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The Formation of Cyanoketene (NCCHCO) and the Isomer NCCCHO from Anionic Precursors in the Gas Phase. The Rearrangement of NCCCHO to NCCHCO

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It has been reported that irradiation of cyanoacetylene and ozone on a water ice surface at 255 nm yields both hydrogen peroxide and cyanoacetylene (NCCHCO), and it has been proposed that this overall process may involve a crucial step where NCCCHO rearranges to NCCHCO.The isomers NCCHCO and NCCCHO have been prepared in this study by one-electron vertical oxidation of $[NCCHCO]^{-\bullet}$ and $[NCCCHO]^{-\bullet}$ in collision cells of a VG ZAB 2HF mass spectrometer. $^{-}NR^{+}$ experiments indicate that singlet NCCHCO is stable for the microsecond duration of the experiment. In contrast, calculations at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory indicate that singlet NCCCHO does not occupy a minimum on the singlet neutral potential surface, but rearranges to singlet NCCHCO. Some of the singlet NCCHCO neutrals formed in this way are stable, whereas others have sufficient excess energy to effect decomposition to give NCCH and CO. Triplet NCCCHO is stable but, when energized, may (i) rearrange over a barrier of 49.0 kcal mol^{-1} to give triplet NCCHCO, which is energized and decomposes to NCCH and CO, and/or (ii) undergo intersystem crossing to yield singlet NCCHCO. It is concluded that, in principle, the rearrangement NCCCHO to NCCHCO could occur in regions of interstellar ice.

Introduction

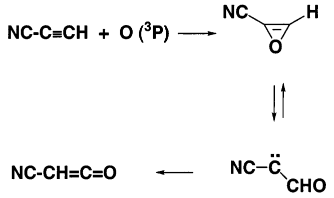
There has been debate recently concerning whether cyanoacetylene and cyanoacetaldehyde (together with urea) can effect “efficient prebiotic syntheses” of cytosine.[1−7] A problem with the hypothesis of an RNA-like substance playing a role in the origin of life is that cytosine has not been found in meteorites nor is it among the products of electric spark discharge experiments.[3] However, cyanoacetylene is a known constituent of interstellar dust clouds[8,9] and it has also been detected in the gaseous phase of comets, e.g., P/H Levy[10,11] and Hale-Bopp.[12]

A recent report[13] has described that irradiation of cyanoacetylene and ozone on a water ice surface at 255 nm yields both hydrogen peroxide and cyanoketene. Several mechanisms have been proposed for the formation of cyanoketene; one of those involves the reaction between cyanoacetylene and atomic oxygen shown in Scheme 1.[13] Neither cyanoketene nor the other isomers shown in Scheme 1 have been detected as stellar molecules. In principle, however, these molecules could be the precursors of pyrimidine bases in interstellar dust clouds, circumstellar envelopes or, more likely, in regions containing interstellar ice.

A number of studies of cyanoketene have been reported:[14−24] cyanoketene may be prepared by a variety of methods including flash vacuum thermolyses of cyanoacetic acid derivatives.[22] Cyanoketene is highly reactive, with neat cyanoketene reported to “disappear” below 80 K.[22] The photoelectron,[14] microwave,[23] and infrared[22] spectra of cyanoketene have been determined. Cyanoketene undergoes cyclotrimerization in the presence of P_4O_{10}/H_2O to yield 2,4,6-tricyanophloroglucinol.[21]

The aims of the present study are to attempt the syntheses of both cyanoketene (NCCHCO) and NCCCHO in the gas phase and to determine whether NCCCHO converts to NCCHCO as proposed in Scheme 1.

SCHEME 1



Experimental Section

A. Mass Spectrometric Methods. For a detailed description of the experiment and the instrument used, see ref 25. In brief, the experiments were performed using a two-sector modified VG ZAB 2HF mass spectrometer with BE configuration, where B and E represent magnetic and electric sectors, respectively. The precursor anion radical to NCCHCO was formed in the chemical ionization ion source by the reaction between $NCCH_2CO_2Et$ and HO^- as shown in eq 1

$$NC-CH_2-CO_2Et + HO^- \rightarrow [NC-CH{=}C{=}O]^{-\bullet} + H_2O + EtO^\bullet \quad (1)$$

This is a standard process[26] in which reaction between $NCCH_2CO_2Et$ and HO^- produces the enolate anion $NC-{}^{-}CHCO_2Et$ which then loses $EtO^\bullet$ to yield $[NCCH{=}C{=}O]^{-\bullet}$. The formation of $[NCCCHO]^{-\bullet}$ is more challenging. The reaction we wish to effect is the standard reaction[27] of $NCCH_2CHO$ with $O^{-\bullet}$ (formed by dissociative resonance capture of nitrous oxide[27]) as shown in eq 2. This aldehyde is unstable and we were unable to use it directly. Instead, we used the acetal derivative $[NCCH_2CH(OMe)_2]$ to form the required and transient aldehyde by a

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10.1021/jp031289k CCC: $27.50

method that we have reported previously.[28] The procedure involves the introduction of this acetal through the septum inlet (heated to 100°) into the ion source. The acetal converts to the aldehyde, and the reaction shown in eq 2

$$\mathrm{NC{-}CH_2{-}CHO} + \mathrm{O}^{-\bullet} \rightarrow [\mathrm{NCCCHO}]^{-\bullet} + \mathrm{H_2O} \quad (2)$$

occurs in the chemical ionization ion source to give the required radical anion $[\mathrm{NCCCHO}]^{-\bullet}$.

Typical source conditions were as follows: source temperature, 200 °C; repeller voltage, −0.5 V; ion extraction voltage, 7 kV; mass resolution $m/\Delta m \geq 1500$. Each neutral precursor was inserted into the ion source through the septum inlet, which was heated to 100 °C to give a measured pressure of ca. 10^{-6} Torr inside the source housing. The reagent gas [H_2O for HO^-; N_2O (for $O^{-\bullet}$)] was introduced through a gas inlet into the ion source, to give a measured total pressure of ca. 10^{-5} Torr in the source housing. The estimated total pressure in the ion source is 10^{-1} Torr.[29] Collisional-induced (CID) spectra were determined using the magnetic sector to select $m/z = 67$ in each case, and utilizing argon as the target gas in the first collision cell following the magnetic sector. The pressure of argon in the first cell was maintained such that 80% of the parent ion beam was transmitted through the cell. This corresponds to an average of 1.1−1.2 collisions per ion.[30] Product anion peaks resulting from CID processes were recorded by scanning the electric sector.

Neutralization-reionization[31−33] ($^-NR^+$) experiments were performed for mass-selected anions utilizing the dual collision cells located between the magnetic and electric sectors. Neutralization of anions was effected by collisional electron detachment using O_2 at 80% transmittance (of the main beam) as the collision gas in the first collision cell, while reionization to cations was achieved by collision of the neutrals with O_2, (80% transmittance) in the second collision cell. To detect a reionization signal due to the parent neutral, the neutral species must be stable for the one microsecond time frame of this experiment. Charge reversal ($^-CR^+$) spectra[34,35] were recorded using single-collision conditions in collision cell 1 (O_2, 80% transmission of main beam).

A reviewer has asked for an explanation of what information is provided by a comparison of the $^-NR^+$ and $^-CR^+$ spectra. This is explained in detail in ref 33, but in summary: (i) If the $^-CR^+$ spectrum is consistent with neither rearrangement of the precursor anion nor the product cation, and if the $^-NR^+$ spectrum shows both a peak corresponding to the mass of the neutral and a spectrum identical with the $^-CR^+$ spectrum, then the Franck−Condon one-electron oxidation has produced neutrals with the same bond connectivity as the anion, and (at least) some of those neutrals are stable for the microsecond duration of the NR experiment, (ii) if the $^-NR^+$ spectrum shows a parent peak, but is different in some way from the $^-CR^+$ spectrum, then depending on what that difference is, some neutrals are either rearranging to an isomer, and/or undergoing some decomposition during the microsecond time frame of the NR experiment, (iii) if the CID spectrum of the negative ion indicates that it retains structural identity during excitation, and the $^-CR^+$ spectrum of the anion indicates that there is partial rearrangement of the first formed cation to another isomer, and if the $^-NR^+$ spectrum is identical to the $^-CR^+$ spectrum, then this comparison gives no information about the structure(s) of the neutral(s), and (iv) if the $^-NR^+$ spectrum shows no peak corresponding to the reionized neutral, the neutral formed by the Franck−Condon oxidation is not stable within the microsecond time frame of the NR experiment.

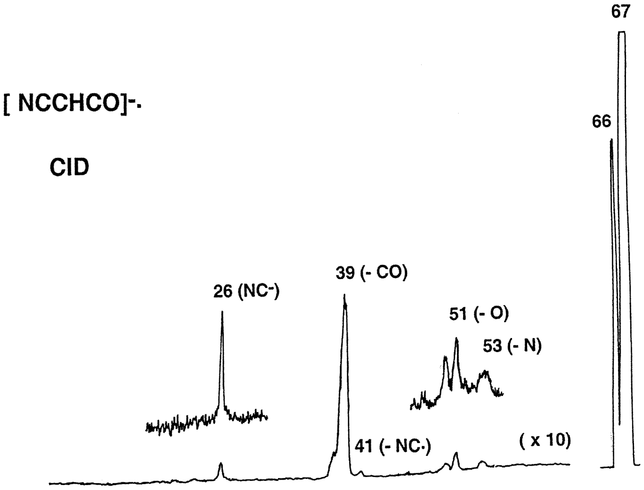


Figure 1. CID mass spectrum (MS/MS) of $[\mathrm{NCCHCO}]^{-\bullet}$. VG ZAB 2HF mass spectrometer. For experimental conditions see Experimental Section.

B. Synthetic Procedures. Ethyl cyanoacetate and 3,3-dimethoxypropionitrile were commercially available and were used without purification. Ethyl (^{13}C-cyano) acetate was made by a reported method ($^{13}C = 99\%$).[36]

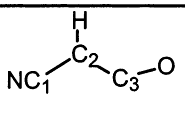
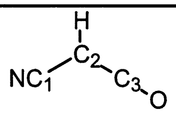
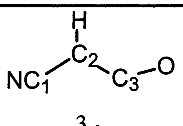
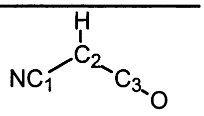
C. Theoretical Methods. Geometry optimizations were carried out with the Becke 3LYP method[37,38] using the 6-31G(d) basis set[39] basis set within the GAUSSIAN 98 suite of programs.[40] Stationary points were characterized as either minima (no imaginary frequencies) or transition structures (one imaginary frequency) by calculation of the frequencies using analytical gradient procedures. The minima connected by a given transition structure were confirmed by intrinsic reaction coordinate (IRC) calculations. The calculated frequencies were also used to determine zero-point vibrational energies which were scaled by 0.9804[41] and used as a zero-point correction for the electronic energies. We have previously reported the success of the B3LYP method in predicting geometries of unsaturated chain structures, and that this method produces optimized structures, at low computational cost, that compare favorably with higher level calculations.[42] More accurate energies for the B3LYP geometries were determined using the CCSD(T) method including zero-point energy correction (calculated by vibrational frequencies at the B3LYP/6-31G(d)G level of theory). All calculations were carried out on the Alpha Server at the Australian Partnership for Advanced Computing (APAC) National Facility (Canberra).

Results and Discussion

Formation of NCCH=C=O from $[\mathrm{NCCHCO}]^{-\bullet}$. The anion radical of cyanoketene is formed as shown in eq 1 (Experimental Section). The collision-induced mass spectrum (CID MS/MS) of this anion is shown in Figure 1. The parent anion decomposes by losses of $H^\bullet$, O, ($H^\bullet$ + O), CO, and HCCO: these decompositions are consistent with anion connectivity NCCHCO. The geometry of the anion radical [calculated at the B3LYP/6-31G(d) level of theory] is quite unusual, in that the CCO angle is 132° (see Table 1 for full details of the geometry and energy of $[\mathrm{NCCHCO}]^{-\bullet}$.

The charge-reversal mass spectrum ($^-CR^+$) of $[\mathrm{NCCHCO}]^{-\bullet}$ is shown in Figure 2a. This characteristic spectrum shows major losses of $H^\bullet$, N, O, $NC^\bullet$, CO, (CO + $H^\bullet$), and HCCN−losses consistent with a decomposing cation radical with connectivity NCCHCO. The data to this point indicate that (i) the anion radical $[\mathrm{NCCHCO}]^{-\bullet}$ does not rearrange when energized, and

TABLE 1: Calculated Properties of NCCHCO Anion, Neutrals, and Cation[a]

	 $1^{-\bullet}$	 $^{1}1$	 $^{3}1$	 $1^{+\bullet}$
State	^{2}A’	^{1}A’	^{3}A”	^{2}A”
Energy (Hartrees)	-224.264826	-244.231000	-244.157565	-243.869052
Dipole moment (Debye)	1.56	3.55	1.85	3.37
NC_1 (Å)	1.177	1.165	1.174	1.182
C_1C_2	1.406	1.418	1.392	1.381
C_2H	1.096	1.086	1.091	1.094
C_2C_3	1.395	1.331	1.466	1.394
C_3O	1.232	1.162	1.197	1.133
NC_1C_2 (°)	178.0	179.0	179.5	179.1
C_1C_2H	116.7	120.9	118.8	122.8
$C_1C_2C_3$	122.5	121.4	121.3	119.8
C_2C_3O	132.5	178.9	125.5	178.8
NC_1C_2H	0.0	0.0	0.0	0.0
HC_2C_3O	0.0	0.0	0.0	0.0

[a] Geometries optimized at the B3LYP/6-31G(d) level of theory. Energies calculated at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory.

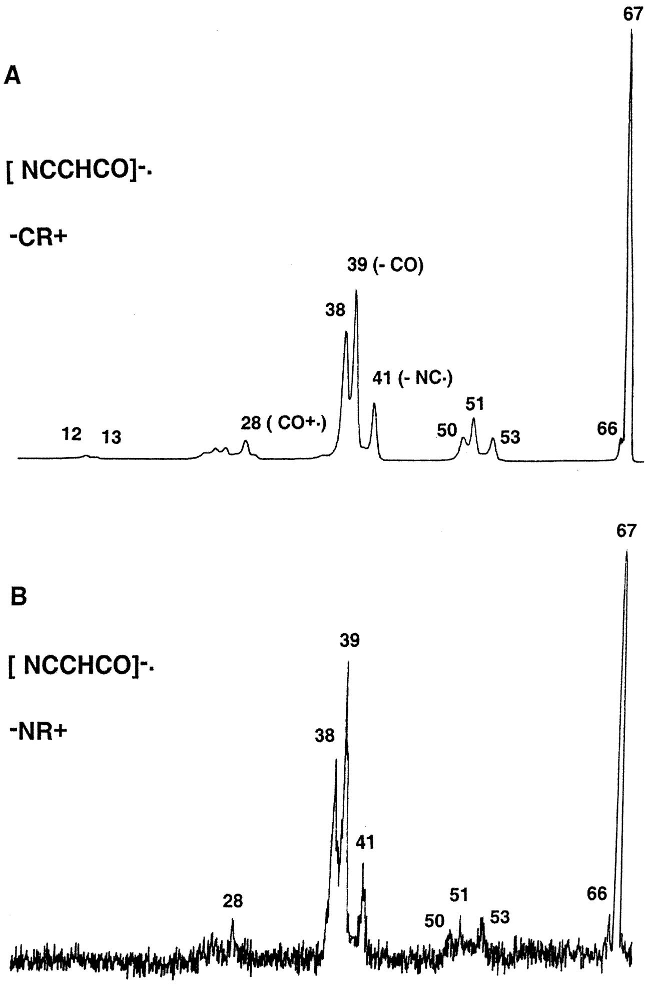


Figure 2. (A) $^{-}CR^{+}$, and (B) $^{-}NR^{+}$ mass spectra of $[NCCHCO]^{-\bullet}$. VG ZAB 2HF mass spectrometer. For experimental conditions see Experimental Section.

as such is an appropriate precursor for neutral NCCHCO, and (ii) the cation radical $[NCCHCO]^{+\bullet}$ does not rearrange when energized, and is thus an appropriate probe to test for any rearrangement of neutral NCCHCO (formed by neutralization of the anion radical).

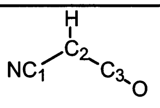
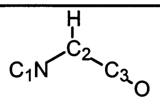
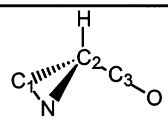
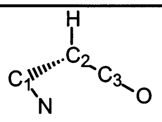
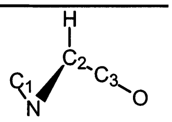
The neutralization−reionization mass spectrum of $[NCCHCO]^{-\bullet}$ is shown in Figure 2b. This spectrum is very similar to the corresponding $^{-}CR^{+}$ spectrum. The observation that the $^{-}CR^{+}$ and $^{-}NR^{+}$ spectra are very similar and that there is a pronounced peak at $m/z = 67$ in the $^{-}NR^{+}$ spectrum indicates that neutral NCCHCO (formed by one-electron vertical oxidation of $[NCCHCO]^{-\bullet}$) is stable for at least the microsecond duration of the neutralization−reionization processes.

There are two forms of neutral NCCHCO, the ground-state singlet and the triplet state. These are separated by 46.1 kcal mol^{-1} [at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory]. The geometries of these two species are significantly different (see Table 1). In particular, the singlet has the classical ketene structure (NC−CH═C═O) (the CCO angle is 178.9°), whereas the triplet has a structure similar to that of the radical anion [the triplet CCO angle is 125.5°, whereas that of the anion is 132.5° (see Table 1)]. Singlet cyanoketene has an adiabatic electron affinity of 0.92 eV and an ionization energy of 9.85 eV (experimentally 9.93 ± 0.26 eV[17]), calculated at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory.

One of the features of nitriles is that they may rearrange, when energized, to the isomeric and less stable isonitrile. For example, we have shown that neutral NCCCN rearranges to CNCCN over a barrier of 57.8 kcal mol^{-1}, with the process being endothermic by only 8 kcal mol^{-1} [at the B3LYP/6-31+G(d)//B3LYP/6-31+G(d) level of theory].[43] Thus we need to check whether it is possible for singlet NCCH═C═O to rearrange to CNCH═C═O under the conditions of the neutralization process. Calculations at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory are summarized in Figure 3, with full details contained in Table 2. The data in Figure 3 show this isomerism to be an unfavorable process: it is endothermic by 28.2 kcal mol^{-1} with the first transition state being 58.7 kcal mol^{-1} above NCCHCO.

We have also determined the CID MS/MS, $^{-}CR^{+}$, and $^{-}NR^{+}$ spectra of the ^{13}C-labeled derivative $[N^{13}CCH{=}C{=}O]^{-\bullet}$ (pro-

TABLE 2: Calculated Properties of Singlet Neutrals Shown in Figure 3[a]

	 ^{1}**1**	 ^{1}**2**	 ^{1}**3**	 **TS1**	 **TS2**
State	$^1A'$	$^1A'$	-	-	-
Relative Energy (kcal mol^{-1})	0.0	28.2	52.7	58.7	52.8
Dipole moment (Debye)	3.55	2.99	2.38	2.0	1.93
NC_1 (Å)	1.165	1.183	1.232	1.203	1.221
NC_2		1.374	1.526		1.494
C_1C_2	1.418		1.766	1.575	
C_2C_3	1.086	1.331	1.338	1.329	1.328
C_3O	1.331	1.166	1.161	1.166	1.167
C_2H	1.162	1.085	1.084	1.083	1.086
C_1NC_2 (°)		177.5	78.8		90.5
NC_1C_2	179.0		58.0	85.2	
NC_2C_3		121.8	120.0		120.7
$C_1C_2C_3$	121.4		115.2	123.0	
C_2C_3O	178.9	178.3	178.8	176.3	178.8
HC_2C_3	117.7	119.5	117.9	119.3	120.9
$C_1NC_2C_3$		180.0	95.9		82.1
NC_2C_3O		180.0	-115.7		144.6
C_1NC_2H		0.0	-102.6		-104.3
$NC_1C_2C_3$	180.0		-107.8	-73.9	
NC_1C_2H	0.0			104.7	
$C_1C_2C_3O$	180.0			-102.8	

[a] Geometries optimized at the B3LYP/6-31G(d) level of theory. Energies calculated at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory and are relative to ^{1}**1** (−244.231000 Hartrees).

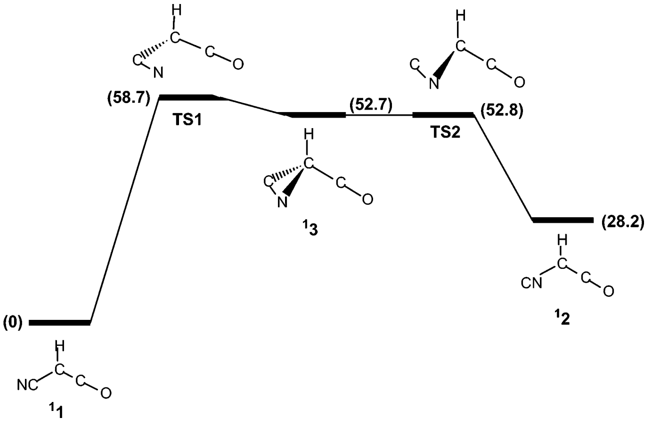


Figure 3. The singlet NCCHCO to singlet CNCHCO rearrangement. Geometries at the B3LYP/6-31G(d) level of theory. Energies at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. Relative energies in kcal mol^{-1} relative to singlet NCCHCO (0 kcal mol^{-1}).

duced as shown in eq 1, but using the labeled ester $N^{13}CCH_2CO_2Et$) in order to confirm that there is no deep-seated rearrangement of the backbone of NCCH═C═O. These spectra, listed in Table 3, are completely consistent with the spectra shown in Figures 1 and 2. In particular, they demonstrate that there is no carbon rearrangement along the backbone of the anion, neutral, or cation of NCCH═C═O (compare the complete scrambling of the carbons of energized NCCCN[43]).

The Radical Anion and Neutrals of NCCCHO. The negative ion precursor $[NCCCHO]^{-\bullet}$ is made as shown in eq 2 (Experimental Section). We must now determine whether this species is stable, or rearranges when energized. The collision induced mass spectrum of $[NCCCHO]^{-\bullet}$ is quite different from that of the isomer shown in Figure 1. Loss of $H^\bullet$ is the only significant fragmentation. Thus there is no experimental evidence that $[NCCCHO]^{-\bullet}$ rearranges to $[NCCHCO]^{-\bullet}$. To check this further we have carried out calculations of the reaction coordinate of the rearrangement $[NCCCHO]^{-\bullet}$ to $[NCCHCO]^{-\bullet}$. These calculations are summarized in Figure 4 and Table 4. The rearrangement shown in Figure 4 has a barrier of 36.8 kcal mol^{-1}. This is quite an appreciable barrier for a negative ion rearrangement, and this together with the experimental data indicates that if any such rearrangement occurs at all, it must be a very minor process. We conclude that $[NCCCHO]^{-\bullet}$ is an appropriate precursor for neutral NCCCHO.

TABLE 3: Spectra of $[N^{13}CCHCO]^-$ (Mass (loss or formation) relative abundance in %)

CID (fragment ions only)	67($H^\bullet$)100; 40(CO)35; 27($N^{13}C^-$)
$^-CR^+$	68(parent)100; 67($H^\bullet$)5; 54(N)6; 52(O)10; 51(O + $H^\bullet$)6; 41($N^{13}C^\bullet$)13; 40(CO)46; 39 (CO + $H^\bullet$)29; 29(CHO^+)0.5; 28($CO^{+\bullet}$)4; 27($N^{13}C^+$)1; 13($HC^+$and/or $^{13}C^{+\bullet}$)0.3; 12($C^{+\bullet}$)0.3
$^-NR^+$	68(parent)100; 67($H^\bullet$)6; 54(N)6; 52(O)4; 51 (O + $H^\bullet$)6; 41($N^{13}C^\bullet$)15; 40(CO)45; 39(CO + $H^\bullet$)30; 29(CHO^+)1; 28($CO^{+\bullet}$)3; 27($N^{13}C^+$)1; 13($HC^+$and/or $^{13}C^{+\bullet}$)0.5; 12($C^{+\bullet}$)0.5

The $^-CR^+$ and $^-NR^+$ spectra of $[NCCCHO]^{-\bullet}$ are shown in Figures 5a and 5b. The $^-CR^+$ spectrum is very similar to that of $[NCCHCO]^{-\bullet}$. This tells us that the $^-CR^+$ process of $[NCCCHO]^{-\bullet}$ gives a rearranged and decomposing species $[NCCHCO]^{+\bullet}$. However the $^-NR^+$ and $^-CR^+$ spectra of $[NCCCHO]^{-\bullet}$ are also very similar. As a consequence, this particular experiment does not provide information about the structure(s) of the neutral(s) formed by the one-electron oxidation of $[NCCCHO]^{-\bullet}$. This is because the data do not distinguish between the following scenarios, (i) NCCCHO rearranges to NCCHCO which is then ionized to $[NCCHCO]^{+\bullet}$, or (ii)

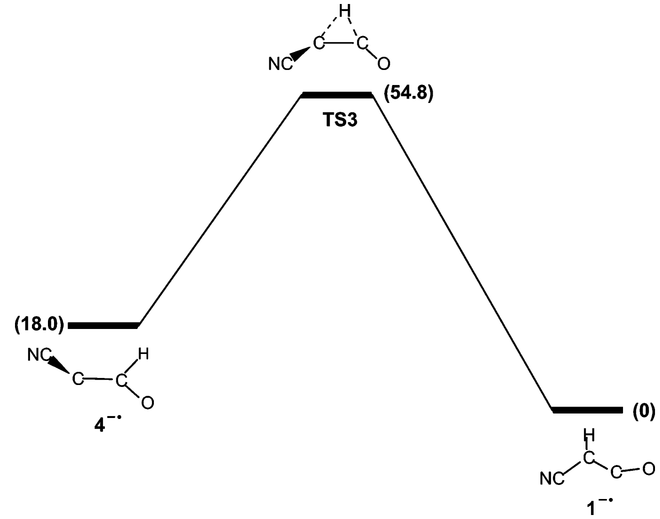


Figure 4. The anion rearrangement $[NCCCHO]^{-\bullet}$ to $[NCCHCO]^{-\bullet}$. Geometries at the B3LYP/6-31G(d) level of theory. Energies at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. Relative energies in kcal mol^{-1} relative to $[NCCHCO]^{-\bullet}$ (0 kcal mol^{-1}).

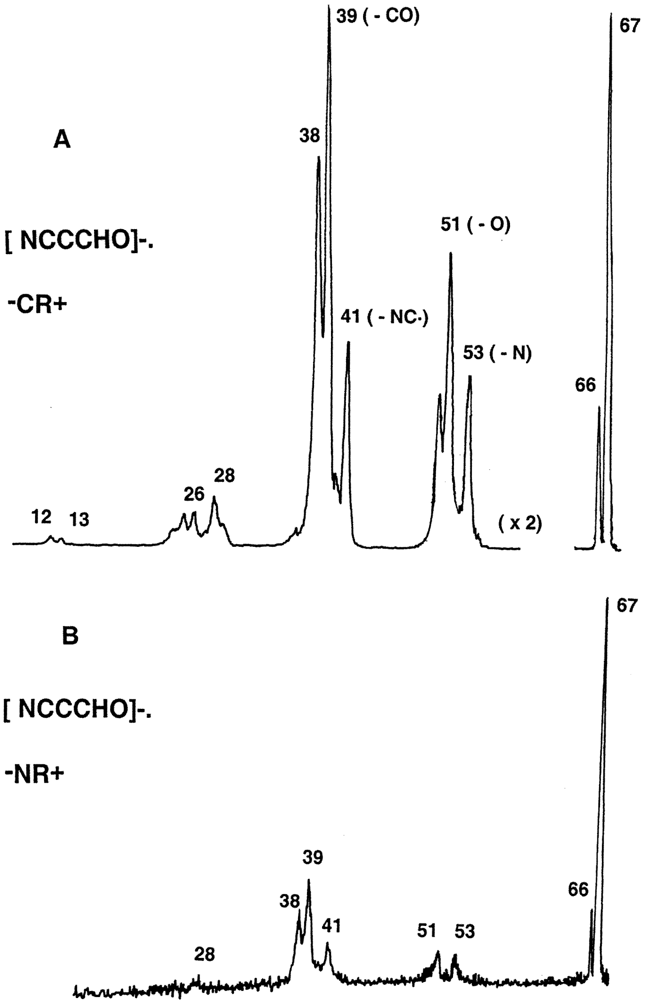
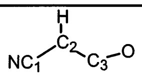
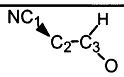
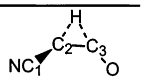


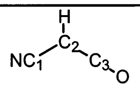
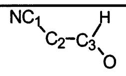
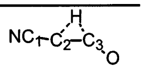
Figure 5. (A) $^-CR^+$, and (B) $^-NR^+$ mass spectra of $[NCCCHO]^{-\bullet}$. VG ZAB 2HF mass spectrometer. For experimental conditions see Experimental Section.

TABLE 4: Calculated Properties of Anions Shown in Figure 4[a]

	 $1^{-\bullet}$	 $4^{-\bullet}$	 TS3
State	$^2A'$	-	-
Relative Energy (kcal mol^{-1})	0.0	18.0	54.8
Dipole moment (Debye)	1.56	1.41	1.65
NC_1 (Å)	1.177	1.198	1.185
C_1C_2	1.406	1.343	1.394
C_2C_3	1.395	1.397	1.349
C_3O	1.232	1.247	1.229
C_2H	1.096		
C_3H		1.131	1.401
NC_1C_2 (°)	178.0	175.1	169.1
$C_1C_2C_3$	122.5	139.0	141.8
C_2C_3O	132.5	130.8	154.8
C_1C_2H	116.7		
C_2C_3H		110.9	58.3
$NC_1C_2C_3$	180.0	175.2	-144.1
$C_1C_2C_3O$	180.0	-138.3	-34.2
$C_1C_2C_3H$		47.6	-174.5

[a] Geometries optimized at the B3LYP/6-31G(d) level of theory. Energies calculated at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory and are relative to $\mathbf{1}^{-\bullet}$ (−224.264826 Hartrees).

TABLE 5: Calculated Properties of Cations Shown in Figure 6[a]

	 $1^{+\bullet}$	 $4^{+\bullet}$	 TS4
State	$^2A''$	$^2A''$	$^2A''$
Relative Energy (kcal mol^{-1})	0.0	74.3	74.6
Dipole moment (Debye)	3.37	1.47	1.33
NC_1 (Å)	1.182	1.196	1.191
C_1C_2	1.381	1.321	1.327
C_2C_3	1.394	1.397	1.356
C_3O	1.133	1.193	1.188
C_2H	1.094		
C_3H		1.154	1.195
NC_1C_2 (°)	179.1	174.3	175.5
$C_1C_2C_3$	119.8	155.8	159.4
C_2C_3O	178.8	143.3	152.4
C_1C_2H	122.8		
C_2C_3H		95.0	84.0
$NC_1C_2C_3$	180.0	180.0	180.0
$C_1C_2C_3O$	180.0	180.0	180.0
$C_1C_2C_3H$		0.0	0.0

[a] Geometries optimized at the B3LYP/6-31G(d) level of theory. Energies calculated at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory and are relative to $\mathbf{1}^{+\bullet}$(−243.869052 Hartrees).

NCCCHO is stable and ionizes to $[NCCCHO]^{+\bullet}$ which then rearranges to $[NCCHCO]^{+\bullet}$.

The Rearrangements of $[NCCCHO]^{+\bullet}$ and NCCCHO. The $^-CR^+$ spectrum of $[NCCCHO]^{-\bullet}$ indicates that the decomposing product cation is $[NCCHCO]^{+\bullet}$, suggesting that the rearrangement of $[NCCCHO]^{+\bullet}$ to $[NCCHCO]^{+\bullet}$ is facile. We have explored this process using molecular modeling. The results are summarized in Figure 6, with full details given in Table 5. The rearrangement is strongly exothermic (−74.3 kcal mol^{-1}), with a barrier of only 0.3 kcal mol^{-1}. It follows that vertical two-electron oxidation of $[NCCCHO]^{-\bullet}$ yields exclusively the rearranged species $[NCCHCO]^{+\bullet}$. The thermochemistries of the decomposition processes of both neutrals and cations are listed in Table 6. The decomposition $[NCCHCO]^{+\bullet} \rightarrow [NCCH]^{+\bullet} + CO$ is endothermic by 69.5 kcal mol^{-1}, so some of the cation radicals formed by the rearrangement shown in Figure 5 will decompose by loss of CO.

TABLE 6: Calculated Dissociation Energies (kcal mol^{-1})^a

NCCHCO$^{-\bullet}$	→	HCCN$^{-\bullet}$	+	CO	32.9
		HCCO^{-}	+	CN$^{\bullet}$	88.6
		NCCCO^{-}	+	H	41.0
^{1}NCCHCO	→	^{1}HCCN	+	CO	66.9
		HCCO$^{\bullet}$	+	CN$^{\bullet}$	117.0
		NCCCO$^{\bullet}$	+	H	99.8
		^{1}NCCHC	+	O	159.1
		CCHCO$^{\bullet}$	+	N	155.1
^{3}NCCHCO	→	^{3}HCCN	+	CO	9.0
		HCCO$^{\bullet}$	+	CN$^{\bullet}$	70.9
		NCCCO$^{\bullet}$	+	H	53.7
		^{1}NCCHC	+	O	113.0
		CCHCO$^{\bullet}$	+	N	109.1
NCCHCO$^{+\bullet}$	→	HCCN$^{+\bullet}$	+	CO	69.5
		^{3}HCCN	+	CO^{+}	146.7
		HCCO^{+}	+	CN$^{\bullet}$	113.3
		HCCO$^{\bullet}$	+	CN^{+}	201.2
		^{3}NCCCO^{+}	+	H$^{\bullet}$	101.3
		CCHCO^{+}	+	N	129.6
		NCCHC$^{+\bullet}$	+	O	209.4

[a] Dissociations were determined using theoretical data from previous tables and the following calculated CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) energies (in Hartrees); −243.700122 (NCCCO^{-}), −243.572586 (NCCCO$^{\bullet}$), −243.208219 (^{3}NCCCO^{+}), −169.051800 (^{1}NCCHC), −168.609705 (NCCHC$^{+\bullet}$), −189.496793 (CCHCO$^{\bullet}$), −189.175492 (CCHCO^{+}), −243.532510, −151.625957 (HCCO^{-}), −151.546954 (HCCO$^{\bullet}$), −151.190929 (^{3}HCCO^{+}), −131.143514 (HCCN$^{-\bullet}$), −131.055458 (^{1}HCCN), −131.074279 (^{3}HCCN), −130.689293 (HCCN$^{+\bullet}$), −92.497621 (CN$^{\bullet}$), −92.001462 (^{1}CN^{+}), −113.068937 (^{1}CO), −112.561040 (CO$^{+\bullet}$), −0.499334 (H$^{\bullet}$), −74.925654 (^{3}O), −54.486982 (^{4}N).

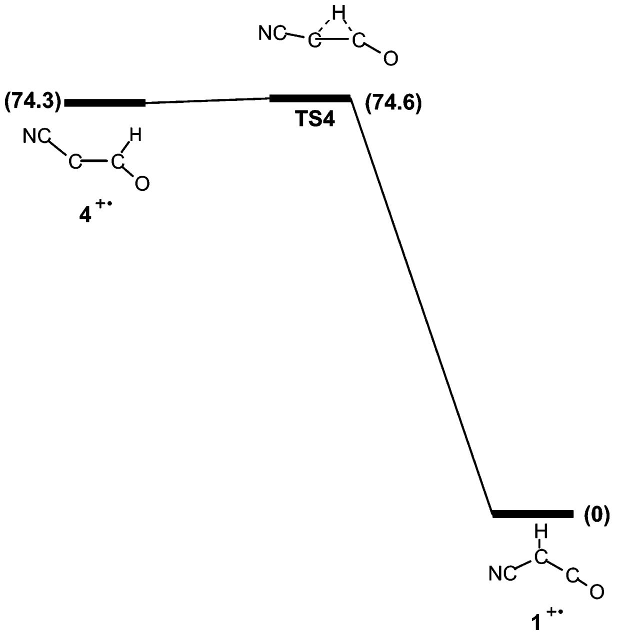


Figure 6. The cation rearrangement [NCCCHO]$^{+\bullet}$ to [NCCHCO]$^{+\bullet}$. Geometries at the B3LYP/6-31G(d) level of theory. Energies at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. Relative energies in kcal mol^{-1} relative to [NCCHCO] $^{+\bullet}$ (0 kcal mol^{-1}).

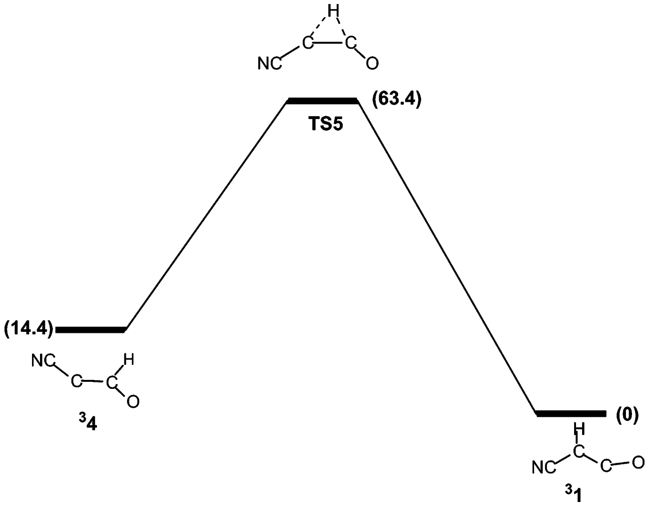
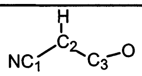
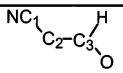
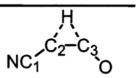


Figure 7. The neutral rearrangement of triplet NCCCHO to triplet NCCHCO$^{\bullet}$ Geometries at the B3LYP/6-31G(d) level of theory. Energies at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. Relative energies in kcal mol^{-1} relative to triplet NCCHCO (0 kcal mol^{-1}).

TABLE 7: Calculated Properties of Neutrals Shown in Figure 7^a

	 ^{3}**1**	 ^{3}**4**	 **TS5**
State	^{3}A"	^{3}A"	-
Relative Energy (kcal mol^{-1})	0.0	14.4	63.4
Dipole moment (Debye)	1.85	1.36	1.99
NC$_1$ (Å)	1.174	1.197	1.178
C$_1$C$_2$	1.392	1.324	1.375
C$_2$C$_3$	1.466	1.435	1.387
C$_3$O	1.197	1.223	1.210
C$_2$H	1.091		
C$_3$H		1.109	1.349
NC$_1$C$_2$ (°)	179.5	175.2	172.8
C$_1$C$_2$C$_3$	121.3	149.1	146.0
C$_2$C$_3$O	125.5	124.2	139.6
C$_1$C$_2$H	118.8		
C$_2$C$_3$H		114.2	61.9
NC$_1$C$_2$C$_3$	180.0	180.0	171.4
C$_1$C$_2$C$_3$O	180.0	180.0	-10.8
C$_1$C$_2$C$_3$H		0.0	-138.3

[a] Geometries optimized at the B3LYP/6-31G(d) level of theory. Energies calculated at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory and are relative to ^{3}**1** (−244.157565 Hartrees).

The experimental data to date provide no information as to whether neutral NCCCHO is stable, or rearranges to NCCHCO.[44] We have explored this question by molecular modeling. Only the triplet of NCCCHO is stable. Singlet NCCCHO is not a stable species on the singlet potential surface. The reaction coordinate of the triplet NCCCHO to triplet NCCHCO rearrangement is shown in Figure 7. Full details are listed in Table 7. The exothermic 1,2 H rearrangement (−14.4 kcal mol^{-1}) has a barrier of 49.0 kcal mol^{-1}. Since the geometries of triplet NCCCHO and the precursor anion are similar (see Tables 4 and 7), the excess energy that the neutral has as a consequence of the Franck Condon oxidation (the difference in energy between the anion geometry and the triplet NCCCHO structure on the triplet neutral surface) will be small. This energy is computed to be only 4.1 kcal mol^{-1} at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory, significantly less that the 49.0 kcal mol^{-1} required to surmount the barrier for the interconversion. However, an excess energy of 49.0 kcal mol^{-1} is within the range that we have observed before for neutral rearrangements.[45] This excess energy is usually produced by keV collisions of the neutral with collision gas in the collision cell.

The triplet cyanoketene neutrals so formed have a maximum excess energy of 63.4 kcal mol^{-1} as a consequence of the rearrangement shown in Figure 7. However, triplet cyanoketene requires an excess energy of only 9.0 kcal mol^{-1} to effect decomposition to NCCH and CO (Table 6). Thus the rearrangement of triplet NCCCHO (Figure 7) will give energized triplet cyanoketene which will decompose to NCCH and CO.

The $^{-}$NR^{+} spectrum (Figure 5b) clearly shows the formation of stable parent neutrals, i.e., $m/z = 67$, produces the base peak of the spectrum, and this is indicative of the formation of neutrals with lifetimes of at least one microsecond. Some of these neutrals will almost certainly correspond to NCCCHO neutrals which do not have sufficient energy to effect rearrangement to triplet cyanoketene (see Figure 7). However it seems likely that stable cyanoketene should be a major contributor to $m/z = 67$. Since singlet NCCCHO is not stable and triplet NCCCHO yields a decomposing triplet NCCHCO, what then is the process which gives stable cyanoketene?

There seem to be only two possible scenarios, namely, (i) the unstable singlet NCCCHO rearranges to a stable singlet NCCHCO neutral, and/or (ii) triplet NCCCHO undergoes intersystem crossing to unstable singlet NCCCHO which immediately rearranges to yield stable singlet NCCHCO.

Consider the first possibility. Singlet NCCCHO does not occupy a minimum on the singlet neutral potential surface. However, when singlet NCCCHO is explored at the level of theory used in this investigation, it immediately reverts to the singlet NCCHCO structure. If [NCCCHO]$^{-\bullet}$ undergoes vertical Franck−Condon one-electron oxidation onto the singlet neutral potential surface, the initially formed neutral (with the anion geometry) lies 75.2 kcal mol^{-1} above singlet NCCHCO [at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory].

The second possibility is that triplet NCCCHO undergoes intersystem crossing onto the singlet potential surface, and that this energized species rearranges to stable NCCHCO. Using a known program,[46] we calculate that this cross-over point lies 9.9 kcal mol^{-1} [at the B3LYP/6-31G(d) level of theory] above triplet NCCCHO. The product of this process, singlet NCCHCO, has an excess energy of 70.3 kcal mol^{-1}.

The two processes described above yield NCCHCO with (at least initially) significant amounts of excess energy, namely, 75.2 and 70.3 kcal mol^{-1}, respectively (see above). Thermochemical data for the decompositions of singlet cyanoketene are listed in Table 6. Decomposition of NCCHCO to NCCH and CO is calculated to be endothermic by 66.9 kcal mol^{-1} [at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory], and 71.9 kcal mol^{-1} [at the CCSD(T)/aug-pVTZ//B3LYP/6-31G(d) level of theory]. The computed excess energy of singlet cyanoketene neutrals and the energy required to effect decomposition of singlet NCCHCO to NCCH and CO are thus of the same order. Some of the neutrals will decompose to NCCH and CO. However a proportion of the neutrals will lose some of this excess energy (e.g., by radiation); thus, stable cyanoketene molecules will also be formed by either process outlined above.

We conclude: (i) one-electron vertical oxidation of [NCCHCO]$^{-\bullet}$ yields stable singlet NCCHCO, (ii) similar oxidation of [NCCCHO]$^{-\bullet}$ is more complex. The presence of a pronounced recovery signal at $m/z = 67$ in the $^{-}$NR^{+} spectrum of [NCCCHO]$^{-\bullet}$ indicates that there are stable neutrals (with atomic composition C_3HNO) which have lifetimes of at at least a microsecond. Some of these may correspond to triplet NCCCHO neutrals that do not have sufficient excess energy to effect the rearrangement shown in Figure 7. Other neutrals correspond to stable singlet NCCHCO formed either from rearrangement of unstable singlet NCCCHO neutrals, or following intersystem crossing between triplet and singlet neutral potential surfaces.

It is therefore possible to effect the rearrangement between the isomers NCCCHO and NCCHCO in the gas phase, and it follows that this rearrangement (proposed in Scheme 1) could, in principle, occur in interstellar dust clouds and/or in an interstellar ice environment.

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