The Generation of the Thiocyanate Radical and Cation from the Thiocyanate Anion $[SCN]^-$ in the Gas Phase. The Rearrangements of Neutral and Cationic SCN. A Joint Experimental and Theoretical Study

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A comparison of the neutralization reionization and charge reversal mass spectra of the thiocyanate anion $(SCN)^-$ show that, while the majority of SCN radicals and cations formed by these processes retain their connectivity, a minority of both radicals and cations are energized and rearrange to isomers that dissociate by loss of C. Theoretical calculations at the CCSD(T)aug-cc-pVDZ//B3LYP/6-31+G(d) level indicate that the thiofulminate species (SNC) is the likely rearranged product in each case. Doublet neutral SCN rearranges through cyclic SCN to the thiofulminate radical SNC in a reaction endothermic by 29.9 kcal mol^{-1} and requiring neutral SCN to have an excess energy of $\geq$48.5 kcal mol^{-1}; a result in agreement with a previous theoretical study of SCN. Triplet (ground state) $(SCN)^+$ may rearrange to triplet $(SNC)^+$ in a concerted reaction endothermic by 20.6 kcal mol^{-1} and with a barrier of 45.1 kcal mol^{-1}. Singlet $(SCN)^+$, in contrast, rearranges to singlet $(SNC)^+$ through a cyclic SCN intermediate in a stepwise process endothermic by 18.2 kcal mol^{-1}, with a maximum barrier of 39.5 kcal mol^{-1}.

Introduction

The cyanate $(OCN)^-$ and fulminate $(ONC)^-$ anions may be formed in the ion source of a reverse sector mass spectrometer[1] and converted into the stable cyanate and fulminate radicals in a collision cell by the neutralization reionization technique $(^-NR^+)$.[2] The two radicals are stable for the time frame (10^{-6} s) of the experiment, but when these are converted into the corresponding cations, some interconversion between $(OCN)^+$ and $(ONC)^+$ occurs.[1] Our interest in these systems stems from our interest in interstellar chemistry; HNCO is present in the circumstellar envelope of carbon star IRC+10216,[3] while $(OCN)^-$ is suggested to be present in interstellar ice.[4]

In this paper, we compare the OCN/ONC system with the sulfur analogues thiocyanate (SCN) and thiofulminate (SNC).

The sulfur analogue of HNCO (HNCS) is also present in interstellar dust clouds and circumstellar envelopes,[3] and arguably, $(SCN)^-$ could co-occur with $(OCN)^-$ in interstellar ice. The latter point is particularly relevant since the reaction between $(SCN)^-$ and hydrogen peroxide is known to give the antibiotic hypothiocyanite anion $(OSCN)^-$,[5,6] perhaps the first natural antimicrobial species. The present investigation is an $^-NR^+$ study of the thiocyanate anion, initiated to see whether the chemistry of the thiocyanate anion, neutral, and cation mirrors that of the corresponding cyanate system.

An early report indicates that $(SCN)^-$ may be produced by the reaction between CS_2 and NH_2^-.[7] The photoelectron spectrum of $(SCN)^-$ has been studied giving the adiabatic electron affinity of the thiocyanate radical as 3.537 ± 0.005 eV.[8] Theoretical calculations have been reported.[9,10] A reaction-coordinate calculation at the CCSD(T) level of theory indicates that the isomerization of the thiocyanate anion $(SCN)^-$ to the thiofulminate anion $(SNC)^-$ is endothermic by 36.1 kcal mol^{-1} with the barrier to the transition state being 62.6 kcal mol^{-1}.[10]

The thiocyanate radical system and its derivatives have been much studied. There have been reports of the laser-induced fluorescence spectrum,[11] photolysis,[12] photoabsorption,[13] and photodissociation of RNCS and RSCN (R = H, CH_3, C_2H_5).[14,15] Photoionization mass spectrometry gives an adiabatic IP of 10.689 ± 0.005 eV and $\Delta H^\circ_f \leq 72.7 \pm 0.8$ kcal mol^{-1},[16] and there have been reports of electron resonance spectra,[17] the emission spectrum,[18,19] the microwave spectrum,[20] rovibrational states,[21] and spin−orbit splitting.[22] Some neutral−neutral reactions (e.g., with NO and NO_2) have been described.[23] A number of theoretical studies have been carried out for the thiocyanate radical;[19,22,24−27] the latest involves large-scale MRCI calculations, which indicate that the conversion of the thiocyanate radical to the thiofulminate radical is endothermic by 29.7 kcal mol^{-1}, with an overall barrier of 57.5 kcal mol^{-1}.[27]

In comparison, the thiofulminate system has been less studied. Thiofulminate ligands are known in inorganic systems,[28] and a number of nitrile N-sulfide analogues have been prepared.[29] As mentioned above, the SNC−SCN anion[10] and radical[27] interconversions have been investigated from a theoretical viewpoint and suggest these reactions to be facile.

Experimental Section

A. Mass Spectrometric Methods. For a detailed description of the experiments and the instrument used, see ref 30. 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 $(SCN)^-$ anion was 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 precursor CH_3SCN was introduced into the ion source via the septum inlet at 100 °C to give a measured source pressure of 10^{-5} Torr inside the source housing followed by water (the

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precursor of the HO$^-$ anion) to give a total pressure of 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 (SCN)$^-$ 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.[31] Product ions resulting from CID were recorded by scanning E.

Neutralization−reionization[2] ($^-$NR$^+$ and $^+$NR$^+$) experiments were performed for B mass-selected anions and cations (respectively), utilizing the dual collision cells located between sectors B and E. Neutralization of ions was achieved by collisional electron detachment using O_2 (at 80% transmittance) as collision gas, while 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[32] were recorded using single collision conditions in collision cell 1 (O_2, 80%T).

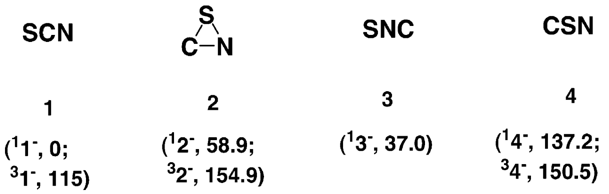
B. Precursor Neutrals. Methylthiocyanate, carbon disulfide, and acetonitrile were commercial samples and were used without further purification.

C. Theoretical Methods. Geometry optimizations were carried out with the Becke 3LYP method[33,34] using a modest 6-31+G(d) basis set within the Gaussian 98 suite of programs.[35] 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 then scaled[36] by 0.9804 and used as a zero-point correction for the electronic energies calculated at this and higher levels of theory. B3LYP/6-31+G(d) has previously been used for geometry optimizations of anionic carbon clusters and has demonstrated good correlation with structures calculated using high-level coupled-cluster approaches.[37,38] 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,[39] but the method continues to be used with success.[40,41] More accurate energies for the B3LYP geometries were determined using the CCSD(T) method,[42−47] together with the Dunning aug-cc-pVDZ basis set.[48,49] All calculations were carried out on Power Challenge supercomputers at the Australian National University Supercomputing Facility (Canberra).

Results and Discussion

Theoretical Calculations of Anions ($\mathbf{1}^-$−$\mathbf{4}^-$). The initial aims of this study were to make the thiocyanate and thiofulminate anions [(SCN)$^-$ and (SNC)$^-$ respectively], to convert these anions to the corresponding neutrals by vertical one-electron oxidation, and to ascertain whether these neutrals are stable or rearrange during or after the neutralization step. Before undertaking the experimental part of this project, it is necessary to determine (i) how many stable isomers are present on the anion potential surfaces and (ii) whether any of these anions could interconvert under the experimental conditions used for the neutralization experiment. Theoretical studies show that there are seven such structures. The bond connectivities of these structures are shown in Chart 1. There are singlet anions $^{1}\mathbf{1}^-$−$^{1}\mathbf{4}^-$ and triplet anions $^{3}\mathbf{1}^-$, $^{3}\mathbf{2}^-$, and $^{3}\mathbf{4}^-$. The triplet form of the thiofulminate anion $^{3}\mathbf{3}^-$ is not stable at this level of theory. The relative energies of the seven structures are shown in Chart 1. The singlet state is the ground state of each anion. Since the singlet states of the anions are significantly more stable than the corresponding triplets, we have not considered the triplet states of the anions further in this study.

CHART 1



The geometries of the four singlet anions were calculated at the B3LYP/6-31+G(d) level of theory. Energies of the four anions were calculated at the CCSD(T)aug-cc-pVDZ//B3LYP/6-31+G(d) level. The data for $^{1}\mathbf{1}^-$−$^{1}\mathbf{3}^-$ are similar to those obtained previously for this system.[10] The structures of thiocyanate anion $^{1}\mathbf{1}^-$ and thiofulminate anion $^{1}\mathbf{3}^-$ may be approximated by the valence bond structures $^-$S−C≡N and $^-$S−N$^+$≡C$^-$, while the thio-oxazirinyl anion $^{1}\mathbf{2}^-$ essentially has an N═C bond with two long NS and CS single bonds. The relative energies of the four anions with respect to the thiocyanate anion [$^{1}\mathbf{1}^-$, (SCN)$^-$, 0 kcal mol^{-1}] are the thio-oxazirinyl anion ($^{1}\mathbf{2}^-$, +58.9 kcal mol^{-1}), the thiofulminate anion ($^{1}\mathbf{3}^-$, +37.0 kcal mol^{-1}), and (CSN)$^-$ ($^{1}\mathbf{4}^-$, +137.2 kcal mol^{-1}).

Possible interconversions of the minima on the singlet anion potential surface are shown in Figure 1. Full details of the minima and transition states shown in Figure 1 are listed in Table 1. These results are qualitatively similar to those reported earlier,[9,10] but there are differences in the detail. The results shown in Figure 1 indicate that $^{1}\mathbf{1}^-$ can rearrange through $^{1}\mathbf{2}^-$−$^{1}\mathbf{3}^-$, provided the system has an excess energy of ≥60.4 kcal

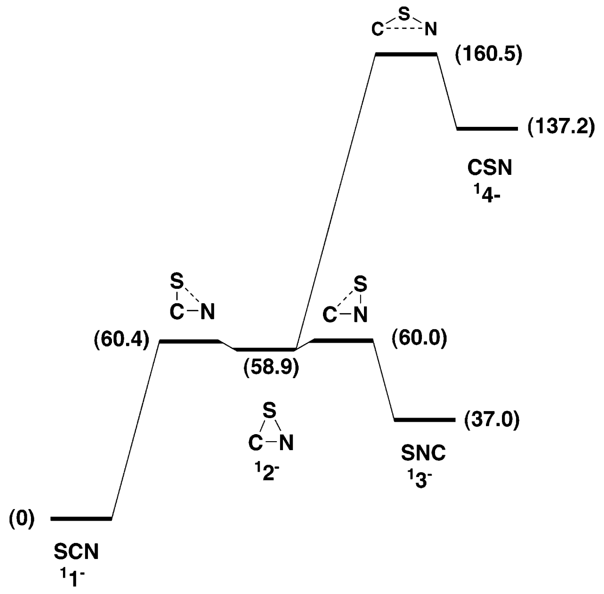
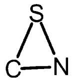
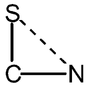
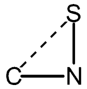
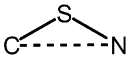


Figure 1. Interconversion of singlet (SCN)$^-$ to singlets (SNC)$^-$ and (CSN)$^-$. Geometries are at the B3LYP/6-31+G(d) level of theory. Relative energies are in kcal mol^{-1} (CCSD(T)-aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory). Formulas drawn in the figure show bond connectivities only; for full structural details, see Table 1.

TABLE 1: Singlet Anion Potential Surface

	S—C—N		S—N—C	C—S—N			
	1	**2**	**3**	**4**	**TS 1/2**	**TS 2/3**	**TS 2/4**
State	$^1\Sigma$	$^1A'$	$^1\Sigma$	$^1\Sigma$	$^1A'$	$^1A'$	$^1A'$
Symmetry	$C_{\infty v}$	C_s	$C_{\infty v}$	$C_{\infty v}$	C_s	C_s	C_s
Energy (Hartrees)[a]	-490.37718	-490.28337	-490.31824	-490.15850	-490.28087	-489.80118	-490.12138
Relative Energy (kcal.mol^{-1})	0.0	58.9	37.0	137.2	60.4	60.0	160.5
Dipole Moment	1.62	0.64	1.41	0.50			
Bond lengths (Å)[b]							
NC	1.183	1.222	1.184		1.206	1.209	2.751
CS	1.672	2.044		1.577	1.945	2.375	1.666
SN		1.977	1.687	1.536	2.227	1.907	1.571
Bond angle (o)[b]							
NCS	180.0	69.3			86.6		
SNC		75.3	180.0			96.8	
CSN		35.3		180.0			116.4

[a] CCSD(T)/aug-cc-pVDZ level of theory, including zero-point energy (calculated from vibrational frequencies at the B3LYP/6-31+G(d) level of theory and scaled by 0.9804). [b] B3LYP/6-31+G(d) level of theory.

TABLE 2: Singlet Anion Dissociation Energies (kcal mol^{-1})[a]

NCS	→	NC^-	+	S	115.4
NCS	→	CS^-	+	N	237.8
SNC	→	NS^-	+	C	170.5
SNC	→	NC^-	+	S	78.4

[a] Energies are from the CCSD(T)/aug-cc-pvdz/B3LYP/6-31+G(d) (scaled by 0.9804) level of theory.

mol^{-1} at this level of theory. The rearrangement to give $^1\mathbf{4}^-$ $(CSN)^-$ is a high energy process and need be considered no further. Our previous experience with negative-ion rearrangements suggests that a barrier of 60.4 kcal mol^{-1} is too high to effect conversion of the thiocyanate anion to the thiofulminate anion under the experimental conditions used for the formation of (and one-electron oxidation of) the thiocyanate anion. However, the reverse process, the conversion of the thiofulminate anion to the more stable thiocyanate anion, requires an excess energy of ≥23 kcal mol^{-1}; this process might well occur under the collisional conditions used to effect the Franck−Condon oxidation of $(SNC)^-$ to SNC.

The thermochemistry of possible decomposition processes of $^1\mathbf{1}^-$ and $^1\mathbf{3}^-$ have been calculated and are shown in Table 2. These are all more energetic than the rearrangements between $^1\mathbf{1}^-$ and $^1\mathbf{3}^-$.

Attempted Formation of $(SCN)^-$ and $(SNC)^-$: $^-CR^+$ and $^-NR^+$ Data. The thiocyanate anion is a particularly stable species and can be formed by electron impact on methylthiocyanate, i.e., $CH_3SCN + e \rightarrow (SCN)^- + CH_3^\bullet$. The situation is not so clear cut for the fulminate anion. Wentrup et al. have reported that the reaction between CS_2 and nitriles gives neutral nitrile N-sulfides.[29] Dissociative electron capture of such species should yield the fulminate anion, e.g., $CH_3CNS + e \rightarrow (SNC)^- + CH_3^\bullet$. When CS_2 is allowed to react with CH_3CN in the chemical ionization source of the ZAB 2HF mass spectrometer, a pronounced peak at *m*/*z* 58 is observed.

The CID mass spectrum of the thiocyanate anion shows minor fragmentations to give small peaks at *m*/*z* 44 ($CS^{\bullet-}$), 32 ($S^{\bullet-}$), and 26 (NC^-). These dissociations are consistent with an anion bond connectivity SCN. The CID spectrum of the supposed thiofulminate anion "$(SNC)^-$" is identical with that of the thiocyanate anion (Table 3). Whether this means that the reaction between carbon disulfide and acetonitrile gives (i) the thiocyanate anion directly or (ii) the thiofulminate anion as the initial product, which then rearranges under CID conditions to the thiocyanate anion (cf. Figure 1, the barrier for this reaction is only 23 kcal mol^{-1}), is not clear. We have also measured the spectra of the analogous positive ion *m*/*z* 58 formed from CS_2 and CH_3CN. The CID and $^+NR^+$ spectra of *m*/*z* 58 are shown in Table 3. These data are consistent with a decomposing thiocyanate cation, not a thiofulminate cation.

TABLE 3: CID Spectra of $(SCN)^-$ and "$(SNC)^-$" and CID and $^+NR^+$ Spectra of ("SNC)$^+$"

	negative ion spectra (fragment ions only, *m*/*z* (loss) relative abundance)
CID $(SCN)^-$	44 (N) 100; 32 (CN) 75; 26 (S) 30
CID "$(SNC)^-$"	44(N): 32 (CN): 26 (S) (ca 3:2:1) − very weak spectrum, background noise significant
	positive ion spectra (*m*/*z* (loss) relative abundance)
CID "$(SNC)^+$"	58(parent)100; 44 (N) 10; 32 (CN) 5; 26 (S) 1
$^+NR^+$ "$(SNC)^+$"	58(parent)100; 44 (N) 15; 32 (CN) 26; 26 (S) 2

The $^-CR^+$ and $^-NR^+$ spectra of $(SCN)^-$ are recorded in Figure 2. Both spectra are very intense and reproducible. The $^-CR^+$ and $^-NR^+$ spectra of *m*/*z* 58 (from carbon disulfide and acetonitrile) are identical with those of $(SCN)^-$. The $^-CR^+$ spectrum is produced by two-electron vertical oxidation of the anion to the corresponding cation. The cation so formed may then undergo collisions with neutrals and, as a consequence, show fragmentations in the $^-CR^+$ spectrum. The majority of fragment peaks in Figure 2A are consistent with a cation of connectivity $(SCN)^+$ [e.g., *m*/*z* 44 ($^-$N), 32 ($^{-\bullet}$CN), and 26 ($^-$S)]. However, there is a small peak at *m*/*z* 56, corresponding to loss of C, a fragmentation that cannot come from $(SCN)^+$ but may arise from the corresponding thiofulminate cation $(SNC)^+$.

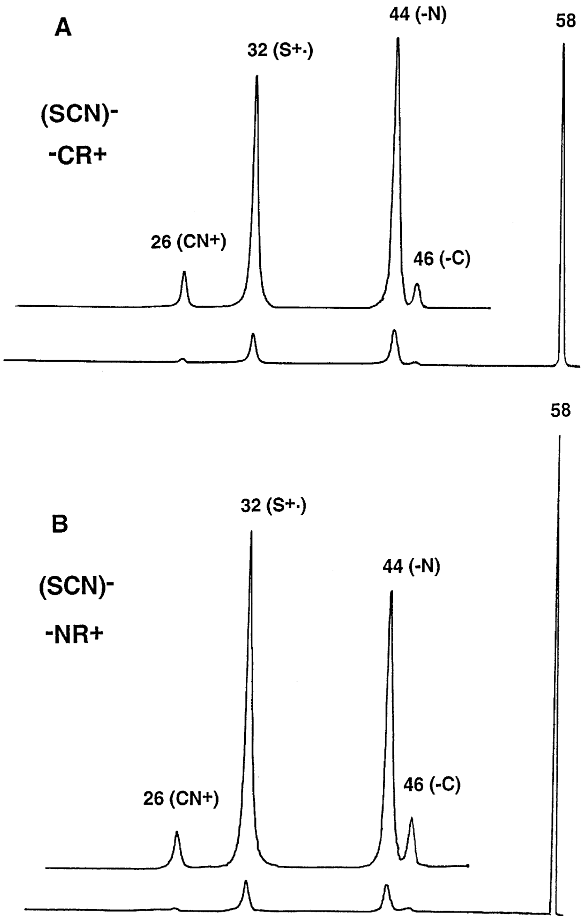


Figure 2. (A) $^{-}$CR^{+} and (B) $^{-}$NR^{+} spectra of (SCN)$^{-}$. For experimental details, see Experimental section. VG ZAB 2HF mass spectrometer.

The $^{-}$NR^{+} spectrum of (SCN)$^{-}$ shows the same peaks as the $^{-}$CR^{+} spectrum, but the two spectra differ in the relative intensity of some peaks. The $^{-}$NR^{+} spectrum is a composite positive ion spectrum arising from ionization of all neutrals formed during the neutralization process of (SCN)$^{-}$ in the first collision cell. The most obvious difference between the two spectra is that m/z 32 ($S^{\bullet -}$) is larger in the $^{-}$NR^{+} spectrum. This means that a neutral is decomposing to elemental sulfur, which is then ionized in the second collision cell. This could come from either SCN or SNC. To investigate these possibilities, we have calculated dissociation energies for various neutrals (and their cationic analogues). These are listed in Table 4. Dissociations of the neutrals SCN and SNC to S and CN are endothermic by 91 and 61 kcal mol^{-1} respectively. Since dissociation of SNC is favored by 30 kcal mol^{-1}, this suggests the possibility that some of the initially formed thiocyanate radicals are rearranging to decomposing thiofulminate radicals. This evidence by itself is purely circumstantial but, taken together with the observation of a larger loss of C in the NR spectrum (loss of C, NR, and CR ≈ 2:1), means that some of the neutral thiocyanate species are rearranging, probably to thiofulminate radicals. This is a different result than that we obtained for the analogous cyanate and fulminate NR study; in these cases, the neutrals were stable, with rearrangements observed solely for the cations.[1]

The Neutral Rearrangements: Theoretical Considerations. The experimental data outined above indicate that, while the majority of the neutral and cationic SCN species retain that connectivity during the time frame of the NR experiment, there is a minority of both neutrals and cations that rearrange, possibly to thiofulminate species. We have probed the neutral potential surface to investigate these possible rearrangements.

TABLE 4: Dissociation Energies (kcal mol^{-1})

doublet netural dissociation energies (kcal mol^{-1})[a]					
NCS	→	NC	+	S	91.1
NCS	→	CS	+	N	158.4
SNC	→	NS	+	C	126.0
SNC	→	NC	+	S	61.2
triplet cation dissociation energies					
NCS	→	NC^{+}	+	S	163.7
NCS	→	CS^{+}	+	N	179.4
SNC	→	NS^{+}	+	C	96.1
SNC	→	NC^{+}	+	S	143.1
singlet cation dissociation energies					
NCS	→	NC^{+}	+	S	141.6
NCS	→	CS^{+}	+	N	153.7
SNC	→	NS^{+}	+	C	108.7
SNC	→	NC^{+}	+	S	123.4

[a] Energies are from the CCSD(T)/aug-cc-pvdz/B3LYP/6-31+G(d) level of theory (scaled by 0.9804).

Details of the doublet SCN surface are shown in Table 5, with the rearrangement processes shown pictorially in Figure 3. The results are qualitatively similar to those obtained previously using MRCI calculations.[17] The structures of the doublet neutrals are very similar to those of their precursor anions (compare Table 1 and Table 4). The thiocyanate and thiofulminate radicals have similar dipole moments and adiabatic electron affinities (thiocyanate, 2.36 D and 3.36 eV; thiofulminate, 2.22 D and 3.06 eV), and the two radicals are different in energy by only 29.9 kcal mol^{-1}. The mechanisms of the neutral rearrangements are similar to those of the possible anion rearrangements (Figure 1), except that the barriers are less for the neutral processes. The rearrangement of SCN (**1**) through cyclic **2** to SNC has a barrier of 48.5 kcal mol^{-1}. The geometries of $^{1}\mathbf{1}^{-}$ and **1** are very similar (compare Tables 2 and 5), and the calculated excess energy of SCN as a consequence of the vertical Franck−Condon process is close to zero. Thus the excess energy of 48.5 kcal mol^{-1} needed to effect the rearrangement must come from collisions of SCN with neutrals in the first collision cell after the oxidation process, and this value is within the range that we have observed for other neutral rearrangements which occur during $^{-}$NR^{+} experiments.[50] The

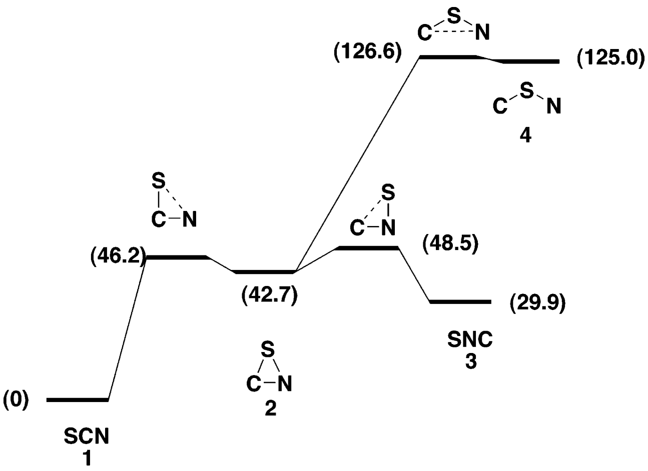
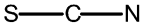
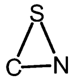
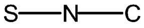
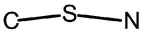
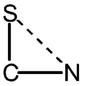
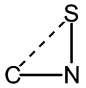
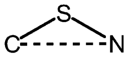


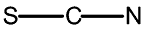
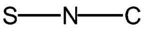
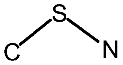
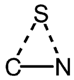
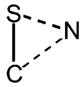
Figure 3. Interconversion of doublet SCN to doublets SNC and CSN. Geometries are at the B3LYP/6-31+G(d) level of theory. Relative energies are in kcal mol^{-1} (CCSD(T)-aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory). Formulas drawn in the figure show bond connectivities only; for full structural details, see Table 5.

TABLE 5: Doublet Neutral Potential Surface

							
	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)[a]	-490.25341	-490.18536	-490.20577	-490.05414	-490.17976	-490.17617	-490.05169
Relative Energy (kcal.mol^{-1})	0.0	42.7	29.9	125.0	46.2	48.5	126.6
Dipole Moment	2.36	1.77	2.22	0.55			
Adiabatic EA (eV)	3.36	2.67	3.06	2.84			
Bond lengths (Å)[b]							
NC	1.186	1.255	1.196		1.204	1.222	3.097
CS	1.637	1.927		1.606	1.851	2.338	1.625
SN		1.79	1.625	1.556	2.201	1.764	1.572
Bond angle (o)[b]							
NCS	180.0	64.5			89.6		
SNC		76.3	180.0			101.6	
CSN		39.2		158.2			151.3

[a] CCSD(T)/aug-cc-pVDZ level of theory, including zero-point energy (calculated from vibrational frequencies at the B3LYP/6-31+G(d) level of theory and scaled by 0.9804). [b] B3LYP/6-31G+(d) level of theory.

TABLE 6: Triplet Cation Potential Surface

					
	$^{3}1^{+}$	**$^{3}3^{+}$**	**$^{3}4^{+}$**	**TS 1/3**	**TS 1/4**
State	$^3\Sigma$	$^3\Sigma$	$^3A''$	$^3A''$	$^3A''$
Symmetry	$C_{\infty V}$	$C_{\infty V}$	C_S	C_S	C_S
Energy (Hartrees)[a]	-489.87300	-489.84011	-489.71060	-489.80118	-489.71051
Relative Energy (kcal.mol^{-1})	0.0	20.6	101.9	45.1	102.0
Dipole Moment	2.25	2.07	1.41		
Bond lengths (Å)[b]					
NC	1.213	1.232		1.228	2.066
CS	1.594		1.676	1.989	1.648
SN		1.561	1.693	1.728	1.775
Bond angle (o)[b]					
NCS	180.0			59.5	55.7
SNC		180.0		82.7	50.1
CSN			90.8	37.7	74.2

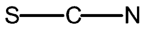
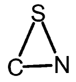
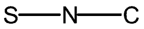
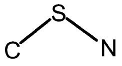
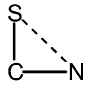
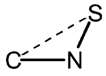
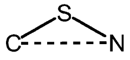
[a] CCSD(T)/aug-cc-pVDZ level of theory including zero point energy (calculated from vibrational frequencies at the B3LYP/6-31+G(d) level of theory and scaled by 0.9804). [b] B3LYP/6-31G+(d) level of theory.

energies of the dissociation processes shown in Figure 2 that occur for the neutrals (in the first cell) and the cations (in the second cell) are recorded in Table 4. It is interesting that some SCN radicals rearrange to SNC, while the cyanate to fulminate rearrangement does not occur under similar conditions. The mechanisms of the cyanate and thiocyanate rearrangements are similar. The difference between the two is that the SCN to SNC rearrangement has a barrier of 48.5 kcal mol^{-1}, whereas the corresponding OCN to ONC rearrangement requires OCN to have an excess energy of ≥91.7 kcal mol^{-1}.[1]

The reverse process SNC to SCN is favorable; the barrier is only 18.6 kcal mol^{-1}, and the reaction is exothermic by 29.9 kcal mol^{-1} at the level of theory used in this study.

Cationic Rearrangements: Theoretical Considerations. The $^-$CR$^+$ spectrum of (SCN)$^-$ (Figure 2A) shows that two-electron vertical oxidation gives mainly (SCN)$^+$ but that there is a minor process in which some (SCN)$^+$ species rearrange to give parent cations that fragment by loss of carbon. The cation situation is complex, because the singlet and triplet forms of each of **1**, **3**, and **4** are within 25 kcal mol^{-1} of each other,

TABLE 7: Singlet Cation Potential Surface

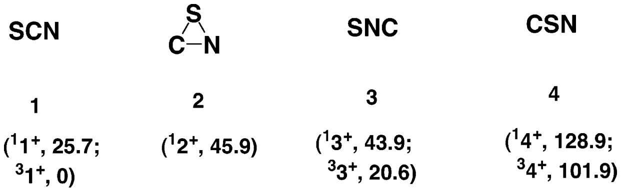
							
	^{1}1$^+$	**^{1}2$^+$**	**^{1}3$^+$**	**^{1}4$^+$**	**TS 1/2**	**TS 2/3**	**TS 2/4**
State	$^1\pi$	$^1A'$	$^1\pi$	$^1A'$	$^1A'$	$^1A'$	$^1A'$
Symmetry	$C_{\infty}V$	C_S	$C_{\infty}V$	C_S	C_S	C_S	C_S
Energy (Hartrees)[a]	-489.83203	-489.79986	-489.80298	-489.66753	-489.78295	-489.76905	-489.64156
Relative Energy (kcal.mol^{-1})	0.0	20.2	18.2	103.2	30.8	39.5	119.5
Dipole Moment	1.98	1.78	1.63	1.76			
Bond lengths (Å)[b]							
NC	1.211	1.354	1.245		1.219	1.266	2.638
CS	1.593	1.824		1.711	1.770	2.326	1.773
SN		1.638	1.547	1.534	2.175	1.647	1.574
Bond angle (o)[b]							
NCS	180.0	59.9			91.5		
SNC		74.5	180.0			105.2	
CSN		45.7		129.5			115.9

[a] CCSD(T)/aug-cc-pVDZ level of theory, including zero-point energy (calculated from vibrational frequencies at the B3LYP/6-31+G(d) level of theory and scaled by 0.9804). [b] B3LYP/6-31G+(d) level of theory.

while cyclic **2** has only a singlet state (see Chart 2). As a consequence, rearrangements of both ^{1}**1**$^+$ and ^{3}**1**$^+$ must be considered. The triplet states of **1**, **3**, and **4** are the ground states of those species. The structures of the cations (Tables 6 and 7) are very similar to those of the corresponding anions and neutrals, with the exceptions of high-energy ^{1}**4**$^+$ and ^{3}**4**$^+$, which are significantly bent with the neutral less so and the anion linear.

The triplet and singlet cation rearrangement coordinates are shown in Figures 4 and 5. Full details of all minima and transition states shown in Figures 4 and 5 are given in Tables 6 and 7, respectively. The rearrangement of ^{3}**1**$^+$ to ^{3}**3**$^+$ is concerted, the barrier is 45.1 kcal mol^{-1}, and the reaction is endothermic by 20.6 kcal mol^{-1} (Figure 4). In contrast, the rearrangement of ^{1}**1**$^+$ to ^{1}**3**$^+$ is stepwise, proceeding through the stable singlet thio-oxazirinyl cation (^{1}**2**$^+$) (Figure 5). The process forming ^{1}**2**$^+$ is endothermic by 20.2 kcal mol^{-1} with a barrier of 30.8 kcal mol^{-1}. If ^{1}**1**$^+$ has an excess energy of ≥39.5 kcal mol^{-1}, further rearrangement to the thiofulminate cation ^{1}**3**$^+$ will proceed. The $^-$CR$^+$ process of (SCN)$^-$ will produce both singlet and triplet (SCN)$^+$. The calculations (discussed above) show that both cations can undergo rearrangement to (SNC)$^+$.

CHART 2[a]



[a] Relative energies are in kcal mol^{-1}.

The reverse processes [(SNC)$^+$ to (SCN)$^+$] are facile. Both singlet and triplet rearrangements are exothermic, with barriers of less than 25 kcal mol^{-1} (see Figures 4 and 5).

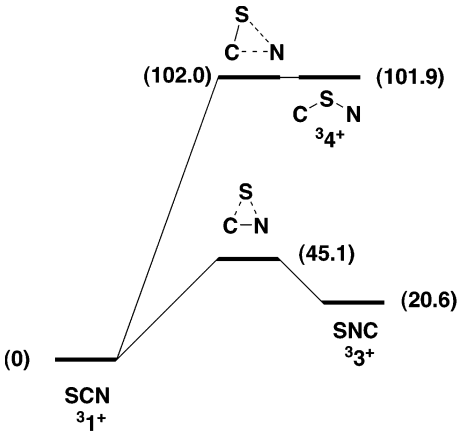


Figure 4. Interconversion of triplet (SCN)$^+$ to triplets (SNC)$^+$ and (CSN)$^+$. Geometries are at the B3LYP/6-31+G(d) level of theory. Relative energies are in kcal mol^{-1} (CCSD(T)-aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory). Formulas drawn in the Figure show bond connectivities only; for full structural details, see Table 6.

Comparison of the energy requirements for the rearrangements (shown in Figures 4 and 5) with the dissociations energies [of (SCN)$^+$ and (SNC)$^+$ (Table 4)] show rearrangements to be favored over dissociation. The lowest-energy cation dissociation is for the loss of C from triplet (SNC)$^+$ (+96.1 kcal mol^{-1}); this is the process in the $^-$CR$^+$ and $^-$NR$^+$ spectra diagnostic of rearrangement.

The excess energies required to effect the thiocyanate to thiofulminate cation rearrangements are significantly higher than the energies given to the cations as a consequence of vertical Franck−Condon oxidations. The cation and anion thiocyanate structures are similar (the differences in CN and CS bond lengths are 0.03 and 0.08 Å), and as a consequence, the calculated Franck−Condon excess energies are small, only 1.5 and 2.1 kcal mol^{-1} for ^{3}**1**$^+$ and ^{1}**1**$^+$, respectively.[51] In order for the rearrangements shown in Figures 4 and 5 to proceed, the thiocyanate cations must be collisionally activated in keV collisions following the vertical oxidation process.

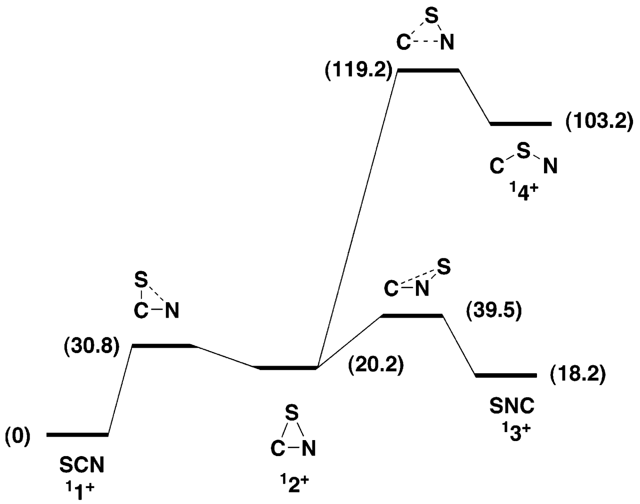


Figure 5. Interconversion of singlet (SCN)$^+$ to singlets (SNC)$^+$ and (CSN)$^+$. Geometries are at the B3LYP/6-31+G(d) level of theory. Relative energies are in kcal mol^{-1} (CCSD(T)-aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory). Formulas drawn in the Figure show bond connectivities only; for full structural details, see Table 7.

Conclusions

1. One-electron vertical oxidation of thiocyanate anions gives thiocyanate radicals, the majority of which are stable for the 10^{-6} s time frame of the neutralization reionization experiment. Some thiocyanate radicals are energized by collision processes occurring after oxidation; the energized species may rearrange to thiofulminate radicals (in agreement with earlier theoretical reports, e.g., ref 27). This should be contrasted with NR experiments with the corresponding cyanate and fulminate anions. These produce both cyanate (OCN) and thiofulminate (ONC) radicals, which are stable for the time frame of the NR experiment.[1]

2. Charge reversal of (SCN)$^-$ yields a majority of cations with SCN bond connectivity, together with some rearranged cations (SNC)$^+$.

3. Theoretical calculations show that (i) anionic and neutral SNC should undergo facile rearrangement to the more stable thiocyanate SCN entity (in agreement with earlier studies)[10,27] and (ii) the cationic rearrangement (SNC)$^+$ to (SCN)$^+$ is more facile than either of the related neutral or anionic rearrangements.

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