Formation of Cyanate (OCN) and Fulminate (ONC) Radicals from Anionic Precursors in the Gas Phase. A Joint Experimental and Theoretical Study

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The cyanate anion (OCN)⁻ may be formed in the ion source of a reverse sector VG ZAB 2HF mass spectrometer by dissociative electron capture of phenyl cyanate (PhOCN). The isomeric fulminate anion (ONC)⁻ is formed by (i) deprotonation of nitromethane (with HO⁻) followed by elimination of H_2O (⁻CH_2NO_2 → [(CHN(O)(OH)]⁻ → (ONC)⁻ + H_2O) and (ii) the reaction between CH_2=N−OCH_3 and O•⁻ [CH_2=N−OCH_3 + O•⁻ → (ONC)⁻ + H_2O + CH_3•]. Neutralization of the cyanate and fulminate anions by Franck−Condon vertical one-electron oxidation (in the first of two tandem collision cells of the mass spectrometer) yields the cyanate (OCN) and fulminate (ONC) radicals, both of which are stable for at least 1 μs. Ionization of these neutrals by one-electron oxidation in a second collision cell produces the cyanate and fulminate cations. A proportion of each of these cations undergoes isomerization. Theoretical and experimental studies show that (i) these rearrangements involve the less stable singlet forms of the cations, (ii) the cationic fulminate to cyanate rearrangement is a major process, and (iii) the corresponding rearrangement of the cyanate cation is a minor process, with the product being either the oxazirinyl cation or the fulminate cation.

Introduction

The history of fulminates, nitrile oxides, cyanates, and isocyanates is a fascinating story and the historical background can be found in the Introduction to ref 1. Mercury fulminate was first used as an explosive some four centuries ago, whereas the nitrile oxide group is found in various organic molecules RCNO. Isocyanates (RNCO) are important precursors in the industrial preparation of urethane polymers,[2] are intermediates in a variety of synthetically useful rearrangement reactions (e.g., the Hofmann, Curtius, Lossen and Schmidt rearrangements)[3] to form organic amines, and the cyanate anion (OCN)⁻ is thought to be implicated in the process involved in oxygen uptake by haemoglobin.[4]

The rearrangements of the silver salts of fulminates (AgONC) and nitrile oxides (AgCNO) to isocyanate (AgNCO) have been reported on a number of occasions.[5−9] X-ray structures of silver isocyanate[10] and silver fulminate[11] have been obtained and show that silver fulminate occurs in two distinct polymorphic forms. The three acid isomers HCNO, HNCO, and HOCN are known and their structures and spectroscopy have been reviewed.[1] It was originally proposed that the fourth isomer, HONC, was also stable,[1] but this proposal has since been shown to be incorrect.[12] High-resolution infrared data have been determined for the cyanate anion [(OCN)⁻] using velocity modulation diode laser spectroscopy,[13] and there has been extensive characterization of the vibrational spectroscopy of this species in the solid state.[14−18] The adiabatic electron affinity of the cyanate radical (OCN) has been measured as 3.609 eV.[19] The organic fulminate to cyanate rearrangement has been described.[20] There have been a number of theoretical studies on the rearrangement of neutral nitrile oxides (RCNO) to isocyanates (RNCO),[21−24] and of the rearrangement of the fulminate anion (ONC)⁻ to the cyanate anion (OCN)⁻,[25−28] The structures of neutral ONC, OCN, and CON,[29,30] and the cation (OCN)⁺ [31−33] have been studied theoretically.

Our interest in fulminates and cyanates comes from our recent syntheses of transient and reactive cumulene and heterocumulene molecules, some of which have been detected in interstellar dust clouds and in circumstellar envelopes of carbon rich stars.[34−36] These neutrals have been produced by Franck−Condon vertical one-electron oxidation of anions of known bond connectivity in the collision cell of a mass spectrometer, with the structures of the neutrals probed by reionization to either decomposing positive or negative ions. This is known as the neutralization-reionization (NR) technique, a method first introduced by McLafferty and co-workers.[37]

There have been 123 molecules and ions so far identified in stellar and interstellar regions, including HCN, HNC, HNCO, CH_3CN, CH_3NC, and a number of other nitrile containing molecules including HC$_n$CN (n = 1−8).[38] Many of these CN containing species have been detected in the circumstellar envelope of the carbon star IRC+10216.[39] The identification of HNCO is of particular interest and raises the question as to whether neutral cyanate (OCN) and other isomers may also be present in stellar regions. This paper reports the formation of cyanate and fulminate neutrals by one-electron oxidation of anions of known bond connectivity.

Experimental Section

A. Mass Spectrometric Methods. For a detailed description of the experiments and the instrument used see ref 40. 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 (OCN)⁻ and (ONC)⁻ anions were generated by chemical ionization (CI) in the negative ion mode, with typical source conditions as follows: source temperature 200 °C, repeller voltage −0.5 V, ion extraction voltage 7 kV, mass resolution $m/\Delta m \geq 1500$. The precursors PhOCN [for (OCN)⁻] and CH_3-NO_2 and CH_2=N−OCH_3 [for (ONC)⁻] were introduced into the ion source via the septum inlet at 100 °C to give a measured

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TABLE 1: Minima and Transition Structures on the OCN Anion Surface Calculated at the B3LYP/6-31G+(d) Level of Theory, with Single Point Energies (Including Zero-Point Energy Correction) Computed at CCSD(T)/aug-cc-pVDZ. The Values Given in Brackets Represent the Available Literature Data for Comparison (see footnotes for references).

	O-C-N	O⟋C—N	O⟋C—N	O-N-C	C-O-N	O⟋C—N	O⟍N—C	C⟍O—N
	1⁻	**2⁻**	**2⁻**	**3⁻**	**4⁻**	**TS 1⁻/2⁻**	**TS 2⁻/3⁻**	**TS 2⁻/4⁻**
State	$^1\Sigma$	$^1A'$	$^3A'$	$^1\Sigma$	$^1A'$	$^1A'$	$^1A'$	$^1A'$
Symmetry	$C_{\infty v}$	C_S	C_S	$C_{\infty v}$	C_S	C_S	C_S	C_S
Energy (Hartrees)	-167.74409	-167.58992	-167.49723	-167.63833	-167.49336	-167.58434	-167.57341	-167.47753
Rel. Energy (kcal mol⁻¹)	0.0	96.7(101.8)[a]	154.9	66.4(67.8)[a]	157.3	100.2(106.9)[a]	107.1(114.1)[a]	167.3
Bond Lengths (Å)								
O-C	1.235 (1.231)[a] (1.26)[b]	1.469(1.465)[a]	1.481		1.193	1.435(1.444)[a]		1.138
C-N	1.197(1.193)[a] (1.17)[b]	1.263(1.257)[a]	1.498	1.188(1.187)[a]		1.237(1.233)[a]	1.224(1.219)[a]	
N-O		1.467	1.384	1.275(1.274)[a]	1.269		1.479(1.487)[a]	2.403
Bond Angles (°)								
O-C-N	180.0	73.7(75.2)[a]	55.4			90.8(92.7)[a]		
O-N-C		58.8	61.7	180.0			99.0(100.6)[a]	
C-O-N		47.4	62.9		173.7			130.2

[a] From ref 27, calculated at CCSD(T)/aug-cc-pVQZ level of theory. [b] Experimental value.[19]

SCHEME 1

OCN   O⟋C—N   ONC   CON

1   **2**   **3**   **4**
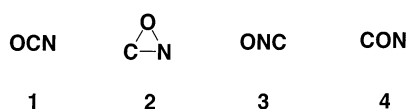
source pressure of 10^{-5} Torr inside the source housing. The precursor anions were produced as shown in Scheme 1: (OCN)⁻ was formed by dissociative electron capture of PhOCN, whereas treatment of CH_3NO_2 with HO⁻ (from water), and the reaction between O•⁻ (from N_2O^{41}) and CH_2=N—OCH_3 gave (ONC)⁻. The total pressure in all cases was ca. 10^{-4} Torr inside the source housing, giving an estimated source pressure of ca. 10^{-1} Torr.

Collisional induced dissociation (CID) of B mass selected anions was effected in the first of the two tandem collision cells positioned between B and E. Argon was used as a target gas. The pressure of the collision gas in the cell was maintained such that 90% of the parent ion beam was transmitted through the cell. This corresponds to an average of 1.1−1.2 collisions per ion.[42] Product ions resulting from CID were recorded by scanning E.

Neutralization−reionization[37] (⁻NR⁺) experiments were performed for B mass-selected anions utilizing the dual collision cells located between sectors B and E. Neutralization of the anions was achieved by collisional electron detachment using O_2 at 80% transmittance as collision gas, whereas reionization to cations was achieved by collision of the neutrals with O_2, again at 80% transmittance. Any ions remaining after the first collision event were deflected from the primary neutral beam using a deflector electrode positioned before the second collision cell. To detect a reionization signal due to the parent, the neutral species must be stable for approximately 1 μs. Charge reversal (⁻CR⁺) spectra[43] were recorded using single collision conditions in collision cell 1 (O_2, 80%T).

B. Precursor Neutrals. Nitromethane was a commercial sample. Phenyl cyanate[44] and formaldehyde *O*-methyloxime (CH_2=N—OCH_3)[45] were prepared by reported methods.

C. Theoretical Methods. Geometry optimizations were carried out with the Becke 3LYP method[46,47] using a modest 6-31+G(d) basis set within the GAUSSIAN 98 suite of programs.[48] 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 that were then scaled[49] by 0.9804 and used as a zero-point correction for the electronic energies calculated at this and higher levels of theory. B3LYP/6-31G(d) has previously been used for geometry optimizations of anionic carbon clusters and has demonstrated good correlation with structures calculated using high level couple-cluster approaches.[50,51] Some problems have been highlighted in the literature regarding the use of the B3LYP method for the accurate prediction of molecular energies for carbon clusters,[52] but the method continues to be used with success.[53,54] More accurate energies for the B3LYP geometries were determined using the CCSD(T) method[55−60] together with the Dunning aug-cc-pVDZ basis set.[61,62] This level of theory gives a calculated adiabatic electon affinity of 3.408 eV for the cyanate radical: the experimental value is 3.609 eV.[20] All calculations were carried out on Power Challenge Supercomputers at either the South Australian Supercomputing Centre (Adelaide) or the Australian National University Supercomputing Facility (Canberra).

Results and Discussion

Theoretical Calculations on Anions 1⁻−4⁻ and the Syntheses of 1⁻ and 3⁻. The major aim of this study is to form, by unequivocal pathways, the cyanate anion (OCN)⁻ and the fulminate anion (ONC)⁻ and to convert them by vertical one-electron oxidation to the corresponding cyanate (OCN) and fulminate (ONC) radicals. Before undertaking a synthesis of these anions, it is necessary to determine how many stable isomers are present on the anion potential surfaces. Theoretical studies indicate that there are five such structures. These are singlet anions **1⁻−4⁻**, and triplet **2⁻**: the corresponding triplet forms of the **1⁻**, **3⁻**, and **4⁻** isomers are not stable. The connectivities of these anions are shown in Scheme 1. Full details of the geometries and energies of the five anion isomers are recorded in Table 1.
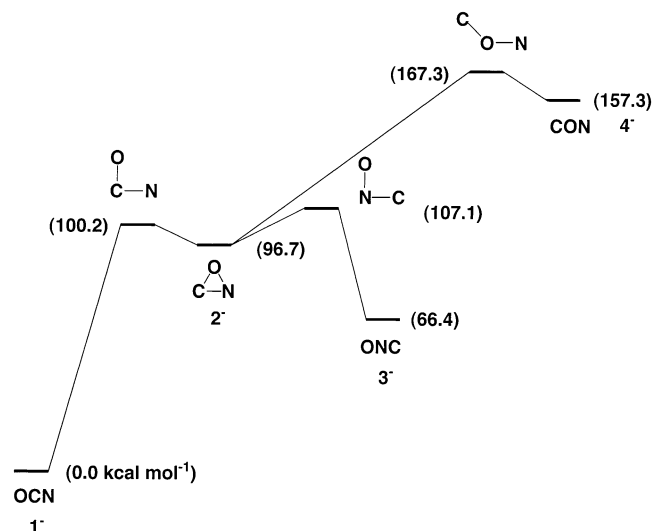
Figure 1. Calculated pathway for conversion of OCN isomers on the singlet anion potential energy surface. The energies are given in kcal mol^{-1} and are calculated at CCSD(T)/aug-cc-pVDZ/B3LYP/6-31+G(d) level of theory. For details of minima and transition states see Table 1.

The geometries of the five anions were calculated at the B3LYP/6-31+G(d) level of theory: in the case of (OCN)$^-$, the calculated bond lengths are within 0.03 Å of the experimental values[20] (see Table 1). Energies of all species were determined at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level; these values are similar to those for of $1^- - 3^-$ calculated at the CCSD-(T)/aug-cc-pVQZ level of theory[28] (Table 1). The relative energies of the five anions in relation to the cyanate anion [(OCN)$^-$, 1^-] (0 kcal mol^{-1}), are the singlet oxazirinyl anion ($^1 2^-$, +96.7 kcal mol^{-1}), the triplet oxazirinyl anion ($^3 2^-$, +154.9 kcal mol^{-1}), the fulminate anion (3^-, +66.4 kcal mol^{-1}), and (CON)$^-$ (4^-, +157.3 kcal mol^{-1}).

If we are to form the cyanate (OCN) and the fulminate (ONC) neutral radicals from their anions, the anions must not undergo rearrangement under the conditions necessary to charge-strip them to the neutral radicals. Possible interconversions of minima on the singlet anion potential surface are shown in Figure 1: full details of minima and transition states shown in Figure 1 are listed in Table 1. Conversion of the cyanate anion (1^-) through the oxazirinyl anion ($^1 2^-$) to the fulminate anion (3^-) is endothermic by 66.4 kcal mol^{-1} with a maximum barrier of 107.1 kcal mol^{-1} at the level of theory that we have used. These results are similar to those determined earlier.[26-28] If 1^- and 3^- are formed by soft ionization procedures, the calculations suggest that it is unlikely that either would rearrange under these reaction conditions. The data in Figure 1 show that although the high energy isomer 4^- will not be formed from any of the other anions, it can convert to 1^- if it has excess energy of ≥10 kcal mol^{-1}. Finally, conversion through $^3 2^-$ is unlikely to occur because it is a high energy process that also involves spin inversion.
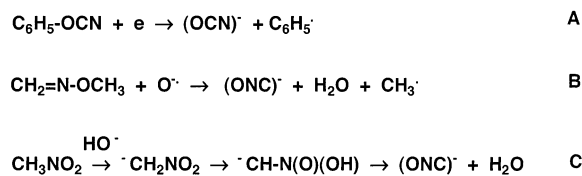
The anions 1^- and 3^- were prepared by reactions A−C shown in Scheme 2. The cyanate anion is produced by process A. The fulminate anion can be produced by the reaction between O$^{•-}$ and CH$_2$=N−OCH$_3$ (process B) or from nitromethane (sequence C) by a known reaction.[63,64]

The charge reversal ($^-$CR$^+$) mass spectra of the anions (OCN)$^-$ and (ONC)$^-$ are shown in Figures 2A and 3A, respectively. The $^-$CR$^+$ spectra of the two anions are reproducibly different. That of (OCN)$^-$ shows major peaks corresponding to CO$^{+•}$ (m/z 28) and CN$^+$ (m/z 26), consistent with
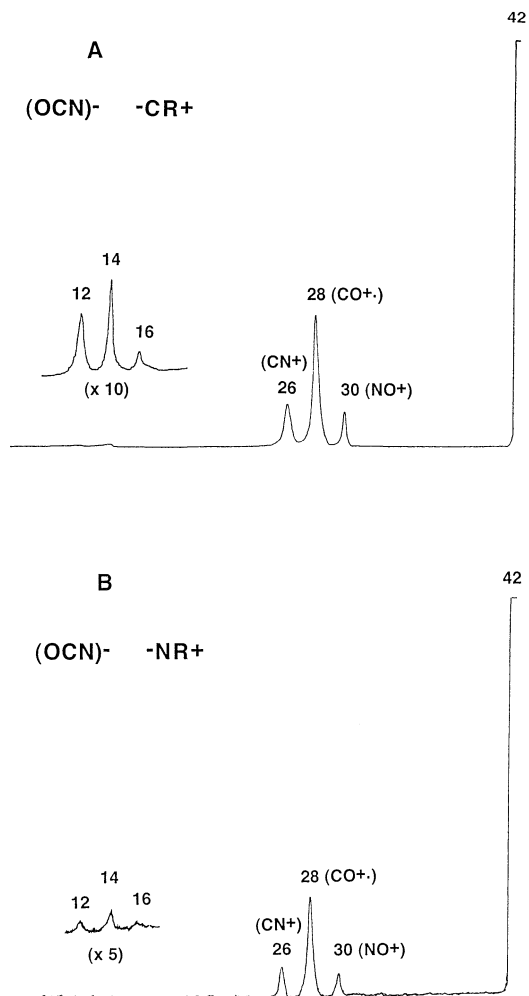
Figure 2. $^-$CR$^+$ (A) and $^-$NR$^+$ (B) mass spectra of (OCN)$^-$. For experimental details see the Experimental Section. VG ZAB 2HF mass spectrometer.

SCHEME 2

C$_6$H$_5$-OCN + e → (OCN)$^-$ + C$_6$H$_5^•$ **A**

CH$_2$=N-OCH$_3$ + O$^{•-}$ → (ONC)$^-$ + H$_2$O + CH$_3^•$ **B**

CH$_3$NO$_2$ $\xrightarrow{\text{HO}^-}$ $^•$CH$_2$NO$_2$ → $^•$CH-N(O)(OH) → (ONC)$^-$ + H$_2$O   **C**

the major proportion of (OCN)$^-$ and (OCN)$^+$ retaining their positional integrity during and following the two-electron oxidation.

There is also a smaller peak at m/z 30 (NO$^+$) in this spectrum (Figure 2A) suggesting that there is some rearrangement of charged OCN, perhaps to charged ONC during or following the CR process. A similar scenario can be seen in the $^-$CR$^+$ spectrum of (ONC)$^-$ (Figure 3A). There is a major fragment peak at m/z 30 (NO$^+$) and smaller peaks at m/z 28 (CO$^{+•}$) and 26 (CN$^+$). Thus some species retain the ONC connectivity throughout the CR process, with others rearranging, perhaps to a charged OCN structure. It will be shown later that these are rearrangements of the cations. It follows that there is no rearrangement of either (OCN)$^-$ or (ONC)$^-$ prior to or during the charge reversal process.

Structures of the Neutral Isomers and Formation of Stable OCN and OC. The structures of the four neutral doublets **1** to **4** are shown in Table 2. The cyanate radical (OCN) (**1**) is the

TABLE 2: Minima and Transition Structures on the OCN Neutral Surface Calculated at the B3LYP/6-31G+(d) Level of Theory, with Single Point Energies (Including Zero-Point Energy Correction) Computed at CCSD(T)/aug-cc-pVDZ. The Values Given in Brackets Represent the Available Literature Data for Comparison (see footnotes for references).

	O-C-N	O / C—N (ring)	O-N-C	C-O-N	O / C-N (ring)	O / N-C (ring)	C / O-N (ring)
	1	2	3	4	TS 1/2	TS 2/3	TS 2/4
State	$^2\Pi$	$^2A''$	$^2\Pi$	$^2A'$	$^2A''$	$^2A''$	$^2A'$
Symmetry	$C_{\infty v}$	C_s	$C_{\infty v}$	C_s	C_s	C_s	C_s
Energy (Hartrees)	-167.61886	-167.50121	-167.52080	-167.43067	-167.58434	-167.47276	-167.42122
Rel. Energy (kcal mol^{-1})	0.0	73.8	61.5	118.1	82.1	91.7	124.0
Adiab. EA(eV)	3.408 (3.609)[b]	2.414	3.198	1.706			
Bd Length(Å)							
O-C	1.186 (1.176)[a] (1.206)[b]	1.402		1.179	1.413		1.145
C-N	1.230 (1.233)[a] (1.200)[b]	1.339	1.211 (1.212)[a]		1.246	1.250	
N-O		1.429	1.228 (1.216)[a]	1.339		1.375	2.040
Bond Angles (°)							
O-C-N	180.0	62.8			86.9		
O-N-C		60.8	180.0			99.8	
C-O-N		56.4		165.0			120.1

[a] From ref 28, calculated at CCSD(T)/aug-cc-pVQZ level of theory. [b] From ref 19, experimental value.
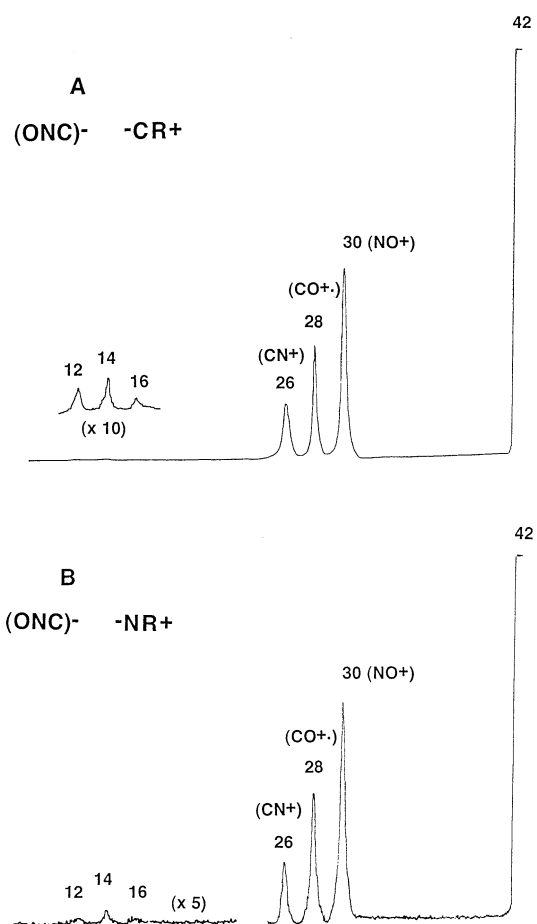
Figure 3. $^-$CR$^+$ (A) and $^-$NR$^+$ (B) mass spectra of (ONC)$^-$. For experimental details see the Experimental Section. VG ZAB 2HF mass spectrometer.

global minimum on the neutral potential surface, with the oxazirinyl radical (**2**), the fulminate radical (**3**), and CON (**4**), being higher in energy than (**1**) by 73.8, 61.5, and 118.1 kcal mol^{-1}, respectively, at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory. The data for **1**−**3** are similar to those reported by Pak et al.[28] The calculated bond lengths of the

cyanate radical (using our level of theory) are within 0.03 Å of the experimental values (see Table 2), with the calculated adiabatic electron affinity being 3.408 eV (experimental 3.609 eV[20]). The adiabatic electron affinity of the fulminate radical is calculated to be 3.198 eV. The structures of these radicals are difficult to describe using simple valence bond theory. For example the cyanate radical (**1**) has OC and CN bonds with (short) double bond character; the closest valence bond structure is **D**. In contrast, the ON and NC bonds of the fulminate radical (**3**) show (short) single bond and (long) triple bond character, respectively; the closest valence bond representation being **E**.[65]

$$O=C=N \cdot \qquad \cdot \overset{+}{O-N} \equiv C^-$$

$$\mathbf{D} \qquad\qquad \mathbf{E}$$
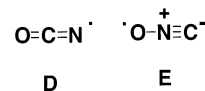
Is is now necessary to ascertain the likelihood of rearrangement of either (OCN) (**1**) or (ONC) (**3**) during the experimental conditions of the one-electron oxidation process of the respective anions. The potential surface describing the interconversion of the four neutrals is shown in Figure 4, and details of the minima and transition states shown in Figure 4 are listed in Table 2. The interconversion of **1** through **2** to **3** is endothermic by 61.5 kcal mol^{-1}, with a maximum barrier of 91.7 kcal mol^{-1}. This energy requirement is too high for isomerization of neutral **1** to either **2** or **3** in a neutralization experiment. The rearrangement of the fulminate radical (ONC) (**3**) through the oxazirinyl radical (**2**) to the cyanate radical (**1**) is strongly exothermic (−61.5 kcal mol^{-1}) with a barrier of 30.2 kcal mol^{-1}. This rearrangement could occur if the fulminate radical contains ≥30.2 kcal mol^{-1} of excess energy following the vertical one-electron oxidation of the corresponding anion.

The excess energies of the neutrals produced by Franck−Condon one-electron oxidation of the cyanate and fulminate anions should be small, because the structures of the anions and neutral radicals are similar in both cases (Tables 1 and 2). The Franck−Condon excess energy of the neutral formed by vertical oxidation is equal to the difference in energy between the ground state neutral, and that of the neutral with the anion geometry on the neutral surface. This is only 2.7 and 2.0 kcal mol^{-1} for the neutrals OCN and ONC formed by vertical one-electron oxidation of (OCN)$^-$ and (ONC)$^-$, respectively. These
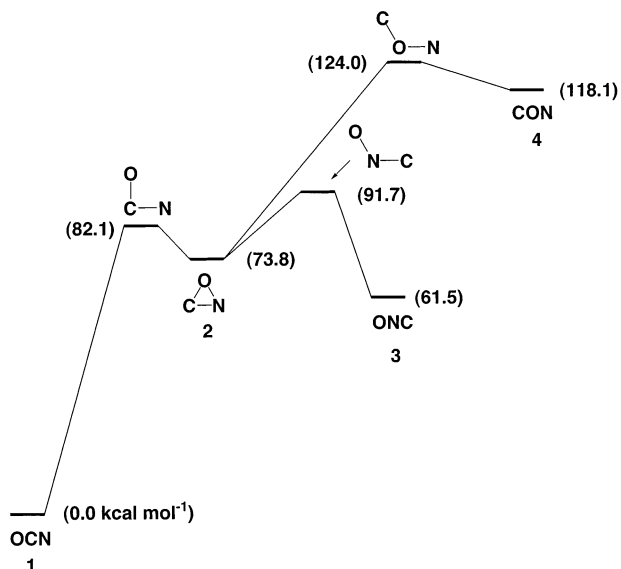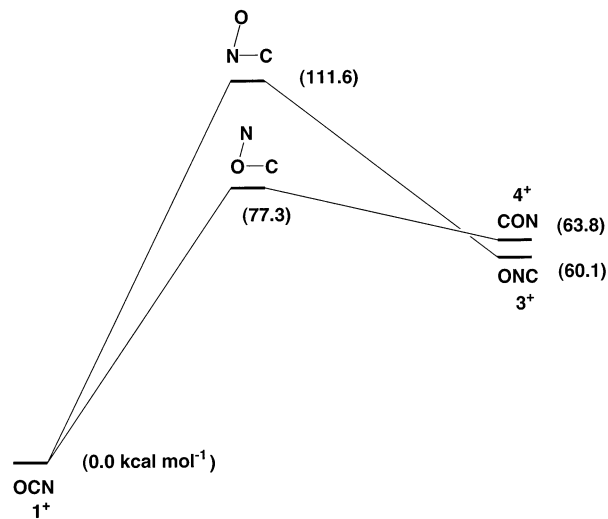
Figure 4. Calculated pathway for conversion of OCN isomers on the neutral potential energy surface. The energies are shown in kcal mol^{-1} and are calculated at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory. For details of minima and transition states see Table 2.

Figure 5. Calculated pathway for conversion of OCN isomers on the triplet cation potential energy surface. The energies are shown in kcal mol^{-1} and are calculated at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory. For details of minima and transition states see Table 4.

are minimum energies; it is possible for the neutrals to have higher excess energies as a consequence of (i) some formation energy of the precursor anions being transferred during the neutralization process and (ii) some collision energy being transferred to the neutral accompanying or following formation. Even so, it is debatable whether even the rearrangement ONC (**3**) to (OCN) (**1**) (see Figure 4) could occur under NR conditions.

The $^{-}$NR^{+} and $^{-}$CR^{+} spectra shown in Figures 2 and 3 should now be compared. The first thing to note is that both $^{-}$NR^{+} spectra show pronounced recovery signals at m/z 42: this means that the neutrals formed are stable for the period of the $^{-}$NR^{+} experiment (10^{-6} s). The second observation is that the abundances of the fragment peaks noted in the $^{-}$NR^{+} and $^{-}$CR^{+} spectra of (OCN)$^{-}$ are the same (Figure 2).

The same scenario pertains for the two spectra of (ONC)$^{-}$ (Figure 3). Because the $^{-}$NR^{+} and $^{-}$CR^{+} spectra show the same amount of (partial) rearrangement, this means that (i) the rearrangements must be reactions of the cations formed in both $^{-}$NR^{+} and $^{-}$CR^{+} spectra and (ii) there is no detectable neutral decomposition process operating for either OCN or ONC. It can be concluded from these observations that stable cyanate and fulminate radicals are formed by Franck−Condon oxidation of their anions, and they neither rearrange nor decompose during their microsecond lifetime. The lack of decomposition of neutral cyanate and fulminate is supported by the data (determined at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G+(d) level of theory) listed in Table 3 (Supporting Information). None of the decomposition processes listed for **1** or **3** have energies less than 100 kcal mol^{-1}.[66]

Rearrangement Pathways of the Cations [OCN]$^{+}$ and [ONC]$^{+}$. Each of the cationic isomers **1^{+}**−**4^{+}** has a singlet and a triplet form: in each case, the triplet is the lower energy state. Structures and energies of triplet and singlet cations are listed in Tables 4 and 5 (Supporting Information). There is very little difference in the structure of each triplet and singlet pair. The differences in energy of triplet and singlet cations are **1^{+}** (36.3), **2^{+}** (the triplet state of **2^{+}** is unstable), **3^{+}** (16.8), and **4^{+}** (47.2 kcal mol^{-1}). One difference noted in both Tables 4 and 5 (Supporting Information) is that the cyanate cations are linear,

whereas the fulminate cations are bent (the ONC angles are 160 and 163° for the triplet and singlet respectively).

Comparison of the spectra recorded in Figures 2 and 3 shows that there is more rearrangement of the fuminate cation (Figure 3) than of the cyanate cation (Figure 2). This can be seen qualitatively by comparing the relative abundances of the peaks formed by rearrangement in each spectrum; i.e., m/z 28 (CO$^{+\bullet}$) in Figure 3 is significantly larger than m/z 30 (NO^{+}) in Figure 2. It is also necessary to take account of the energetics of these two decomposition processes: that producing NO^{+} from (ONC)$^{+}$ needs significantly less energy than the process that forms CO$^{+\bullet}$ from (OCN)$^{+}$ [these two processes are endothermic by 54.1 and 125.7 kcal mol^{-1}, respectively (see Table 3, Supporting Information)]. Rearrangement of the fulminate cation is therefore a significant process, whereas rearrangement of the cyanate cation is minor in comparison.

The energies of the collision processes in the vertical one-electron ionizations of the cyanate and fulminate radicals cannot be controlled, so both triplet and singlet cations will be accessed in reionization experiments. The calculated Franck−Condon excess energies consequential on the vertical oxidation to the respective cations are quite small and are as follows:- OCN → ^{1}(OCN)$^{+}$ (+3.6 kcal mol^{-1}), OCN → ^{3}(OCN)$^{+}$ (+8.9 kcal mol^{-1}), ONC → ^{1}(ONC)$^{+}$ (+11.1 kcal mol^{-1}), and ONC → ^{3}(ONC)$^{+}$ (+7.2 kcal mol^{-1}). These excess energies, would not, by themselves, be expected to provide sufficient energy to effect rearrangement of the cations.

Both triplet and singlet cationic potential surfaces have been investigated. The results are summarized in Figures 5 and 6, with all details of minima and transition states listed in Tables 4 and 5 (Supporting Information). The triplet surface is shown in Figure 5. Conversion of ^{3}**1^{+}** to either ^{3}**3^{+}** or ^{3}**4^{+}** seems most unlikely; both processes are strongly endothermic with barriers of 111.6 and 77.3 kcal mol^{-1}, respectively. The triplet oxazirinyl cation is not an intermediate in either rearrangement pathway. The possibility of rearrangement of the fulminate cation (^{3}**3^{+}** to ^{3}**1^{+}**) is more difficult to assess. The process is exothermic by 60 kcal mol^{-1} with the barrier to the transition state being 51.5 kcal mol^{-1} at the level of calculations used.

A comparison of the data in Figures 5 and 6 shows that the rearrangements involve the higher-energy singlet cations and

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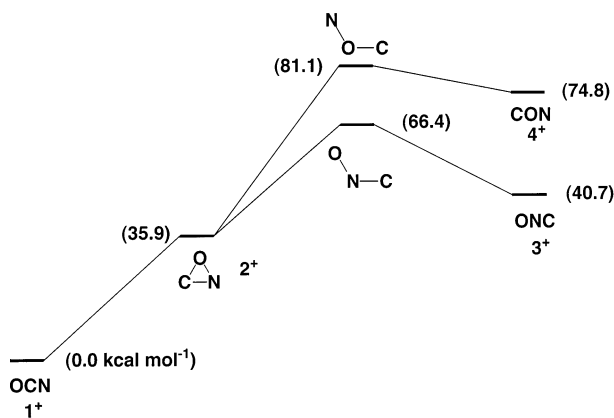
Figure 6. Calculated pathway for conversion of OCN isomers on the singlet cation potential energy surface. The energies are shown in kcal mol^{-1} and are calculated at CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory. For details of minima and transition states see Table 5.

also confirms that the cationic fulminate rearrangement is more energetically favorable than the cationic cyanate rearrangement, as observed experimentally. The rearrangement of the singlet fulminate cation to the singlet cyanate cation is exothermic by 40.7 kcal mol^{-1} on the singlet cation surface and the barrier is only 25.7 kcal mol^{-1}.

The singlet cyanate rearrangement is more difficult to assess. The rearrangement $^1\mathbf{1}^+$ to $^1\mathbf{3}^+$ is endothermic by 40.7 kcal mol^{-1}, with the maximum barrier for the stepwise reaction being 66.4 kcal mol^{-1}. For this reaction to occur, rearranging cations need 55 kcal mol^{-1} in addition to the Franck–Condon energy. It is interesting that this reaction goes via the oxazirinyl cation $^1\mathbf{2}^+$ and that the process $^1\mathbf{1}^+$ to $^1\mathbf{2}^+$ requires 35.9 kcal mol^{-1} (see Figure 6). Perhaps the cyanate cation rearrangement stops at the oxazirinyl cation (rather than proceeding to the fulminate cation), and it is this species that fragments directly to give m/z 30 (NO$^+$). The decomposition $^1\mathbf{2}^+ \rightarrow$ NO$^+$ + C is endothermic by 58.9 kcal mol^{-1} (Table 3, Supporting Information). In contrast, the process $^1\mathbf{2}^+$ to $^1\mathbf{3}^+$ has a barrier of 30.5 kcal mol^{-1} (Figure 6), and the subsequent decomposition of $^1\mathbf{3}^+$ to NO$^+$ requires an additional 54.1 kcal mol^{-1} (Table 4, Supporting Information). The problem here is that it is not possible to say whether the excess energy to enable dissociation of the rearranged cation is imparted (i) as a direct consequence of the collision process effecting the oxidation of the neutral to the cyanate cation or (ii) to a subsequent collision event occurring after the rearranged ion ($^1\mathbf{2}^+$ or $^1\mathbf{3}^+$) has formed. So it is not possible to argue, from available data, whether the minor rearrangement involving the cyanate cation gives the oxazirinyl cation ($^1\mathbf{2}^+$) or the fulminate cation ($^1\mathbf{3}^+$).

Conclusion

(i) Stable cyanate and fulminate anions have been produced in the mass spectrometer by unequivocal syntheses,

(ii) Vertical one-electron oxidations of cyanate and fulminate anions in a collision cell of the mass spectrometer form the cyanate and fulminate radicals which are stable for the microsecond before they are reionized, and

(iii) Following reionization of cyanate and fulminate radicals in a second collision cell, some of the resulting cyanate and fulminate cations rearrange. Available evidence suggests that (a) it is the higher energy singlet states of these two cations that rearrange, (b) the major rearrangement is that which involves conversion of the fulminate cation to the more stable

cyanate cation, and (c) rearrangement of the cyanate cation is a minor process: the rearrangement produces either the oxazirinyl cation $^1\mathbf{2}^+$ and/or the fulminate cation $^1\mathbf{3}^+$.

Supporting Information Available: Table 3 provides information concerning the thermochemistry of the decomposition pathways of neutrals and cations of 1−4. Tables 4 and 5, respectively, give energy and geometry data for minima and transition states on the triplet (Figure 4) and singlet (Figure 5) ONC$^+$ potential surfaces. This material is available free of charge via the Internet at http://pubs.acs.org.

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(64) Normally, the collision induced (negative ion) spectrum of a polyatomic anion can be used as a probe to investigate the energized anion undergoes rearrangement. Both (OCN)$^-$ and (ONC)$^-$ give pronounced parent peaks. The only peaks corresponding to fragment anions are so small as to be only observable at the maximum sensitivity of the instrument (10^6 greater than the sensitivity required to observe the parent anion). The fragment ions correspond to CN$^-$ (*m/z* 26) in both spectra.

(65) Standard bond lengths are taken from the *Handbook of Chemistry and Physics*, 56th ed; CRC Press: 1975; p F-211. C=N (1.322), C≡N (1.158), C–O (1.430), C=O (1.230), and N–O (1.240 Å).

(66) Although CON is a minimum on the neutral potential surface, it is essentially unstable, because it decomposes (presumably over a small barrier) to yield CO and N, in a reaction exothermic by 13.1 kcal mol^{-1}.