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Electron capture of tetracyanoethylene oxide in the gas phase. Rearrangement of the parent radical anion to form $[(NC)_3C]^-$. A joint experimental and ab initio study

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Abstract

Capture of an electron by tetracyanoethylene oxide can initiate a number of decomposition pathways. One of these decompositions yields $[(NC)_3C]^-$ as the ionic product. Ab initio calculations (at the B3LYP/6-31+G* level of theory) indicate that the formation of $[(NC)_3C]^-$ is initiated by capture of an electron into the LUMO of tetracyanoethylene oxide to yield the anion radical $[(NC)_2C\text{–}O\text{–}C(CN)_2]^{-\cdot}$ that undergoes internal nucleophilic substitution to form intermediate $[(NC)_3C\text{–}OCCN]^{-\cdot}$. This intermediate dissociates to form $[(NC)_3C]^-$ (*m/z* 90) as the ionic product. The radical $(NC)_3C^\cdot$ has an electron affinity of 4.0 eV (385 kJ mol^{-1}). Ab initio calculations show that $[(NC)_3C]^-$ is trigonal planar with the negative charge mainly on the nitrogens. A pictorial representation of this structure is the resonance structure formed from three degenerate contributing structures $(NC)_2\text{–}C{=}C{=}N^-$. The other product of the reaction is nominally $(NCCO)^\cdot$, but there is no definitive experimental evidence to indicate whether this radical survives intact, or decomposes to $NC^\cdot$ and CO. The overall process $[(NC)_2C\text{–}O\text{–}C(CN)_2]^{-\cdot} \rightarrow [(NC)_3C]^- + (NCCO)^\cdot$ is calculated to be endothermic by 21 kJ mol^{-1} with an overall barrier of 268 kJ mol^{-1}. (Int J Mass Spectrom 194 (2000) 165–170) © 2000 Elsevier Science B.V.

Keywords: Tetracyanoethylene oxide radical anion; Rearrangement; Tricyanomethyl anion.

1. Introduction

We have recently studied the radical anion $(NC_3N)^{-\cdot}$ and the corresponding neutral as part of an ongoing study of heterocumulene anions and their neutrals [1]. This anion was first formed by Dawson and Nibbering using the process shown in Eq. (1) [2]. We thought that the tetracyanoethylene oxide radical anion should also be a useful precursor of this anion and its corresponding neutral, i.e. both neutral NC_3N and the NC_3N radical anion should be formed by the processes shown in Eqs. (2) and (3). Dissociative electron capture of tetracyanoethylene oxide in the ion source of the mass spectrometer does indeed yield the two product anions [of Eqs. (2) and (3)] in high yield, together with three other anions formed in smaller yield, *m/z* 90 {$[(NC)_3C]^-$, see below}, *m/z* 118, and *m/z* 144. The anion radical *m/z* 144 is formed by capture of an electron by tetracyanoethylene oxide, and the collision induced (CID) tandem mass spectrum of this ion is shown in Fig. 1. Peaks correspond-

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Dedicated to Professor James D. Morrison on the occasion of his 75th birthday.

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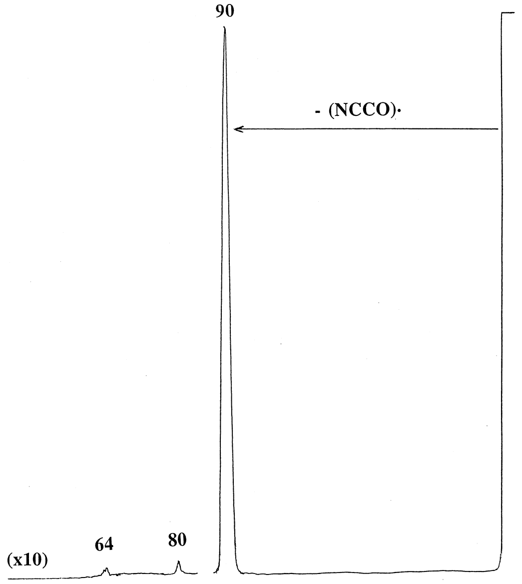
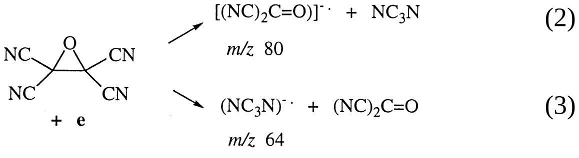


Fig. 1. CID tandem mass spectrum of the anion formed by capture of an electron by tetracyanoethylene oxide (VG ZAB 2HF mass spectrometer). For experimental conditions see Sec. 2.

ing to the ions $(NC_3N)^{-\cdot}$ and $[(NC)_2CO]^{-\cdot}$ are less than 1% in abundance compared with the base peak (*m/z* 90) that is formed by loss of 54 Da from the parent radical anion. The species at *m/z* 144 that produces *m/z* 90 must be different from that which forms the products of Eqs. (2) and (3). The metastable ion spectrum of *m/z* 144 (i.e. that exhibited by *m/z* 144 without any gas in the collision cell) also shows only a peak corresponding to *m/z* 90, but this peak is some hundred times less abundant than that observed in the corresponding CID spectrum

$$CH_2(CN)_2 + O^{-\cdot} \rightarrow \underset{m/z\ 64}{(NC_3N)^{-\cdot}} + H_2O \qquad (1)$$

In this article, we discuss the formation of *m/z* 90



from the detectable species formed by capture of an electron by tetracyanoethylene oxide.

2. Experimental

Collisional induced dissociation (CID), charge reversal (CR), and neutralisation reionisation ($^{-}NR^{+}$) mass spectra (MS/MS) were obtained with a reverse sector VG ZAB 2HF instrument [3]. Full details of the operation of the instrument have been given previously [4]. Specific details were as follows: the chemical ionisation slit was used in the ion source, the ionising energy was 70 eV, the ion source temperature was 150 °C, and the accelerating voltage 7 kV. The sample was introduced into the ion source via the direct probe that was unheated. The measured source pressure of the sample was typically 5×10^{-6} Torr. Tetracyanoethylene oxide readily captures an electron under these conditions. The parent anion was focused using the magnet, fired through the second collision cell (that immediately following the magnetic sector) which contained dioxygen [measured pressure outside the cell, 2×10^{-7} Torr (giving a 10% reduction in the ion beam signal, equivalent to single collision conditions)], and mass-analyzed ion kinetic energy (MIKE) (MS/MS) data were obtained by scanning the electric sector. Charge reversal spectra were obtained in the same manner except that the electric sector voltage was reversed to enable the transmission of positive ions [5]. Neutral reionisation mass spectra ($^{-}NR^{+}$) were carried out using the second and third collision cells operating in tandem (both cells are positioned between the magnetic and electric sectors of the spectrometer). Dioxygen was used in each of the collision cells (pressure 5×10^{-6} Torr) equivalent to a reduction in the main beam of 20% through each collision cell. Full details of the method have been described previously [6].

Tetracyanoethylene oxide was a commercial product. The potassium salt of tricyanomethane was made by a reported method [7].

Ab initio calculations with GAUSSIAN 94 [8] were carried out (using the South Australian Super Computing facility) at the following levels of theory: (1) Full geometry optimisations for all species shown in Fig. 2 were carried out with the Becke 3LYP method [9] using the 6-31+G* basis set. Stationary points were characterised as minima (no imaginary frequencies) by calculation of the frequencies using analytical

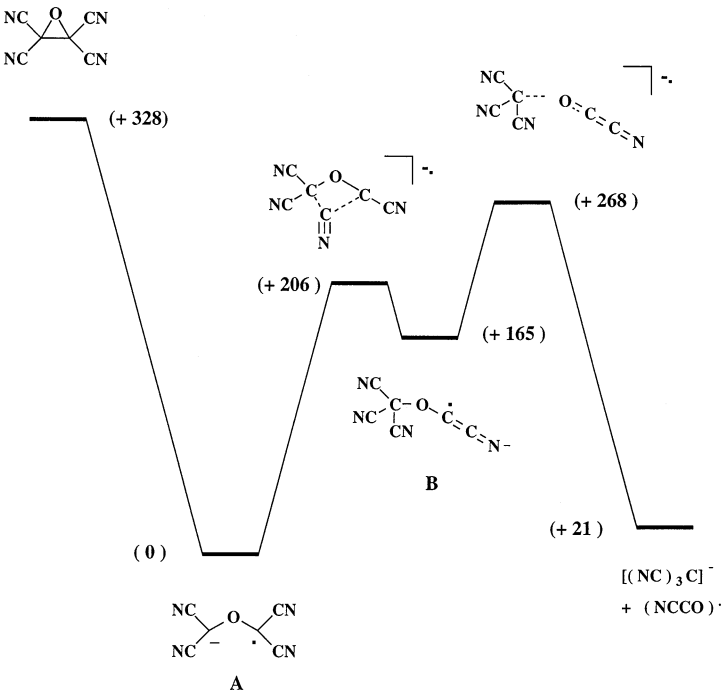


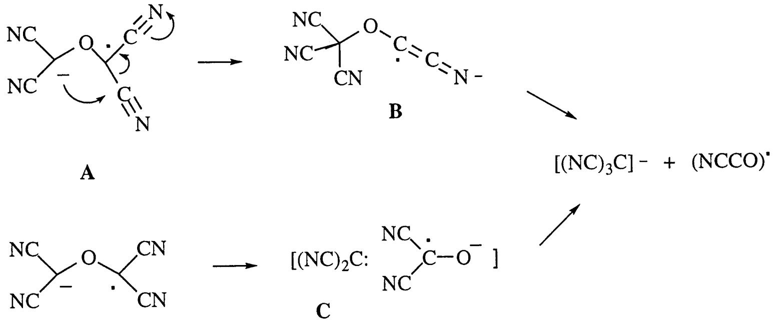
Fig. 2. Ab initio calculations for the reaction forming $[(NC)_3C]^-$. All geometries and energies were computed at the B3LYP/6-31+G* level of theory, with the exception of transition state 2, which was optimised at the HF/6-31G* level of theory and the single point energy calculated at the B3LYP/6-31+G* level.

gradient procedures. Transition states were characterised with one imaginary frequency using analytical gradient procedures. The calculated frequencies were used to determine the zero-point vibrational energies, which were then scaled [10] by 0.9804 and used as a zero-point energy correction for the electronic energies calculated at this or higher levels of theory. (2) The dipole moment of neutral $(NCCO)^{\cdot}$ was deter-

Table 1
CID, CR, and $^-NR^+$ spectra of the *m/z* 144 and 90 ions from tetracyanoethylene oxide, and of $[(NC)_3C]^-$ from $(NC)_3C^-K^+$

Ion (*m/z*)	Mode	Spectrum [*m/z* (relative abundance)]
144	CID	see Fig. 1
	CR	144(58), 118(24), 102(14), 90(29), 76(44), 64(98), 54(100), 50(24), 38(62), 28(2), 26(3), 24(1).
	$^-NR^+$	144(60), 118(100), 102(18), 90(75), 76(76), 64(68), 54(76), 38(78).
90	CID	90, 76(5), 64(100), 50(6), 26(8).
	CR	90(100), 76(33), 64(64), 50(12), 38(32), 26(6).
	$^-NR^+$	90(63), 76(21), 64(100), 50(25), 38(98), 26(8).
$(NC)_3C-$	CID	90, 76(7), 64(100), 50(7), 26(9).
(90)[a]	CR	90(100), 76(32), 64(74), 50(10), 38(22), 26(4).
	$^-NR^+$	90(58), 76(20), 64(100), 50(22), 38(89), 26(7).

[a] When $CH(CN)_3$ is allowed to react with HO^- in the chemical ionisation ion source, the parent anion $[CH(CN)_3]^{-\cdot}$ is formed to the exclusion of $[(NC)_3C]^-$. The ion $[(NC)_3C]^-$ is generated from $KC(CN)_3$ under the conditions of fast atom bombardment mass spectrometry. Argon was used as the FAB gas, and the matrix was meta-nitrobenzyl alcohol/dimethylformamide (1:1). The CID and CR mass spectra of $[(NC)_3C]^-$ were measured as described in Sec. 2.



Scheme 1.

mined using the QCISD/6-311+G** level of theory, in order to be compatible with recent calculations of this system [11]. (3) Calculations of $(NCCO)^-$ were carried out at the B3LYP/aug-cc-pVDZ level of theory.

3. Results and discussion

The base peak in Fig. 1 occurs at *m/z* 90: this corresponds to $[(NC)_3C]^-$ as shown by comparison of the CID, CR, and $^-NR^+$ spectra of source formed *m/z* 90 with those of authentic $[(NC)_3C]^-$ formed by fast atom bombardment mass spectrometry from $K^+(NC)_3C^-$ (Table 1). The CID spectrum of *m/z* 90 is simple, showing loss of $NC^\cdot$ to form $(NC_3N)^{-\cdot}$, whereas both the CR and $^-NR^+$ spectra show the presence of pronounced parent cations together with daughter cations formed by losses of N, $NC^\cdot$, and $2NC^\cdot$ from the parent.

We have explored this unusual rearrangement using ab initio calculations at the B3LYP/6-31+G* level of theory. The initial and key result of the calculations is that addition of an electron to tetracyanoethylene oxide does not produce a stable tetracyanoethylene oxide radical anion. Addition of an electron to the LUMO of tetracyanoethylene oxide initiates specific cleavage of the ring C–C bond to produce a symmetrical ring opened species **A**. Intermediate **A** is 328 kJ mol^{-1} more negative in energy than neutral tetracyanoethylene and must be at least partially collisionally deactivated in the ion source in order for *m/z* 144 to be detected. We can find no evidence on the potential surface of a reaction channel involving electron capture followed by ring opening of the ethylene oxide ring by cleavage of an O–C bond. There are, in principle, two ways that $[(NC)_3C]^-$ might be formed from **A**. The first involves an S_Ni reaction to form intermediate **B*** (see Scheme 1), which cleaves to give $[(NC)_3C]^-$. The second mechanism involves cleavage of the C–O bond of **A** to form reactive intermediate **C** followed by nitrile anion transfer from the dicyanoketone radical anion to the electron deficient site of $(NC)_2C$.

We have investigated both of these processes using ab initio calculations. We believe that the second pathway is the less likely process, because: (1) we have been unable to find a pathway from **A** to intermediate **C** (**C** lies 145 kJ mol^{-1} above **A**), and (2) nitrile anion donation within intermediate **C** is unfavourable because the dicyanoketone radical anion is a particularly poor nitrile anion donor (the reaction $[(NC)_2CO]^{-\cdot} \rightarrow NC^- + (NCCO)^\cdot$ is endothermic by 276 kJ mol^{-1} at the B3LYP/6-31+G* level of theory. Although formation of CN^- via the above process is unfavourable, this may be offset to some extent by the exothermicity of the overall process forming $[(NC)_3C^-]$.

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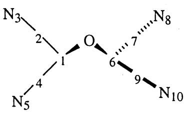
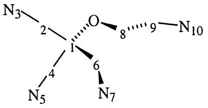
* This S_Ni reaction could, in principle, proceed first to a substituted oxetan ring intermediate which could ring open to yield **B**. Ab initio calculations indicate that there is no reactive intermediate formed on the potential surface between **A** and **B**.

Table 2
Energies and geometric parameters of all species shown in Fig. 2 (B3LYP/6−31+G*)



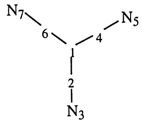
epoxide anion A

Energy	-522.78224Hartrees
Symmetry	C_1
C_1C_2	1.4009Å
C_2N_3	1.1740Å
C_1O	1.3793Å
$C_2C_1C_4$	121.5°
C_1OC_6	120.0°
Dih $C_1OC_6C_7$	31.1°



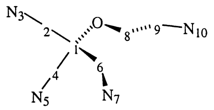
transition state 1

Energy	-522.70394 Hartrees
Symmetry	C_1
C_1C_2	1.5011Å
C_2N_3	1.1607Å
C_1C_6	1.5135Å
C_6N_7	1.1667Å
C_1O	1.3868Å
OC_8	1.4462Å
C_8C_9	1.3946Å
C_9N_{10}	1.1857Å
$C_2C_1C_4$	107.9°
$C_1C_6N_7$	159.4°
C_1OC_8	106.5°
OC_8C_9	109.7°
$C_8C_9N_{10}$	171.5°



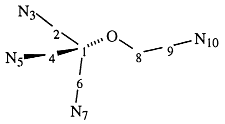
Product [(NC)₃C]⁻

Energy	-316.69244 Hartrees
Symmetry	Cs
C_1C_2	1.4126Å
C_2N_3	1.1732Å
$C_2C_1C_4$	120°



Intermediate B

Energy	-522.68019 Hartrees
Symmetry	C_1
C_1C_2	1.4971Å
C_2N_3	1.1331Å
C_1O	1.3469Å
OC_8	1.4764Å
C_8C_9	1.4169Å
C_9N_{10}	1.1589Å
$C_2C_1C_4$	106.8°
C_1OC_8	108.9°
OC_8C_9	104.7°
$C_8C_9N_{10}$	174.6°



transition state 2

Energy	-522.70394 Hartrees
Symmetry	C_1
C_1C_2	1.4534Å
C_2N_3	1.1370Å
C_1O	1.7376Å
OC_8	1.3487Å
C_8C_9	1.3905Å
C_9N_{10}	1.1613Å
$C_2C_1C_4$	113.1°
C_1OC_8	110.5°
OC_8C_9	112.1°
$C_8C_9N_{10}$	175.2°

[a] Full geometric details are available as supplementary data from the author.

We propose that $[(NC)_3C]^-$ is formed from **A** following the S_Ni process **A** to **B**. Ab initio calculations for this process are summarised in Fig. 2. Details of geometries and energies of all species shown in Fig. 2 are listed in Table 2. The overall reaction is endothermic by 21 kJ mol^{-1}, a reaction clearly assisted by the stability of $[(NC)_3C]^-$ $[(NC)_3C^{\cdot}$ is calculated to have an electron affinity of 4.0 eV (386 kJ mol^{-1})]. The anion $[(NC)_3C]^-$ is trigonal planar with the negative charge shared mainly by the nitrogen atoms. This structure may be represented in valence bond terms as the resonance hybrid of the three degenerate canonical structures $(NC)_2$–C=C=N$^-$.

The neutral product of the rearrangement reaction summarised in Fig. 2 is shown as the radical $(NCCO)^\cdot$. Does this neutral survive intact during the reaction conditions, or is it sufficiently energised to decompose to carbon monoxide and the nitrile radical? The positive ion spectrum produced by all the neutrals formed from *m/z* 144 (the $^{-}NR^{+}$ spectrum) [12] is listed in Table 1. The abundances of the peaks at *m/z* 54 $[(NCCO)^{+}]$ are 76% and 100% (the base peak) of the $^{-}NR^{+}$ and CR spectra, respectively. The larger abundance of *m/z* 54 in the CR spectrum suggests that $(NCCO)^{+}$ is formed principally by decomposition of the charged reversed parent cation *m/z* 144 rather than by ionisation of neutral $(NCCO)^\cdot$. Thus we are unable to provide evidence for, or against, the formation of stable $(NCCO)^\cdot$ during the rearrangement process.

Even so, radical $(NCCO)^\cdot$ is an interesting species because it is intermediate in structure between the short-lived species OCCO [13] and stable cyanogen NCCN. Neutral $(NCCO)^\cdot$ has been made previously by electron capture of $(NCCO)^{+}$, and since the $^{+}NR^{+}$ spectrum [of $(NCCO)^{+}$] shows a recovery signal at *m/z* 54, neutral $(NCCO)^\cdot$ has a lifetime of at least 10^{-6} s [14]. A recent ab initio study (at the QCISD/6-311+G** level of theory) of NCCO and $(NCCO)^{+}$ has explored the structures and energies of these species [11], but has not reported the dipole moment or the adiabatic electron affinity of the neutral. The neutral radical may be represented in valence bond terms O=C–C≡N with an OCC angle of near 130° [11]. We have calculated the dipole moment of $(NCCO)^\cdot$ (at the QCISD/6-311+G* level of theory) to be 1.17 Debye. We have also investigated the anion $(NCCO)^{-}$ at a number of levels of theory (the highest being B3LYP/aug-cc-pVDZ) and report that this anion is unstable with respect to decomposition to NC^{-} and CO. This explains why no peak at *m/z* 54 is observed in the CID mass spectrum of *m/z* 144.

In conclusion, we have provided evidence, based on both experimental and ab initio studies that capture of an electron by tetracyanoethylene oxide forms symmetrical intermediate **A**, which then undergoes an internal cyclisation/dissociation sequence, terminating with the formation of $[(NC)_3C]^{-}$ as the ionic product. The other product is nominally $(NCCO)^\cdot$, but there is no definitive experimental evidence to indicate whether this radical survives intact or decomposes to CO and $NC^\cdot$.

Acknowledgements

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