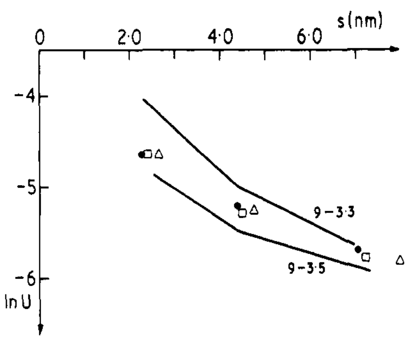

Figure 6. The inversion of experimental argon-graphite second virial coefficients. The data points refer to different initial approximate potentials: (●) 9-3; (□) 9-3.5; (△) Steele. The solid lines show the 9-3.3 and 9-3.5 potentials.

tained by the minimization procedure outlined above. The value of ϵ_{IS} used in this study was instead taken from Steele's analysis of graphite-rare gas interactions using the "summed 10-4" potential.[9] This gives $\epsilon_{IS} = 959$ K for the argon-graphite system.

The smoothed experimental data were inverted by use of a range of suitable approximate potentials to calculate $G^{(0)}(T^*)$, as shown in Figure 6. The results show a clear convergence from the common potential functionality with an attractive exponent of 3.4 ± 0.1. However, this convergence is slow due to the sensitivity of the inverted potential to the initial approximate potential in this range of separations.

Conclusions

The inversion method proposed is clearly of value when data of sufficient accuracy and temperature range are available. With the low-temperature data currently available a successful inversion requires both an initial approximate potential which closely resembles the true potential and an accurate, independent estimate of ϵ_{IS}. The inversion of this low-temperature data can be used to establish upper and lower bounds to the long-range behavior of the gas-surface interaction. In general, however, to realize the full potential of the inversion method we require measurements over a larger temperature range. For the argon-graphite system, in order to define the potential function over the main region of interest without resorting to additional data we would need the low pressure adsorption isotherms at temperatures up to 1500 K.

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Photochemistry of Acetylene, Hydrogen Cyanide, and Mixtures

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Photolyses of HCN, C_2H_2, and mixtures were accomplished including various ratios of HCN/C_2H_2 and time periods. The photolysis of HCN yielded $(CN)_2$, CH_4, NH_3, CH_3NH_2, $(NH)_2$, and a brown polymer. The products from C_2H_2 were diacetylene (C_4H_2), C_2H_4, C_6H_6, vinylacetylene, phenylacetylene, and a polymer. Products from a relatively low HCN/C_2H_2 ratio (5:1) where 90% of the light is absorbed by C_2H_2 were similar to those of C_2H_2 except for the additional formation of acrylonitrile (C_2H_3CN). At relatively higher ratios of HCN/C_2H_2 where 37-56% of the light is absorbed by HCN, cyanoacetylene (C_2HCN) was formed in addition to the foregoing products and the C_4H_2 substantially reduced. The proposed principal path for formation of C_4H_2 is attack of $C_2H\cdot$ on C_2H_2, while for C_2H_3CN the principal path is attack of $C_2H_3\cdot$ on HCN. The proposed principal path for production of C_2HCN is via $CN\cdot$ attack on C_2H_2. Several products from HCN are proposed to be the result of progressive H atom addition. Other products from C_2H_2 and HCN are the result of radical-radical recombination. We believe these results could have relevance to Jovian atmosphere chemistry and formation of several molecules found in interstellar space.

Introduction

Direct photolysis of HCN in the gas phase at 185 nm has been shown to yield $(CN)_2$, H_2, CH_4, NH_3, N_2H_4, C_2H_6, and CH_3NH_2 as well as undefined polymeric material.[1] Photolysis of C_2H_2 at 185 nm gave C_4H_2 (diacetylene), C_2H_4, C_6H_6, vinylacetylene, and undefined polymer.[2] There have been no previous studies involving the photolysis of HCN-C_2H_2 mixtures.

Our interest in HCN and C_2H_2 arises from the rather broad distribution of each of these in the universe. Furthermore, potential products of each of these separately, or from reaction of fragments of each, exist in interstellar space. For example, C_4H, $C_2CN\cdot$, $C_2H\cdot$, C_2HCN, and C_4HCN (cyanodiacetylene) through C_8HCN have been identified in interstellar space.[3]

HCN is considered as one of the more abundant molecules in interstellar clouds,[3] has been found in nearby galaxies, is a constituent of comets, appears to be a constituent of the Jovian atmosphere,[5] and is considered an important intermediate in prebiotic earth chemistry.[6]

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C_2H_2 also exists in interstellar clouds[3] and in the Jovian atmosphere[7,8] and is formed[9] as a principal product in the photolysis of CH_4, which is believed to have been a major constituent of the primitive earth. Many of the compounds produced in our gas-phase study have been found in interstellar clouds and are considered as important in prebiotic earth chemistry. We have reported on the results of H atom (from H_2S) reactions involving C_2H_2, C_2H_4, NH_3, and H_2O particularly as related to Jovian atmosphere chemistry.[10]

Experimental Section

HCN was synthesized by reacting 12 N H_2SO_4 with solid NaCN. The HCN was purified by bulb-to-bulb distillation and passage through a P_2O_5 trap to remove any last traces of water. It is essential that water be removed to avoid polymerization of the HCN. The HCN contained no impurities on the basis of GC/MS analysis.

C_2H_2 obtained from Matheson was purified by several distillations in vacuo (from a trap at −78 °C to one at −196 °C) to remove traces of acetone in which the acetylene was dissolved for shipment in the cyclinder. Mass-spectrometric analysis showed that no impurities were present.

Prepurified argon (99.99%) from Matheson was used as received.

A low-pressure mercury lamp with a Suprasil-1 body was used as light source. The light intensity was determined by O_2 actinometry and was estimated to be 10^7 quanta/s at 185 nm. A mercury-free cyclindrical quartz reaction vessel having an absorption path of 10 cm was fitted with two 2-in. diameter Suprasil-1 quartz windows. Since both HCN and C_2H_2 do not absorb 254 nm, no filter was used to eliminate this wavelength. Both the lamp and the reaction vessel were covered by a glass cyclinder and air was replaced with flowing nitrogen to prevent absorption of the 185-nm light by oxygen. The irradiation time was usually of the order of 2 min after which the lamp was turned off and the gaseous products were analyzed by GC/MS or GC. Even with these short exposures, the windows often had a thin polymeric film. As a precaution against irregular irradiation intensity because of this from experiment to experiment, the vessels were cleaned with concentrated NaOH, rinsed with distilled water, dried with nitrogen, and evacuated before each experiment.

A high vacuum ($\sim 10^{-5}$ torr) system with greaseless Teflon stopcocks was used for gas handling. Gas mixtures in the reaction vessel were allowed to equilibrate to homogeneity by sitting overnight prior to irradiation.

All analyses were done by GC/MS (Hewlett-Packard GC Model 5710A/MS Model 5930A/Data System Model 5933A) and GC (Perkin-Elmer Model 990). In general, a 6 ft × 0.25-in. o.d. glass column packed with Tenax was used at 30 °C. Porapak Q or N and Chromsorb 103 packed columns were occasionally used for light hydrocarbons and amines. Diacetylene and cyanoacetylene were separated by using a 3.6-m ($^1/_8$ in. diameter) stainless-steel column packed with 1,2,3-tris(2-cyanoethoxy)propane on Gas-Chrom Q at 30 °C.

The identification of products was accomplished by direct comparison of GC retention times and mass spectra of authentic compounds where available. For those cases where authentic compounds were not available, products were identified soley on mass-spectral data obtained from the literature.[11]

Results and Discussion

The high sensitivities of GC/MS and GC made it possible to study the photolysis of acetylene and acetylene–HCN at a very low extent of reaction (<5%). This has distinct advantages since many initially formed products would begin to absorb an appreciable portion of incident light if their concentration were allowed to become sizable.

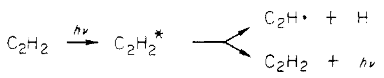
Direct photolysis of HCN in the gas phase at 185 nm yielded $(CN)_2$, CH_4, NH_3, CH_3NH_2, $(NH_2)_2$, and a brown polymer. Our products are similar to those of others[1] except for H_2 and C_2H_6. H_2 is believed to be present but instrumental limitation prevented its positive identification. Photolysis of C_2H_2 at 185 nm produced C_4H_2 (most abundant), C_2H_4, C_6H_6, vinylacetylene, phenylacetylene, and polymer. Again H_2 is believed to be present. All products except phenylacetylene were found by previous investigators.[2]

Both C_2H_2 and HCN absorb at 185 nm with absorption coefficients of 20 and 0.5 cm^{-1} atm^{-1}, respectively. Because of this large difference in absorption intensity, the pressure of HCN relative to C_2H_2 must be kept high in a mixture in order to obtain appreciable photolysis of HCN. Experiments were conducted by varying the pressure ratios of HCN/C_2H_2 such that the percent light absorbed by HCN varied between ~10% and ~60% (the nature of the principal absorbing species was altered from C_2H_2 to HCN). The effect of this variation in the identity of the principal absorbing species and the consequences upon the nature of the photochemical products are distinct and will be discussed.

Products obtained from a 5:1 ratio of HCN/C_2H_2, where only 10% of the light is absorbed by HCN, were similar to those from the photolysis of C_2H_2 alone *except* for the formation of a significant amount of C_2H_3CN (acrylonitrile) (diacetylene was predominant). When the fraction of light absorbed by HCN was increased to 37%, the rate (and amount) of diacetylene formation was substantially reduced (~60%) and the formation of C_2HCN (cyanoacetylene) occurred. There was no appreciable change in the rate of C_2H_3CN formation. When 56% of the light was absorbed by HCN, C_2HCN and C_4H_2 were formed in approximately equal amounts. In the latter case, as the irradiation time was increased, the C_4H_2 reached a maximum and then rapidly decreased while C_2HCN continued to increase rapidly and showed a tendency to plateau at the longest time (Figure 1). This result may well be the consequence of further photopolymerization of C_4H_2 since C_4H_2 has an absorption maximum at 246 nm which is near one of the other wavelengths of light (254 nm) emitted by the light source. C_2HCN has a maximum near 228 nm and is less affected by the 254-nm irradiation.

Light absorption by C_2H_2 leads to both predissociation and excited molecules[2,12] which can either dissociate or deactivate by collision

$$C_2H_2 \xrightarrow{h\nu} C_2H\cdot + H \qquad (1)$$



$$C_2H_2 \xrightarrow{h\nu} C_2H_2^* \longrightarrow \begin{cases} C_2H\cdot + H \\ C_2H_2 + h\nu \end{cases}$$

For HCN, the primary step is proposed[1] to be

$$HCN \xrightarrow{h\nu} H + CN\cdot \qquad (3)$$

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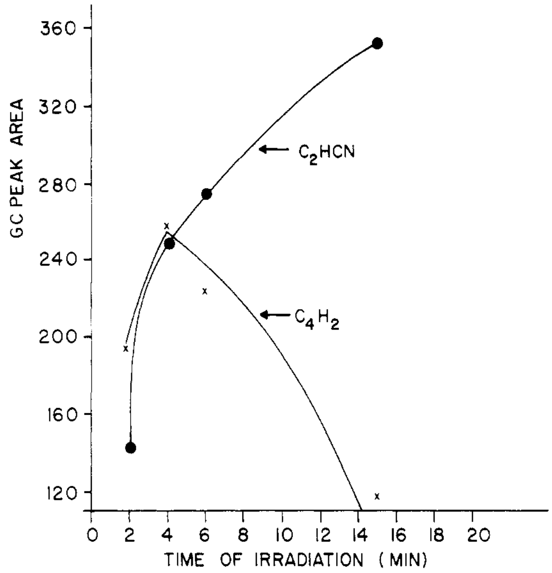

Figure 1. Relative amounts of C_2HCN and C_4H_2 formed as a function of time; also see text (irradiation at 185 nm).

At a 5:1 ratio of HCN/C_2H_2 where 90% of the incident light was absorbed by C_2H_2, C_4H_2 was always the dominant product. There are at least three paths that would direct the formation of C_4H_2 in general:

$$C_2H\cdot + C_2H\cdot + M \rightarrow C_4H_2 + M \tag{4}$$

$$C_2H\cdot + C_2H_2 \rightarrow C_4H_2 + H \tag{5}$$

$$C_2H_2^* + C_2H_2 \rightarrow (C_4H_4^*) \rightarrow C_4H_2 + H_2 \tag{6}$$

Reaction 4 requires three-body collision; hence, its contribution would be very small compared to reaction 5, which has $\Delta H^{13} = -23$ kcal/mol and is expected to be very fast. Reaction 6 involves excited C_2H_2. Excited C_2H_2 formed by initial light absorption has been suggested to have a relatively long lifetime[12] with respect to dissociation and to live long enough to collide with ground-state C_2H_2 resulting in polymer formation.[2,12] However, our results showed that the yields of diacetylene, C_4H_2, did not vary whether 5 torr of C_2H_2 was photolyzed in the presence or absence of 200 torr of argon, indicating that the contribution from reaction 6 is not significant. When all arguments are taken into consideration, reaction 5 is therefore proposed as the major source of diacetylene formation.

To interpret the fact that at a 5:1 ratio of HCN/C_2H_2 (90% light absorbed by C_2H_2) C_2H_3CN was formed in relatively large amounts while C_2HCN was formed only in trace amounts requires us to minimize the importance of radical recombination as the only source of product formation. The radical recombination reaction for the formation of C_2H_3CN would be

$$C_2H_3\cdot + CN\cdot + M \rightarrow C_2H_3CN + M \tag{7}$$

where $C_2H_3\cdot$ has been formed by H atom addition to C_2H_2. However, if this were to happen, the radical reaction for formation of C_2HCN

$$C_2H\cdot + CN\cdot + M \rightarrow C_2HCN \tag{8}$$

should also occur and to a considerably greater extent than reaction 7 since 90% of the light is absorbed by C_2H_2. However, recall that C_2HCN is formed only in trace quantities relative to C_2H_3CN. Both of these reactions involve three-body collisions.

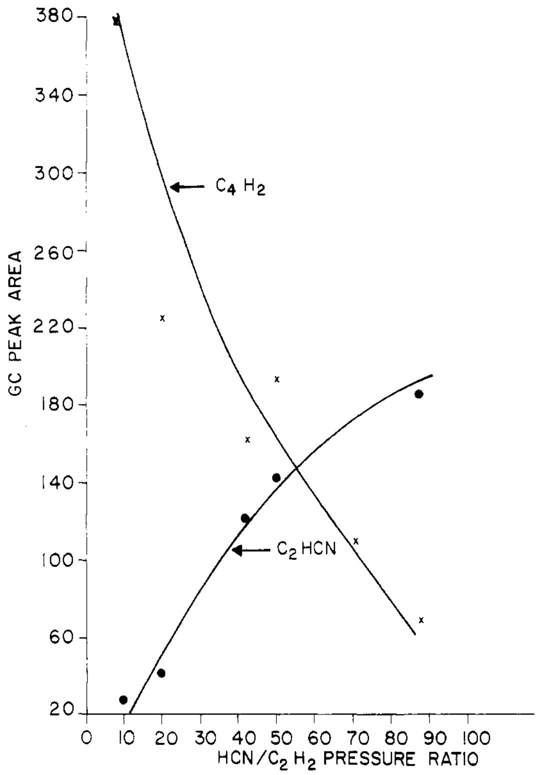

Figure 2. Relative amounts of C_2HCN and C_4H_2 formed as a function of the magnitude of the ratio of HCN/C_2H_2 (irradiation at 185 nm).

Aside from the radical recombination reaction, we propose that the most probable path for the formation of C_2H_3CN is

$$C_2H_3\cdot + HCN \rightarrow C_2H_3CN + H\cdot \qquad \Delta H = 0 \text{ kcal/mol} \tag{9}$$

Another possible reaction is reaction 10, but reaction 9 is

$$C_2H_3\cdot + HCN \rightarrow C_2H_4 + CN\cdot \qquad \Delta H = +25 \text{ kcal/mol} \tag{10}$$

favored over reaction 10 by 25 kcal/mol. Even though HCN is in large excess ($HCN/C_2H_2 = 5$), the ultimate products resulting from H addition to HCN would not lead to C_2H_3CN but to other products such as CH_3NH_2.

The next consideration is the mechanism of formation of C_2HCN. It has been proposed[14] that the reactions

$$C_2H\cdot + HCN \rightarrow C_2HCN + H \qquad \Delta H = -17 \text{ kcal/mol} \tag{11}$$

$$CN\cdot + C_2H_2 \rightarrow C_2HCN + H \qquad \Delta H = -20 \text{ kcal/mol} \tag{12}$$

are the primary paths in the uncatalyzed pyrolytic reaction of HCN and C_2H_2 where the ΔH data are our estimations. Because of the small difference in ΔH, this factor alone does not permit a clear choice between reaction 11 or 12 as the dominant reaction. However, the absence of C_2HCN from a 5:1 ratio of HCN/C_2H_2 (90% light absorbed by C_2H_2) clearly would not be expected if reaction 11 was dominant. The formation of relatively large amounts of C_4H_2 at a 5:1 ratio of HCN/C_2H_2 indicates that reaction 5 is competing with reaction 11; in addition, the relatively low concentration of CN· expected at a 5:1 ratio of HCN/C_2H_2 results in reaction 12 being insignificant. Consequently, C_2HCN is not observed at a 5:1 ratio of HCN/C_2H_2 but is at a still higher ratio of HCN/C_2H_2

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where 40–60% of the light is absorbed by HCN. In the latter case CN· is increased via reaction 3 and reaction 12 becomes the major process. Figure 2 summarizes the results obtained.

We believe these results have relevance to planetary atmosphere chemistry, particularly that of Jupiter, and could have relevance to interstellar chemistry regarding the existence and formation of $C_2H\cdot$, C_4H_2, C_2HCN, and cyanodiacetylene through C_8HCN.

Registry No. HCN, 74-90-8; $(CN)_2$, 460-19-5; CH_4, 74-82-8; NH_3, 7664-41-7; CH_3NH_2, 74-89-5; $(NH_2)_2$, 302-01-2; C_2H_2, 74-86-2; C_4H_2, 460-12-8; C_2H_4, 74-85-1; C_6H_6, 71-43-2; C_2H_3CN, 107-13-1; C_2HCN, 1070-71-9; vinylacetylene, 689-97-4; phenylacetylene, 536-74-3.

Nuclear Spin Relaxation and Molecular Motion of a Highly Ordered Spin Probe in a Nematic Liquid Crystal

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Nuclear magnetic relaxation times of deuterium have been used to determine the spectral densities of motion $J_1(\omega_0)$ and $J_2(2\omega_0)$ for a 5.0 mol % solution of *p*-diethynylbenzene (DEB) in Merck Licristal Phase 5. Relaxation of the quite strongly ordered acetylenic deuterons is heavily influenced by quasi-coherent fluctuations of the nematic director via frequency-dependent contributions to $J_1(\omega_0)$. The order-director contributions to $J_1(\omega_0)$ are roughly proportional to $\omega_0^{-1/2}$ but may be accounted for quantitatively only by including a negative cross term between the order-director fluctuations (ODF) and molecular reorientation. The relaxation of the aromatic deuterons is frequency independent and dominated by fast reorientational motion. Treated as a symmetric top *p*-diethynylbenzene is found to reorient ~10 times faster about the long (z) axis than about the perpendicular (x or y) axes.

Introduction

The long-range orientational order which is characteristic of nematic liquid crystalline media influences the relaxation behavior of nuclear spins in two separate and distinct ways. The most direct effect arises because the time-dependent tensor interactions responsible for spin relaxation decay to nonzero average values, which must be subtracted from the relaxation Hamiltonian before attempting to calculate correlation functions.[1,2] These residual nonzero (equilibrium) averages ultimately lead to a dependence of the motional spectral densities upon equilibrium order parameters for the interaction in question. In addition, the anisotropic forces which are responsible for long-range order will generally perturb the reorientational motion of individual molecules. The latter effect is much more difficult to evaluate than the former, and several models have been developed[3-7] in efforts to account for the empirical observation[8] of slow processes in nematic media. Of these, long-range, quasi-coherent fluctuations of the order director are especially important[3,8] for nuclear magnetic relaxation, because the highest frequency components of the order-director fluctuations (ODF) overlap the range of commonly used nuclear Larmor frequencies.

The present report on the relaxation behavior and molecular motion of deuterated *p*-diethynylbenzene dissolved in Merck Licristal Phase 5 is part of a continuing effort[9-11] to develop techniques for the determination of individual spectral densities of motion in partially ordered systems. As a nuclear relaxation probe of liquid crystal dynamics *p*-diethynylbenzene (DEB), deuterated either in the ring or on the acetylenic carbons, has many desirable properties. This molecule is long enough (ca. 11.5 Å) so that it is beginning to look like a nematogen, and its molecular geometry is such that one can comfortably treat it as a symmetric top for the purpose of evaluating its reorientational anisotropy. It contains deuterons located on the long molecular axis, for which the order parameter $S_{zz} > 0.3$ over most of the nematic range, and the acetylenic deuterons are therefore particularly susceptible to the effects of coherent fluctuations of the nematic director. At the same time the ring deuterons of DEB have very small order parameters and can be expected to behave much like aromatic deuterons in the liquid crystal molecules themselves.

Experimental Methods

p-Diethynylbenzene-*2,3,5,6-d*$_4$ (DEB-d_4) was obtained from Merck Isotopes, Inc. As received from Merck it had a dull tan color and a brown threadlike precipitate was observed to form in a Phase 5 solution of this material; it

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