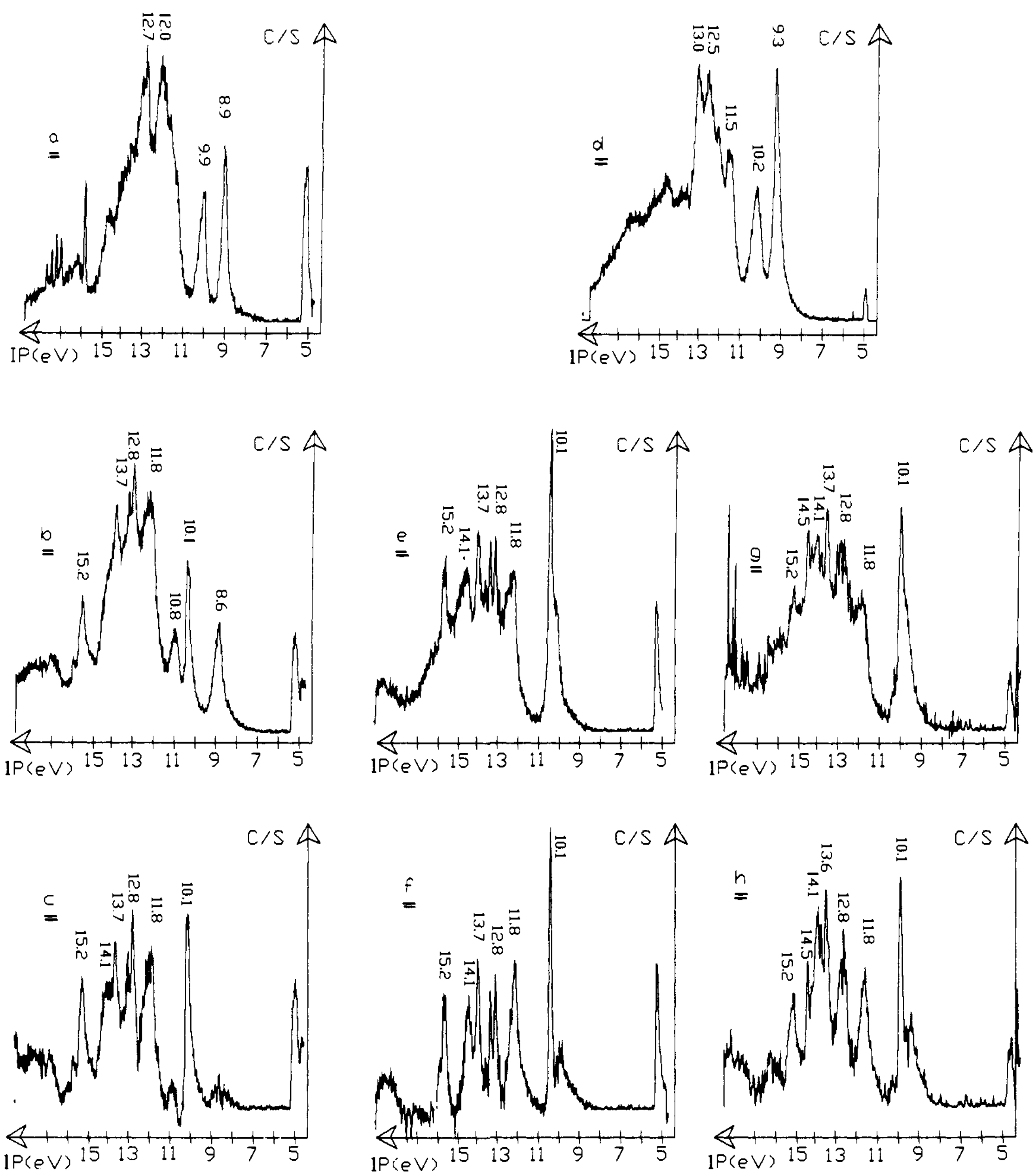

Figure 1. PE spectra of precursor 3 (a), FVT of 3 at 788 K (b), thioformyl cyanide (1), obtained by subtracting cyclopentadiene from b (c), precursor 2 (d), FVT of 2 at 1123 K (e), 1, obtained by subtracting propene from e (f), FVT of 2 at 1300 K (g), and subtraction of propene from spectrum g (h).

calculated from equilibrium geometries and quantic centrifugal distortion constants, are in good agreement with the experimental results.[4]

The coupling of FVT with photoelectron spectroscopy (PES) is an excellent method for the observation of reactive molecules in the gas phase, and we applied it recently to formyl cyanide HCOCN, obtained by retro-ene decomposition of allyloxyacetonitrile.[5] This result as well as recent ones showing that the stability of formyl cyanide can be enhanced by thorough elimination of water and other impurities[6] led us to investigate by PES the FVT of two precursors of thioaldehyde **1**: compound **2**[2,3] and 3-cyano-2-thiabicyclo[2.2.1]hept-5-ene (**3**).[1d,7] The complete PE spectrum of **1**, and the evidence of its stability toward the unimolecular decomposition into CS and HCN, are presented in this paper.

The FVT-PES experiments were performed on a Helectros 0078 spectrometer using a short-path internal oven (pressure 10^{-5} hPa, see ref 5 for experimental details) and the PE spectra of starting materials **3** and **2** recorded before thermolysis (Figure 1, spectra a and d). The thermal cleavage of **3** appeared to be complete at 788 K (spectrum b). Six ionizations were observed beside those of cyclopentadiene. The FVT of **2** was complete at 1123 K and a new spectrum (e) was observed. By subtracting the spectra of cyclopentadiene and propene from the spectra b and e, respectively,

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(7) Adduct **3** was obtained in 42% yield by treatment of cyanomethyl thiocyanate by triethylamine in the presence of cyclopentadiene.

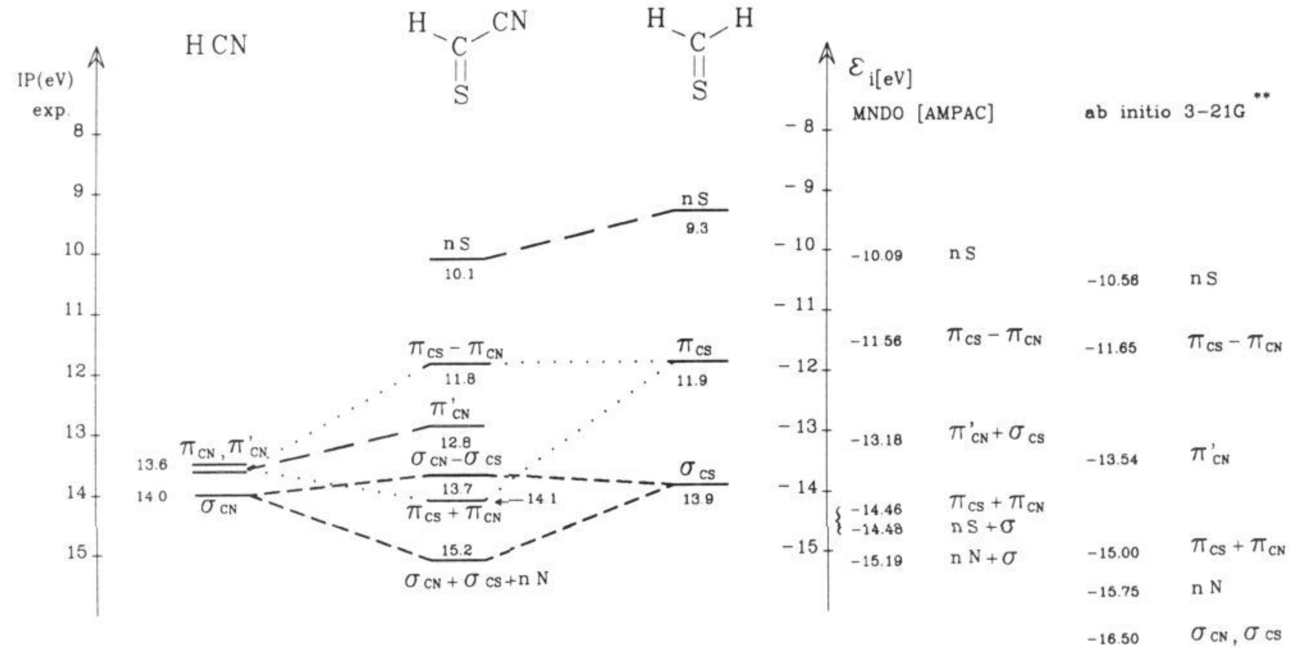

Figure 2. Correlation diagram of the IP's of thioformyl cyanide (**1**), thioformaldehyde, and hydrogen cyanide and calculated energies (MNDO and ab initio 3-21G**).

the identical spectra c and f were obtained, showing the following ionization potentials (IP): 10.1 (strong, narrow), 11.8 (broad, structured), 12.8 (vibrational progression of 1900 cm^{-1}), 13.7 (narrow), 14.1 (broad), and 15.2 eV (strong, broad). When the FVT of **2** was performed at 1300 K (spectrum g), the spectrum h obtained by subtracting propene from g showed, beside the above mentioned IP's, those corresponding to small amounts of carbon disulfide and hydrogen cyanide (14.5 and 13.6 eV, respectively).

The formation of 2,4,6-tricyano-*s*-trithiane (**4**), previously characterized after trapping by NMR and IR in the FVT of **2**,[3] cannot be a priori excluded here in the gas phase, although two bands at ca. 9.0–9.5 eV and a deeper ionization (ca. 12 eV) followed by a poorly-resolved massif should be expected by analogy with the spectrum of unsubstituted *s*-trithiane.[8] Therefore, in order to record the PE spectrum of **4**, we have remade this compound by trapping at 77 K followed by trimerization of thioformyl cyanide (**1**) generated by FVT of sulfide **2** at 1133 K. A deep blue color, vanishing quickly upon warming, was observed in the trap after FVT of **2**. This FVT, performed on 5 μL of **2** with trapping of products in an optical cryostat (see ref 5 for experimental procedures) allowed us to record the visible spectrum of this blue compound on a Jobin-Yvon 201 spectrometer. This absorption, showing a maximum at 611 nm and disappearing rapidly upon warming, is attributable to the n → π* transition of **1** (thiobenzaldehyde, 575 nm; thioacrolein, 580 nm[9]).] It should be noted that the precursor **3** is not suitable in this case, owing to the great dienophilic reactivity of **1**[1] leading to its immediate recombination in the trap with cyclopentadiene to give back the starting compound **3**.

The PE spectrum of the white solid trithiane **4**, obtained above by warming up of the trap, was difficult to record, due to low thermal stability and volatility of this compound. Vaporization of **4** between 333 and 373 K led to a poorly-resolved spectrum showing an ionization at 11.45 eV (CN) accompanied by a broad massif at 9.5–9.8 eV and a band at 12.6 eV, corresponding likely to those expected for the trithiane ring of **4**. It appears, therefore, that the spectrum obtained by short-path internal FVT of precursors **2** and **3** should not be attributed to the trimer **4** but to the monomeric thioaldehyde **1**.

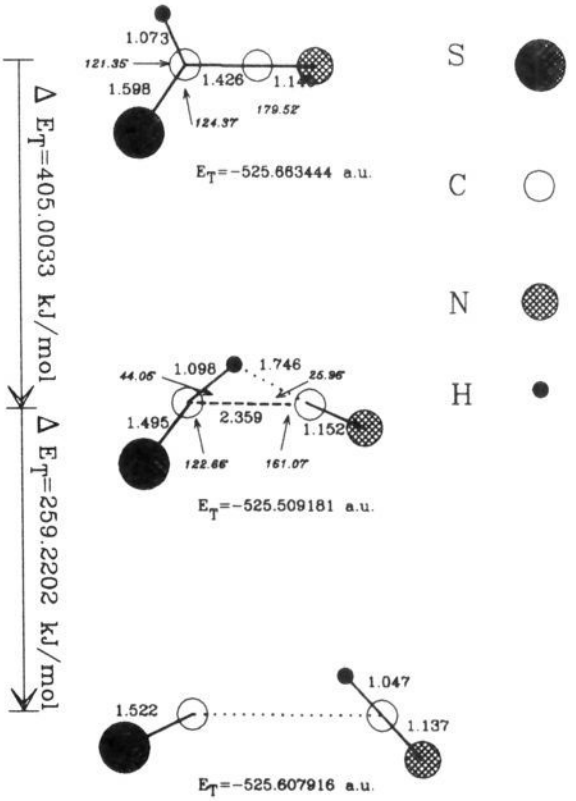

Figure 3. Change in geometry of thioformyl cyanide (**1**), from its ground state, through the transition state, toward the products hydrogen cyanide and carbon monosulfide.

The qualitative interpretation, resulting from an estimation of the interactions between thioformaldehyde[10] and cyano group, has been confirmed by MNDO and ab initio (3-21G** basis set[11]) calculations of the orbital energies (Figure 2). The optimized geometry, close from previously published results,[4] shows a marked

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shortening of the C–C bond, calculated at 1.426 Å (1.434 Å 6311 G** MP_2), this revealing a significative delocalization. The above calculation and correlation diagram (Figure 2) agree with the attribution of the first band (10.1 eV) to the ionization of the sulfur lone pair interacting with the $n^{\perp}{}_{C\equiv N}$ orbital. Any vibrational structure should be expected as weak, the ground-state valence vibration $\nu_{C=S}$ being calculated at 1078 cm^{-1}, and was not observed.

The two ionic states of symmetry A″, calculated to lie at 11.56 eV (11.65) and 14.46 eV (15.00), arise respectively from the ejection of an electron from the delocalized orbitals between the two fragments CS and CN (antisymmetric and symmetric interaction $\pi_{CS} - \pi_{CN}$, $\pi_{CS} + \pi_{CN}$). In the experimental spectrum, we assign the bands at 11.8 and 14.1 eV to these two ionic states.

The three other well-resolved bands arise from ionization into σ radical cation states. The band at 12.8 eV with a vibrational progression of 1900 cm^{-1} is unambiguously associated with the orbital in the plane of the CN group. The ionizations at 13.7 and 15.2 eV therefore correspond to those of the σ_{C-S} orbital and of the cyano group lone pair n_N, respectively.

The relative stability of thioformyl cyanide (**1**) and the formation of only minor amounts of carbon disulfide and hydrogen cyanide at a FVT temperature of 1300 K led us to perform an ab initio calculation (3-21G**) of the unimolecular decomposition pathway of this compound. The results (Figure 3) have been determined at the SCF level but remain comparable, considering the involved energetical and geometrical modifications, to those obtained for formyl cyanide.[6] The stationary point is characterized by a Hessian with one negative eigenvalue. The structure of the transition state shows marked lengthening of the C–C bond and decrease of the CCH angle, accompanied by shortening of the C–S bond. The transition-state energy, calculated to be 405.00 kJ·mol^{-1} above compound **1**, appears especially high. Furthermore, the final state leading to the formation of CS and HCN is energetically less stable than **1**.

These theoretical results support our experimental findings that, under dilute gaseous conditions, thioformyl cyanide (**1**) is relatively stable, its unimolecular decomposition process being thermodynamically disfavored. In contrast, formyl cyanide is unstable and decomposes under the same conditions.[5]

Theoretical Studies of Inorganic and Organometallic Reaction Mechanisms. 7. Ab Initio Potential Energy Surfaces of CO Substitutions on Six-Coordinate *trans*-$W(CO)_4(NO)Cl$ and $Re(CO)_5Cl$

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Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255. *Received August 10, 1992*

Abstract: Carbonyl substitution reactions on *trans*-$W(CO)_4(NO)Cl$ and isoelectronic $Re(CO)_5Cl$ were investigated through the construction of ab initio potential energy surfaces. Hartree–Fock–Roothaan calculations for the substitution by PMe_3 on $W(CO)_4(NO)Cl$ predict an associative mechanism with a 7-coordinate intermediate, in which the W–N–O angle is bent to 135.7°. The Laplacian of the total charge density displays a process in which electrons shift from the metal to the nitrogen, create an additional N lone pair, and vacate a coordinate site for the entering ligand. For a weaker donor, such as PH_3, this associative mechanism is not available because poor donors cannot stabilize an intermediate with a bent W–N–O bond. Substitution by any PR_3 in $Re(CO)_5Cl$ also proceeds by a dissociative or I_d mechanism, since here the CO ligand cannot accommodate an additional electron pair and it resists bending to maintain a strong Re–C bond. We also explored the influences of electron correlation and basis set on the potential energy surfaces.

Introduction

Ligand substitution at a transition-metal center is a basic organometallic reaction as well as a crucial step in homogeneous catalytic reactions. Thus, detailed knowledge about the mechanism of such reactions is of particular significance. As good chemical models, the kinetics of substitution reactions of the CO group in the metal carbonyl derivatives have been studied extensively.[1] Among the metal carbonyl derivatives, metal nitrosyl carbonyls continue to receive attention because their novel associative mechanism results in a rapid substitution rate. For instance, although 4-coordinate $Ni(CO)_4$ slowly undergoes substitution through a dissociative mechanism,[2] its isoelectronic analogs $Co(CO)_3(NO)$,[3] $Fe(CO)_2(NO)_2$,[4] and $Mn(CO)(NO)_3$[5] readily react through an associative process. Carbonyl substitutions of 5-coordinate $Fe(CO)_5$[6] and 6-coordinate $Cr(CO)_6$[7] occur by a dissociative mechanism, while their isoelectronic counterparts $Mn(CO)_4(NO)$[8] and $V(CO)_5(NO)$[9] react by an associative pathway. Recent studies on $W(CO)_4(NO)X$ (X = Cl, Br, or I) show that CO substitution proceeds through an associative route with strong nucleophiles such as $P(n\text{-}Bu)_3$ but through a dissociative or intermediate dissociative mechanism for weaker nucleophiles such as PPh_3.[10] This associative pathway apparently is not accessible

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