Table X. Optimized Geometry of the 1,1-Dilithium Salt 9[a]

Bond Lengths, Å	
C_a–S	1.633
C–S	1.767
S–O	1.510
C_a–Li	2.132
O–Li	1.830
Li–Li	3.596
Bond Angles, deg	
C_a–S–C	118.1
H–C_a–S	116.4
Li–C_a–S	78.2
O–S–O	109.3
Li–C–Li	115.0
C_a–(OSO)[b]	125.6

[a] Energy = −637.03027 au. C_s symmetry enforced during the calculation; see Supplementary Material for complete structural parameters. [b] Angle between the first atom and the plane formed by the atoms in parentheses.

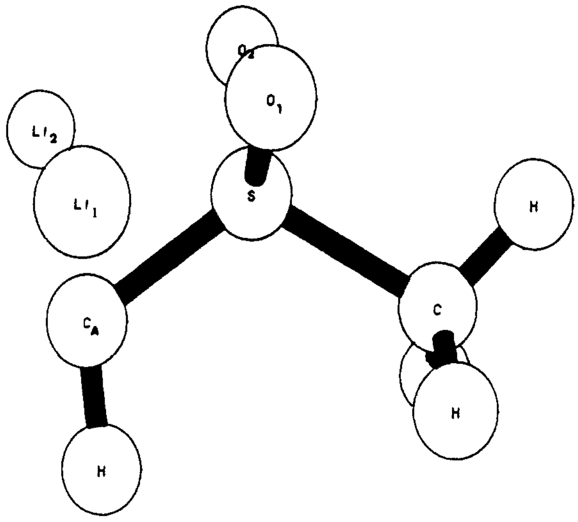
Table XI. Comparative Stabilities of the Dilithium Salts[a]

structure	energy, au	relative energy, kcal/mol
6	−637.13947	0.0
7	−637.12663	8.06
8	−637.12173	11.13
9	−637.12465	9.30

[a] 3-21G*+ basis set with d-orbitals on all heavy centers (except lithium) and diffuse functions on both carbon atoms.

favors the monolithium salt by 14.56 kcal mol^{-1}. Thus, without consideration of the entropy term, the amount of dilithium salt in equilibrium with the monolithium salt is negligible.

Solution-quenching studies show that the 1,3-dilithium salt is the stable species in tetrahydrofuran.[10] However, if one substituent lacks α-hydrogens, generation of the lithium salt of the 1,1-dianion is possible.[26] The search for the structure of this compound on the potential surface was accomplished by using MNDO methods. Only one stable structure resulted, which was further optimized at the ab initio level to give the structure shown (**9**, Table X). Note that in an effort to accommodate the extra charge on the anionic carbon, the basis set of this carbon was augmented with a set of d-orbitals (exponent = 0.65) in addition to the diffuse sp shell.



9

Once again, this structure is an extension of the lithium salt of the monoanion with each lithium associated with one carbanion center and one oxygen atom. In order to compare stabilities of the 1,1-dianion with the 1,3-dianions, the energies of all four lithium salts were calculated by using a larger basis set with the same number of basis functions for each structure. That is, the 3-21G*+ basis set (d-orbitals on all centers except lithium) was augmented with diffuse functions on the anionic centers. The resulting energies (Table XI) show that the dilithium salt of the 1,1-dianion is 9.30 kcal mol^{-1} higher in energy than that of the most stable 1,3-dianion. This value coincides with the lack of products from the 1,1-dianion found from solution-quenching studies.

Acknowledgment. This research was supported in part by NIH grant No. GM-30369. We are indebted to Steven Bachrach for suggesting the application of electrostatic potentials.

Supplementary Material Available: Table of complete optimized structures for structures **2–9** (4 pages). Ordering information is given on any current masthead page.

Isomers of $C_2H_4N^+$ and the Proton Affinities of CH_3CN and CH_3NC

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Abstract: The relative proton affinities of CH_3CN (acetonitrile) and CH_3NC (methyl isocyanide) were determined by using the Selected Ion Flow Tube technique. Two distinct species were observed for the $C_2H_4N^+$ ion: one produced from CH_3CN and one from CH_3NC. The two $C_2H_4N^+$ isomers were readily distinguished in the flow tube by their different reactivity. The association product, $C_2H_4N^+$, of the ion–molecule reaction between CH_3^+ and HCN was shown to be present in both isomeric forms in the ratio 85% protonated acetonitrile and 15% protonated methyl isocyanide.

The proton affinity (PA) of CH_3CN (acetonitrile) has been established by several techniques[1-3] as 788 ± 8 kJ mol^{-1}, whereas that of CH_3NC (methyl isocyanide) has been less well-characterized. Illies et al.[4] quote measurements by Aue et al. of 828 kJ mol^{-1} [5] for the proton affinity of methyl isocyanide. From the known heats of formation of CH_3CN and CH_3NC[23] and their respective proton affinities, the heats of formation of the isomers

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(5) Inferred from the data given in ref 4 and assuming a proton affinity for CH_3OH of 759 kJ mol^{-1}.

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Table I. Ion-Molecule Reactions Used To Establish the Proton Affinity of CH_3CN. Rate Coefficients Are Expressed in $cm^3\ s^{-1} \times 10^9$

reaction	products	branching ratio	rate coeff	reaction tube pressure, torr
$CH_3CNH^+ + CH_3CHO$	$CH_3CHOH^+ + CH_3CN$	0.17	0.91	0.38
	$CH_3CNH^+{\cdot}CH_3CHO$	0.83		
$CH_3CNH^+ + HCO_2CH_3$	$H_2CO_2CH_3^+ + CH_3CN$	0.72	1.7	0.30
	$CH_3CNH^+{\cdot}HCO_2CH_3$	0.28		
$H_2CO_2CH_3^+ + CH_3CN$	$CH_3CNH^+ + HCO_2CH_3$	0.50	1.7	0.30
	$H_2CO_2CH_3^+{\cdot}CH_3CN$	0.50		
$CH_3CHOH^+ + CH_3CN$	$CH_3CNH^+ + CH_3CHO$	0.95	3.4	0.30
	$CH_3CHOH^+{\cdot}CH_3CN$	0.05		

CH_3CNH^+ and CH_3NCH^+ can be deduced.[6] These are sufficiently different to suggest that there are different structures of $C_2H_4N^+$: one derived from proton transfer to CH_3CN and one from CH_3NC. Interest in the isomers of $C_2H_4N^+$ has arisen from attempts to identify the product of the association reaction between CH_3^+ and HCN (reaction 1) which may be radiatively stabilized at low pressures.[7] Illies et al.[4] used the technique of collision-induced dissociation to distinguish between two isomers of $C_2H_4N^+$ and produced evidence for the product of reaction 1 being only CH_3CNH^+. Gilbert and McEwan,[8] however, using a weak collision model for energy transfer with He as the bath gas, inferred that the pressure dependence of the rate coefficient favors the initial formation of CH_3NCH^+. This conclusion does not prevent subsequent isomerization of the CH_3NCH^+ product to CH_3CNH^+.

$$CH_3^+ + HCN\ (+M) \rightarrow C_2H_4N^+\ (+M) \qquad (1)$$

The present study reports measurements of proton transfer and association reactions of CH_3CNH^+ and CH_3NCH^+ from which the proton affinities of the parent neutral compounds are obtained.

A sensitive probe for distinguishing between the isomers of $C_2H_4N^+$ is also presented.

Experimental Section

All measurements were carried out at room temperature 303 ± 5 K in a *S*elected *I*on *F*low *T*ube (SIFT) apparatus described elsewhere.[9,10] The protonated species CH_3CNH^+ and CH_3NCH^+ were formed in the reaction tube in either of two ways: (a) by subjecting a 20/1 mixture of H_2 and CH_3CN (or CH_3NC) to electron impact in the ion source and selecting the appropriate ion at m/e 42 and (b) by proton transfer from HCO^+ to CH_3CN (PA(CO) = 594 kJ mol^{-1}) and from CH_3^+ to CH_3NC (PA(CH_2) ~ 826 kJ mol^{-1}). No difference was observed in the behavior of the CH_3CNH^+ ion generated by either of the above techniques. It was found, however, that it was only possible to generate CH_3NCH^+ free from small traces of a species at the same m/e ratio of 42 but which reacted at a different rate to CH_3NCH^+, when CH_3NCH^+ was formed in the reaction tube by proton transfer to methyl isocyanide from CH_3^+. Evidence presented later indicates that the trace impurity species is almost certainly the isomer CH_3CNH^+. Typical operating conditions were as follows: the pressure in the SIFT upstream quadrupole region was 1×10^{-4} torr with slightly higher pressures in the source region; the ionizing electron energy was ~30 eV and the ion energy was ~15 eV; the flow tube pressures in a helium carrier gas were between 0.25 and 0.40 torr; the downstream quadrupole pressure was typically 7×10^{-6} torr.

Research-grade tetrahydrofuran (THF), tetrahydropyran (THP), acetaldehyde, methyl formate, diethyl ether, and acetonitrile were used. Industrial-grade ammonia was used after vacuum distillation. Hydrogen cyanide was prepared from concentrated H_2SO_4 on KCN followed by trap-to-trap distillation after drying. Methyl isocyanide was prepared by reacting N-methylformamide with p-toluenesulfonyl chloride and freshly distilled quinoline.[11] Further purification was achieved by repeated trap-to-trap distillation.

Table II. Relative Gas-Phase Basicities (GB) (kJ mol^{-1}) such that GB(A) − GB(B) = $\Delta G° = -RT \ln K$ for the Reaction $AH^+ + B \rightleftharpoons BH^+ + A$. The GB of CH_3CN Has Been Assigned a Value of Zero for Comparison Purposes

compd	ref 12	ref 13	ref 14	this work
CH_3CN	0.0	0.0	0.0	0.0
HCO_2CH_3	−2.1	2.9	3.3	0.9
CH_3CHO	−8.4	−8.4	−7.5	−7.6

Results and Discussion

The rate coefficients and branching ratios for the reactions investigated are shown in Tables I, III, IV, VII, and VIII. In most of the reactions studied in this work association competed with proton transfer, and to obtain the proton transfer rate, it was necessary to establish whether the rapid association process interfered with proton transfer.

$$AH^+ + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} BH^+ + A \quad \text{(proton transfer)}$$

$$AH^+ + B + M \rightarrow AH^+{\cdot}B + M \quad \text{(association)}$$

As we could measure only the total rate of removal of AH^+, we had to determine the mass discrimination of the downstream sampling system (nose cone, ion lens system, and quadrupole mass spectrometer) in order to find the branching ratio. Consequently, the equilibrium constant determination ($K = k_f/k_r$) and hence the proton affinity were subject to slightly larger errors than would otherwise be the case. We estimate our error in the relative gas-phase basicity as ±3 kJ mol^{-1}. From the data in Table I, we have calculated the relative gas-phase basicities shown in Table II for CH_3CN, HCO_2CH_3, and CH_3CHO, and it may be noted that these agree well with determinations by other low-pressure techniques. Thus, the competition of association with proton transfer does not appear to influence the proton-transfer rates to any great extent, a conclusion which has also been demonstrated by Davidson et al.[15]

Proton Affinity of CH_3NC. The proton affinity of CH_3NC was found by observing the rate and direction of proton transfer between CH_3NC and NH_3, EtOEt (diethyl ether), THP, and THF. The rate coefficients for these reactions are shown in Table III. For comparison, some of the reactions of CH_3CN (or CH_3CNH^+) with these same reagents are listed in Tables I and IV. Later we will use the differences in reactivities and product distributions to distinguish between the two isomers of $C_2H_4N^+$. In particular, we draw attention to the respective reactions with HCO_2CH_3 (Tables I and III) where CH_3CNH^+ gave rapid proton transfer

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[6] For the purpose of distinguishing between isomers of $C_2H_4N^+$ in this paper, we shall describe the proton-transfer product of CH_3CN as CH_3CNH^+ and the proton-transfer product of CH_3NC as CH_3NCH^+, bearing in mind that these descriptions do not necessarily infer an exact structural representation.

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Table III. Ion–Molecule Reactions Used To Establish the Proton Affinity of CH_3CN. Rate Coefficients Are Expressed in $cm^3\ s^{-1} \times 10^9$

reaction	products	branching ratio	rate coeff	reaction tube pressure, torr
$CH_3NCH^+ + HCO_2CH_3$	$CH_3NCH^+\cdot HCO_2CH_3$	1.0	0.014 0.042	0.29 0.38
$CH_3NCH^+ + THP^a$	$CH_3NCH^+\cdot THP$	1.0	1.0	0.30
$CH_3NCH^+ + THF^b$	$CH_3NCH^+\cdot THF$	1.0	0.81	0.30
$THPH^+ + THF$	$THFH^+ + THP$ $THPH^+\cdot THF$	0.07 0.93	1.3	0.30
$THFH^+ + THP$	$THPH^+ + THF$ $THFH^+\cdot THP$	0.40 0.60	1.1	0.30
$THPH^+ + CH_3NC$	$CH_3NCH^+ + THP$ $THPH^+\cdot CH_3NC$	0.46 0.54	2.4	0.34
$THFH^+ + CH_3NC$	$CH_3NCH^+ + THF$ $THFH^+\cdot CH_3NC$	0.82 0.18	2.0	0.21
$CH_3NCH^+ + NH_3$	$NH_4{}^+ + CH_3NC^c$	1.0	1.9	0.29
$CH_3NCH^+ + EtOEt^d$	$EtOEtH^+ + CH_3NC$ $CH_3NCH^+\cdot EtOEt$	0.10 0.90	1.3	0.30
$NH_4{}^+ + CH_3NC$	$CH_3NCH^+ + NH_3$	1.0	0.16	0.30
$EtOEtH^+ + CH_3NC$	$CH_3NCH^+ + EtOEt$ $EtOEtH^+\cdot CH_3NC$	0.50 0.50	2.1	0.30

[a] Tetrahydropyran. [b] Tetrahydrofuran. [c] A small amount of the association product $CH_3NCH^+\cdot NH_3$ (1–2%) was also observed. [d] Diethyl ether.

Table IV. Ion–Molecule Reactions of CH_3CNH^+ with NH_3, THP, and THF. Rate Coefficients Are Expressed in $cm^3\ s^{-1} \times 10^9$

reaction	products	branching ratio	rate coeff	reaction tube pressure, torr
$CH_3CNH^+ + THP$	$THPH^+ + CH_3CN^a$	1.0	1.3	0.30
$CH_3CNH^+ + THF$	$THFH^+ + CH_3CN$	1.0	1.6	0.30
$CH_3CNH^+ + NH_3$	$NH_4{}^+ + CH_3CN$	1.0	2.0	0.30
$THPH^+ + CH_3CN$	$THPH^+\cdot CH_3CN$	1.0	1.9^b	0.30

[a] A small amount (~1–2%) of the association product $CH_3CNH^+\cdot THP$ was also observed. [b] Pseudo-second-order rate at 0.30 torr.

Table V. Relative Gas-Phase Basicities (GB) (kJ mol^{-1}) such that $GB(A) - GB(B) = \Delta G° = -RT \ln K$ for the Reaction $AH^+ + B \rightleftharpoons BH^+ + A$. The GB of NH_3 Has Been Assigned a Value of Zero for Comparison Purposes

compd	ref 12	ref 13	ref 14	this work
NH_3	0.0	0.0	0.0	0.0
CH_3NC				-6
EtOEt	-14	-15	-13	-11
THP	-13	-17		$\leq -17^a$
THF	-17	-20	-17	$\leq -21^b$

[a] Limit is derived from the nonobservation of proton transfer from CH_3NCH^+ to THP. [b] Limit is derived from *a* and the relative GB(THP) - GB(THF).

(72%) and association (28%), while CH_3NCH^+ gave only slow association without proton transfer. Attempts to generate the ion CH_3NCH^+ by electron impact on a CH_3NC/H_2 mixture in the ion source followed by subsequent mass selection and injection into the reaction tube always gave an *m/e* 42 ion that produced a small proton-transfer signal with methyl formate. We attribute the proton-transfer product to a small amount of isomerization having occurred within the upstream SIFT ion selection section either before or during injection into the flow tube. When CH_3NCH^+ was formed in the reaction tube by proton transfer from $CH_3{}^+$ on to CH_3NC, no subsequent proton transfer from CH_3NCH^+ occurred with HCO_2CH_3. From the data given in Table III, we derive the ladder of gas-phase basicities in Table V.

When the conversion from gas-phase basicity to proton affinity is made by equating the entropy contributions to differences in the rotational symmetry number,[3] the proton affinities in Table VI are obtained. These proton affinities have been referenced to the scale in which NH_3 has a proton affinity of 853.5 kJ mol^{-1}.[3,16] The values listed agree well with the results obtained from other techniques where comparison is possible[3,11-13] and support our new determination of 844 kJ mol^{-1} for the proton affinity of CH_3NC. This result is noticeably higher than the measurement of Aue et al. quoted by Illies et al.[4] of 828 kJ mol^{-1}. However, that measurement was not referenced to a unified scale of proton affinities, as the present measurements have been, but instead to the relative GB's of $C_2H_5OCOCH_3$ and $CF_3CH_2NH_2$. When appropriate scaling factors are made to the Aue et al. result, then little discrepancy occurs.[17,24] Our measured proton affinities lead to $\Delta H_f[CH_3CNH^+] = 816$ kJ mol^{-1} and $\Delta H_f[CH_3NCH^+] = 859$ kJ mol^{-1}.

Table VI. Proton Affinities (kJ mol^{-1} at 300 K) Estimated from GB's of Tables II and V

species	proton affinity[a]	species	proton affinity[a]
NH_3	853.5	THF	≤830
CH_3NC	844	$HCO_2CH_3{}^b$	789
EtOEt	842	CH_3CN^b	788
THP	≤834	CH_3CHO^b	782

[a] These results are referenced to the value $PA(NH_3) = 853.5$ kJ mol^{-1} (see ref 3). [b] These results are referenced to the value $PA(CH_3CN) = 788$ kJ mol^{-1} (see ref 3).

Although the enthalpies of formation of the two isomers are not widely different, their existence as separate entities within the reaction tube is indicative of a substantial barrier to interconversion. We next use the different chemical behavior of CH_3CNH^+ and CH_3NCH^+ with THP, THF, and HCO_2CH_3 to evaluate the isomer distribution of the *m/e* 42 product in reaction 1.

Reaction Products of $CH_3{}^+$ with HCN (Equation 1). The product of this reaction is likely to be either CH_3CNH^+, CH_3NCH^+, or a mixture of both isomers. An analysis of the pressure dependence of the rate coefficient for the reaction has shown protonated methyl isocyanide CH_3NCH^+ to be strongly favored as the initial product in reaction 1.[8] However, in a sufficiently exothermic reaction, there may be enough internal energy to overcome the isomerization barrier, and a mixture might be expected. Very recently, DeFrees et al.[18] in a theoretical study using ab initio chemical methods have confirmed that it is CH_3NCH^+ that is first formed in the collision and that subsequent isomerization can be expected because the energy barrier for isomerization lies significantly below that of the reactants, $CH_3{}^+ + HCN$.

Our results for the reactivity of the $C_2H_4N^+$ ion formed in reaction 1 with NH_3, THP, THF, and HCO_2CH_3 are listed in

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Table VII. Reactions of the *m/e* 42 Ion ($C_2H_4N^+$), Produced in the Reaction CH_3^+ + HCN. Rate Coefficients Are Expressed in $cm^3\ s^{-1} \times 10^9$

reaction	products	branching ratio	rate coeff	reaction tube pressure, torr
$C_2H_4N^+ + NH_3$	$NH_4^+ + C_2H_3N$	0.97	1.8	0.25
	$C_2H_4N^+{\cdot}NH_3$	0.03		
$C_2H_4N^+$ + THP	$THPH^+ + C_2H_3N$	0.80	1.4	0.33
	$C_2H_4N^+{\cdot}THP$	0.20		
$C_2H_4N^+$ + THF	$THFH^+ + C_2H_3N$	0.90	1.7, 0.7[a]	0.30
	$C_2H_4N^+{\cdot}THF$	0.10		
$C_2H_4N^+ + HCO_2CH_3$	$H_2CO_2CH_3^+ + C_2H_3N$	0.65	1.6, 0.01[a]	0.30
	$C_2H_4N^+{\cdot}HCO_2CH_3$	0.35		

[a] These rate coefficients were obtained from a two-exponential fit to the observed decay in $C_2H_4N^+$ signal.

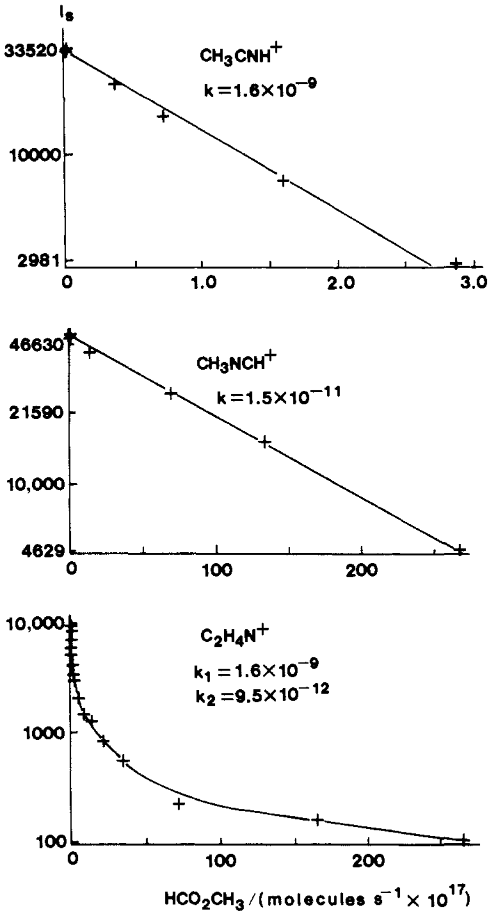

Figure 1. Semilogarithmic plot of I_s, the ion signal at *m/e* 42, against the flow of HCO_2CH_3 for the following ions (reading from top to bottom): CH_3CNH^+ formed by proton transfer from HCO^+ to CH_3CN; CH_3NCH^+ formed by proton transfer from CH_3^+ to CH_3NC; the $C_2H_4N^+$ product of reaction 1. The rate coefficients listed are derived from least-mean-squares fits to the straight lines shown in the upper two plots and from a double-exponential decay fitted to the curve in the lower plot.

Table VII. It was noticeable that in the case of THP, THF, and HCO_2CH_3, the usual plot of ln I_{42} (I_{42} being the observed intensity of $C_2H_4N^+$ signal at *m/e* 42) against neutral reactant flow (f_n) exhibited pronounced curvature. These data, however, gave good fits to double-exponential decays of the form

$$I_{42} = C_1 \exp(-k_1 f_n) + C_2 \exp(-k_2 f_n) \tag{2}$$

(Figure 1 illustrates, for example, the reaction of $C_2H_4N^+$ with HCO_2CH_3.) This is readily explained if it is assumed that the $C_2H_4N^+$ formed by reaction 1 is present in both of the isomeric forms CH_3CNH^+ and CH_3NCH^+ with respective initial concentrations C_1 and C_2 and decay constants k_1 and k_2. In the case of NH_3, the decay of I_{42} was satisfactorily represented by a single exponential which is to be expected since each isomer reacts at a similar rate; i.e., k_1 and k_2 in eq 2 are almost identical (see Tables III and IV). The possibility of substantial internal energy remaining from the initial complex can be discounted as, at a tube pressure ~0.3 torr, the complex has undergone ~4×10^4 collisions with the bath gas before analysis for the isomer ratio. Each collision has been estimated as removing ~8 kJ mol^{-1}.[8] Furthermore, lowering the total number of collisions by a factor of 5 made no measurable difference to the isomer ratio.

Table VIII. Ion–Molecule Reactions of CH_3^+ with HCN, CH_3CN, and CH_3NC. Rate Coefficients Are Expressed in $cm^3\ s^{-1} \times 10^9$

reaction	product	branching ratio	rate coeff	reaction tube pressure, torr
CH_3^+ + HCN	$C_2H_4N^+$	1.0	1.7[a]	0.45
			(~1.6	0.26)
$CH_3^+ + CH_3CN$	$CH_3^+{\cdot}CH_3CN$	1.0	4.0[a]	0.30
$CH_3^+ + CH_3NC$	$CH_3NCH^+ + CH_2$	1.0	1.1	0.30

[a] Pseudobimolecular rate coefficient.

The differing product distributions for reactions of CH_3CNH^+ and CH_3NCH^+ with the reactants THP, THF, and HCO_2CH_3 provide a convenient means of estimating the product isomer ratio in reaction 1. In particular whereas CH_3CNH^+ will rapidly transfer a proton to THP, THF, and HCO_2CH_3, CH_3NCH^+ will form only an association product. The result of this isomer ratio determination showed that reaction 1 leads to a distribution of 85 ± 10% CH_3CNH^+ and 15 ± 10% CH_3NCH^+. Furthermore, the coefficients C_1 and C_2 obtained from least-squares fitting of a double-exponential decay (expression 2) to the $C_2H_4N^+$ signal in reactions with THF and HCO_2CH_3 led to results for the isomer ratio which agree within experimental error with those determined from the observed product distributions.

We conclude therefore that the substantial internal energy provided from the highly exothermic reaction of CH_3^+ with HCN is sufficient to overcome the barrier to isomerization between CH_3NCH^+ and CH_3CNH^+ in agreement with the calculations of DeFrees et al.[18] Subsequent stabilizing collisions with the helium bath gas yield a predominance of the lower energy CH_3CNH^+ isomer. DeFrees et al.[18] have calculated the density of states ratio, $K(E) = N^{\mathrm{vr}}_{\mathrm{iso}}/N^{\mathrm{vr}}$ where N^{vr} is the vibration–rotation density of states at energy E for the more stable CH_3CNH^+ ion and $N^{\mathrm{vr}}_{\mathrm{iso}}$ is the same quantity for the isocyanide ion. The ratio is sensitive to the barrier height (which they estimate as 314 kJ mol^{-1} above CH_3CNH^+) and to the difference in zero-point energies between the two isomers. Their calculated value for the ratio, CH_3NCH^+/CH_3CNH^+, is 1/6 which is in exact agreement with our measurement. Furthermore, our proton affinities lead to a value for the difference in zero-point energies of 43 kJ mol^{-1} (compared to the value of 42 kJ mol^{-1} obtained by DeFrees et al.[18]); however, our measurements indicate that the barrier height to isomerization may be substantially less than 300 kJ mol^{-1}.[19]

Reaction Rates of CH_3^+ with HCN, CH_3CN, and CH_3NC. The reactions of CH_3^+ with HCN, CH_3CN, and CH_3NC are summarized in Table VIII. Only in the reaction with CH_3NC is proton transfer exothermic, and only in this case is it observed. The other two species HCN and CH_3CN rapidly associate at rates

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that are close to the collision limit. The absence of any marked dependence of the rate coefficients on pressure signifies that the two association reactions are approaching the pressure-saturation regime. Schiff and Bohme[20] report a value of 2×10^{-9} cm^3 s^{-1} for the association of CH_3^+ to HCN at pressures of ~0.5 torr. Kemper et al.[21] from low-pressure ICR measurements have estimated a ternary rate coefficient ~2×10^{-25} cm^6 s^{-1} for association with HCN in He as the bath gas. The even more rapid association of CH_3^+ to CH_3CN occurs almost at the ion-dipole collision limit[22] ($k_{AADO} = 5.7 \times 10^{-9}$ cm^3 s^{-1}) and will presumably exhibit an even larger value for the ternary rate coefficient than the reaction of CH_3^+ with HCN.

Conclusions

Protonated CH_3CN and CH_3NC have different structures in the gas phase and maintain their integrity by a substantial isomerization barrier which prevents interconversion. The product ion of reaction 1 is a ~6/1 mixture of the two isomers of $C_2H_4N^+$, with CH_3CNH^+ being produced in the greater amount.

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Registry No. THP, 142-68-7; THPH$^+$, 27659-94-5; THF, 109-99-9; THFH$^+$, 27659-93-4; CH_3N, 75-05-8; CH_3NC, 593-75-9; $CH_3CN{\cdot}H^+$, 20813-12-1; $CH_3NC{\cdot}H^+$, 64709-60-0; CH_3^+, 14531-53-4; HCN, 74-90-8; HC(O)OMe, 107-31-3; NH_3, 7664-41-7; EtOEt, 60-29-7; NH_4^+, 14798-03-9; EtOEtrH$^+$, 17009-83-5; CH_3CHO, 75-07-0.

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(24) **Note Added in Proof.** Recently a value of 834 kJ mol^{-1} for PA-(CH_3NC) has been reported: Meot-ner, M.; Karpas, Z.; Deakyne, C. *J. Am. Chem. Soc.*, in press. This value agrees with the result reported here within the combined experimental uncertainties.

Diabatic Surface Methods for the Study of the Reactivity of Organic Molecules. 1. Cycloaddition of Two Ethylenes

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Abstract: In this paper we discuss the quantitative diabatic surface analysis of the surface associated with the thermal cycloaddition of two ethylene molecules. We show that the main features of a saddle point, such as the index (i.e., the number of negative eigenvalues of the Hessian) and the origin, can be understood by analyzing the behavior of the reactant and product diabatic surfaces computed in a three-dimensional subspace involving two relevant geometrical variables at a time. We show also that the behavior of the constituent diabatic surfaces can be easily rationalized with the simple energy expressions of qualitative MO theory.

I. Introduction

One of the major development areas in quantum chemistry in recent years has involved the computation and characterization of the intermediates and transition structures for model organic reactions. The rapid growth of this research has been facilitated by the development of the MC-SCF method (for a recent review see ref 2) and gradient optimization techniques. In recent work we have been involved in the development of MC-SCF[3] gradient[4] programs and in the subsequent analysis of the reaction profile using diabatic surfaces.[5-8] In ref 6 we have shown that the transition structure geometry of the cyanate-isocyanate rearrangement, the 1,2-sigmatropic shift in propene, the S_N2 reaction of H$^-$ and CH_4, and the addition of singlet methylene to ethylene correlate very accurately with the intersection of appropriate diabatic curves. In the case of the sigmatropic shift we were able to locate the transition structure a priori from preliminary diabatic surface calculations.

In the diabatic surface model[5,6] the adiabatic surface of the reaction is obtained from the interaction of two diabatic surfaces (one associated with reactants and one with products). The transition structure corresponds to the minimum of the surface of intersection of the two diabatic surfaces. This model stems from the very early work of Evans and Polanyi[9] and Evans and Warhurst.[10] The significant feature of the model proposed in ref 5 and 6 is the association of each diabatic surface with the bonding situation in reactants or products through the use of wave functions built from the molecular orbitals of the isolated fragments. Thus the diabatic surfaces are based upon a linear combination of fragment configurations (Heitler-London, no-bond, charge transfer, and locally excited).

In the present paper we discuss the diabatic surface analysis of the potential surface associated with the thermal cycloaddition of two ethylene molecules. The critical points (transition structures, intermediate minima, etc.) have been computed in a previous MC-SCF study.[11]

In our previous work on the diabatic surface model[5,6] we have followed a procedure similar to that used in the qualitative diabatic decomposition schemes[12-16] and considered only cross sections

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