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Reaction of AgOCN with NO, NO_2, $ClNO_2$, ClNO, and BrNO: Evidence of the Formation of $OCN-NO_2$ and OCN−NO

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Reactions of silver cyanate with binary nitrogen oxides, NO and NO_2, and ternary nitrogen oxohalides, $ClNO_2$, ClNO, and BrNO, were studied by means of gas phase IR spectroscopy. The experimental data for the neat reactions of AgOCN with NO_2 and AgOCN with $ClNO_2$ are compatible with the formation of an intermediate, short-lived $OCN-NO_2$ molecule, which undergoes cleavage−rearrangement to give N_2O and CO_2. In contrast, NO does not react with AgOCN. The reaction of XNO (X = Cl, Br) and AgOCN is much more complex, leading to a mixture of NO, NO_2, N_2O, CO_2, NCNCO, and X(CO)NCO. A reaction mechanism that involves the formation of neutral nitrosyl isocyanate, OCN−NO, has been proposed as the initial step. The two neutral intermediates, $OCN-NO_2$ and OCN−NO, were computed by ab initio methods at the correlated MP2 level of theory and are discussed in terms of intramolecular stabilization by donor−acceptor interaction (negative hyperconjugation).

Introduction

The unstable bent halogen isocyanates, XNCO (X = Cl, Br, I), which are isoelectronic to the bent halogen azides, have been extensively investigated in the gas phase.[1] They can easily be prepared from the reaction of silver cyanate with the corresponding dihalogen at high temperatures. The halogen isocyanates are very unstable as they are very sensitive toward hydrolysis and they tend to polymerize.[1]

We have recently been studying the reactions of silver cyanate with bromine.[2] In these studies it has been shown that the final products and their distribution very much depend on the stoichiometry. When a large excess of silver cyanate was used, the only stable, IR-active product in the gas phase was found to be the carbonyl diisocyanate, OCN(CO)NCO (eq 1).[2] The

$$\text{excess AgOCN} + Br_2 \rightarrow AgBr + OC(NCO)_2 + N_2 + Ag + ... \quad (1)$$

formation of diisooxocyan, OCN−NCO, as a likely intermediate in reaction 1 has been discussed on the basis of experimentally observed decomposition products and on the grounds of energetic considerations.[2]

There are also theoretical and experimental reports on the related dipseudohalogen (ONC−CNO, cyanogen di-*N*-oxide).[3] The existence of dipseudohalogen species containing cyanate units has also been postulated by several authors,[4] however, there are no experimental proofs for a compound of the type N−C−O−O−C−N (oxocyanogen, dioxocyan).

In a flash light photolysis experiment, Basco investigated the reaction of cyan radicals with molecular oxygen, finding that a gaseous compound was formed which might be NCOCN, NCNCO, or even NCOOCN.[5]

In 1980 Delgado and Fernandez reported on the formation of oxocyanogen as an intermediate species in the reaction of AgOCN with Br_2.[6] In that paper the authors claimed to have stabilized the "$(OCN)_2$" by subsequent reaction with $TiCl_4$, resulting in the formation of a polymeric compound of the type $\{TiCl_4(OCN)_2\}_n$.[6] However, no direct evidence for the formation of $(OCN)_2$ was found.

Cyanogen isocyanate was first prepared by Mayer from the reaction between silver cyanate and cyanogen chloride, ClCN, yielding a polymeric cyanogen isocyanate which equilibrates with its monomer NCNCO (eq 2).[7] Shortly thereafter, Gottardi

$$n\text{AgOCN} + n\text{ClCN} \rightarrow n\text{AgCl} + (C_2N_2O)_n \quad (2)$$

detected NCNCO as one of the thermal decomposition products of AgOCN.[8] AgOCN decomposes above 335 °C. The only gaseous decomposition products are CO, N_2, CO_2, and NCNCO. A radical mechanism involving OCN radicals has been discussed. The remaining residue is not pure metallic silver but a mixture of metallic silver and polymeric substances which decompose after long strong heating liberating $(CN)_2$ and NCNCO.[8]

In earlier studies it was proposed that the intermediate products formed in the reaction of azide compounds with nitrosonium and nitronium salts (i.e., $ON-N_3$ and O_2N-N_3) decompose according to eqs 3 and 4 in an unimolecular process

$$N_4O \rightarrow N_2O + N_2 \quad (3)$$

$$N_4O_2 \rightarrow 2N_2O \quad (4)$$

via cyclic intermediates (i.e., cyclic N_4O and N_2O).[9,10]

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Similar to the reaction of AgOCN with X−NO (X = Cl, Br), we investigated the reaction of AgSCN with ClNO, which yields ON−SCN.[11] Nitrosyl thiocyanate, ON−SCN, is a very unstable compound known only in solution, which decomposes into NO and $(SCN)_2$.

Lately, we have been investigating the nitration of hydrogen cyanide (reaction of $NO_2{}^+BF_4{}^-$ with HCN) yielding dinitrogen monoxide, N_2O, and carbon monoxide, CO, which is further oxidized by $NO_2{}^+$ to give CO_2 and NO^+. The experimental data are in accord with the intermediate formation of the neutral $CNNO_2$.[12] Furthermore, the reaction of silver cyanide with nitrosyl chloride leads to the blue-green gas nitrosyl cyanide, which is stable at room temperature.[13,14]

In reactions of AgOCN with halides, as well as in the thermal decomposition of AgOCN, OCN radicals seem to be involved.[2,5,8] This naturally led to the attempted preparation of the new compounds $OCN-NO_2$ and OCN−NO using NO and NO_2 as reaction partners. To our knowledge there have been no reports on the reaction of silver cyanate with nitrogen oxides (NO, NO_2) or nitrogen oxohalides. In this paper we report on $OCN-NO_2$ and OCN−NO formed as likely short-lived intermediates in the reaction of silver cyanate with the corresponding binary nitrogen oxides, NO and NO_2, and ternary nitrogen oxohalides, $Cl-NO_2$, Cl−NO, and Br−NO.

Experimental Section

***Caution*!** Halogen isocyanates, binary nitrogen oxides, and ternary nitrogen oxohalides are toxic and appropriate safety precautions should be taken.

(1) Materials. AgOCN was prepared as a white (light-sensitive) solid by precipitation from an aqueous solution of NaOCN and $AgNO_3$.[8] It was thoroughly washed, dried (under vacuum, over P_4O_{10}), and degassed under high vacuum shortly before use. This is an important step since we found that most X−NCO compounds are very susceptible to hydrolysis.

(2) Reactions. For the preparation of samples for IR spectroscopy, a 10 cm gas cell with a directly attached reaction vessel (15 cm^3) separated by a Young PTFE valve was used. In the reaction vessel, dry degassed AgOCN was prepared (1.00 g, 6.7 mmol, 6-fold excess). On the calibrated stainless steel vacuum line (SS 316) 1 mmol of the following gases was condensed onto the silver cyanate at −196 °C: (i) Br_2 (Aldrich)/NO_2 (Aldrich) (1:1, 2:1, 3:1); (ii) NO_2 (Aldrich); (iii) NO_2Cl;[15a] (iv) NO (Aldrich); (v) NOCl;[15b] (vi) NOBr.[15c] The reaction mixture was allowed to warm to room temperature, and IR spectra were measured. The volatile products formed were condensed into the attached IR gas cell, and IR spectra were recorded without delay at 20 °C and 2 Torr and again after different time intervals (see Results and Discussion).

(3) Vibrational Spectroscopy. Infrared spectra were recorded by using a gas cell equipped with NaCl windows on a Philips PU9800 FTIR spectrophotometer.

(4) Computational Methods. The calculations were performed using the program package Gaussian 92.[16] The 6-31G* standard basis sets were employed for the all-electron calculations. All structures were fully optimized at the MP2 level, and the stationary points were characterized by frequency analyses. For the open-shell molecules, the spin-unrestricted Hartree−Fock method (UHF) was applied. In order to give more reliable estimates of the reaction energies involving open-shell species, spin projection techniques were used which eliminate some (but not all) contributions from higher spin states.[17] We present the calculated eigenvalues $\langle S^2 \rangle$ of the S^2 operator and the energies of the spin-projected wavefunctions at the PMP2/6-31G* level.

Results and Discussion

(1) Reaction of NO_2/Br_2, NO_2, and $ClNO_2$ with AgOCN. In the reaction of bromine with a large excess of silver cyanate, it was found (eq 1) that besides AgBr a considerable amount of elemental silver was generated, which was explained by a radical mechanism (eq 5).[2]

$$AgOCN(s) + OCN^{\bullet}(g) \rightarrow Ag(s) + O{=}C{=}N{-}N{=}C{=}O(g) \tag{5}$$

In order to quench the $OCN^{\bullet}$ radicals, we reacted AgOCN with 1:1, 2:1, and 3:1 mixtures of Br_2 and NO_2 and followed the reaction by IR spectroscopy. (Pure NO_2Br is very unstable. N.B. very recently it was found that $BrNO_2$ is formed in good yield in a continuous flow by $ClNO_2$ with a dilute aqueous solution of NaBr).[26] After 10 s reaction time at room temperature CO_2, N_2O, BrNCO, traces of OCN(CO)NCO, and unreacted NO_2 (Table 1) were observed in all cases. However, after a 3 min reaction time *only* CO_2 and N_2O (and traces of OCN(CO)NCO) remained as IR-active gaseous compounds. Moreover, the analysis of the nonvolatile solid revealed beside unreacted AgOCN the presence of AgBr and elemental silver. We do stress that the presence of NO_2 radicals has an influence on the reaction of bromine and silver cyanate since only small amounts of carbonyl diisocyanate were found. This can best be explained by a radical reaction according to eq 6 which was

$$^{\bullet}NO_2(g) + OCN^{\bullet}(g) \rightarrow OCN{-}NO_2(g) \tag{6}$$

estimated to be thermodynamically favorable $\Delta_RH(298K) =$

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Table 1. Vibrational Frequencies (cm^{-1}) of the Experimentally Observed Molecules[a]

species	frequencies	ref
NO	1880 (s)	18
CO_2	3716 (w), 3609 (w), 2326 (vs), 741 (w), 721 (m), 667 (vs)	18, 19
N_2O	3891 (w), 3480 (m), 2809 (w), 2591 (m), 2488 (m), 2457 (m), 2217 (vs), 1890 (w), 1302 (vs), 1275 (vs), 1183 (m), 1155 (m), 694 (w)	18, 20
NO_2	2900 (w), 1750 (s), 1610 (vs), 1260 (s), 750 (m)	18
Br−NO	1799 (vs), 542 (s) 266 (m)	18, 21
Br−NO_2[b]	1667 (s), 1293 (vs), 1200 (w), 787 (s), 605 (w)	26
Cl−NO	1800 (vs), 595 (s), 332 (m)	18
Cl−NO_2	1685 (vs), 1268 (vs), 792 (s), 652 (m)	18, 22
Br−CN	2200 (vs), 574 (s), 342 (m)	18
Cl−CN	2219 (vs), 714 (s), 380 (m)	18
NC−NCO	2280 (vs), 2233 (vs), 1750 (m), 1073 (s), 727 (w), 610 (w)	1f, 7
Br(CO)NCO	2255 (vs), 1178 (m), 1816 (s), 1420 (s), 1399 (m), 987 (sh), 965 (s), 775 (w), 613 (m)	23
Cl(CO)NCO	2260 (vs), 1818 (s), 1780 (m), 1426 (m) 1411 (m), 992 (s), 789 (w), 651 (w), 634 (w)	24
OCN(CO)NCO	2275 (s), 2242 (vs), 1775 (s), 1768 (sh), (1748 (s), 1738 (s), 1428 (vs), 1405 (m), 1075 (vs), 1070 (vs), 730 (m), 725 (sh), 618 (sh), 609 (m)	25

[a] In our studies we could reproduce and confirm all frequencies reported in the literature.[18−25] [b] The reported values for Br−NO_2 were taken from the literature. No attempts were made to reproduce these data.[26]

Table 2. Calculated Reaction Energies and Enthalpies (kcal mol^{-1})

eq	E(MP2/6-31G*)	E(PMP2/6-31G*)	$\Delta_R H$(298K,zpe)[a]
6	-46.8	−39.0	−38.9
7	−83.0		−82.9
9	−5.9		−4.0
10			
X = Cl	−1.7		−1.6
X = Br	−3.6		−2.8
11	−116.5		−115.6
12	−30.1		−29.8
15			
X = Cl	−15.6		−14.9
X = Br	−22.1		−21.0
17	−176.5		−175.6
18	−46.2	−38.2	−38.2
19	−173.0		−172.9

[a] Reaction enthalpy after correction for zpe contributions, rotational and translational degrees of freedom, and the work term at room temperature.

−38.9 kcal mol^{-1} (Table 2). The short-lived intermediate OCN−NO_2, can then undergo a cleavage−rearrangement to give the experimentally observed N_2O and CO_2 (eq 7, Table 1; see

$$\mathrm{OCN{-}NO_2(g) \rightarrow CO_2(g) + N_2O(g)} \tag{7}$$

below, (3) Computations). This decomposition reaction was calculated to be highly exothermic $\Delta_R H(298K) = -82.9$ kcal mol^{-1} (Table 2). A similar thermal decomposition reaction has been reported in literature.[27a] The thermal decomposition of gaseous tetranitromethane, $C(NO_2)_4$, in contact with silver wool was investigated by Bock and Zanathy, yielding NO_2, CO_2, NO, and CO traces.[27a] Carbonyl dinitrite, $(O_2N)_2CO$, has been discussed as an intermediate decomposing into NO_2, NO, and CO_2 (or in the absence of silver, depending on the temperature, into 2NO_2 and CO), indicating a preceding chemisorption at the silver surface.[27a]

On the other hand, NO_2 directly reacts with AgOCN at room temperature forming OCN−NO_2, which decomposes into CO_2 and N_2O as the only IR-active gaseous compounds (eqs 7 and 8, Table 1). This reaction was also predicted to be exothermic

$$\mathrm{{}^{\bullet}NO_2(g) + AgOCN(s) \rightarrow Ag(s) + OCN{-}NO_2(g)} \tag{8}$$

[$\Delta_R H(298K) = -20.0$ kcal mol^{-1}]. The thermodynamic driving force is the formation of CO_2 and N_2O (eq 7).[28,29] Furthermore, analysis of the nonvolatile solid revealed beside unreacted AgOCN the presence of elemental silver. It is known from the literature that excited oxygen atoms, $O(^1D)$, react in a similar way with HNCO leading to CO_2 and $NH(a^1\Delta)$ in a strongly exothermic reaction ($\Delta H = -92$ kcal mol^{-1}).[30] Moreover, the mechanism in that reaction is thought to involve the electrophilic attack of the excited oxygen on the carbon atom of the NCO chain.[31]

We also studied the neat reaction of $ClNO_2$ and AgOCN at room temperature. We found that independently from the molar ratio of the reactants, this exothermic reaction always led to N_2O, CO_2, and AgCl [$\Delta_R H(298K) = -4.0$ kcal mol^{-1};[32] cf. Table 2; eqs 7 and 9].

$$\mathrm{AgOCN(s) + ClNO_2(g) \rightarrow AgCl(s) + OCNNO_2(g)} \tag{9}$$

Due to the only experimentally observed products, CO_2 and N_2O, the proposed reactive short-lived OCN−NO_2 thus would belong to the group of nitrogen-containing compounds, which like nitrosyl azide (→ N_2 + N_2O)[9] and nitryl azide (→ 2N_2O)[10] completely decompose at low temperature yielding only gases. Tetranitromethane (→ 2NO_2 + 2NO + CO_2 for $T > 550$ K or → 3NO_2 + NO + CO),[27a] azodicarbonitrile (→ N_2 + NC−CN),[27b] methyl azide (→ N_2 + H_2 + HCN),[33] or ammonium nitrate (→ N_2O + 2H_2O)[34] completely decompose on heating into thermodynamically favorable, gaseous compounds (eq 7).

(2) Reaction of NO, ClNO, and BrNO with AgOCN. NO is a stable free radical, which in contrast to NO_2 does not react with silver cyanate at room temperature, not even when the reaction mixture was gently heated or activated by ultrasound.

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(28) U_L(AgOCN) = 166.7 kcal mol^{-1};[29c] I_p(Ag) = 175.8 kcal mol^{-1};[29b] $\Delta H_{atom.}$(Ag) = 68.0 kcal mol^{-1};[29b] $I_p(NO_2)$ = 232.7 kcal mol^{-1};[29a] $\Delta_R H°$(298K,eq17) = −175.6 kcal mol^{-1} (see Table 2).

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(31) Although much of the energy released in this reaction comes from the formation of the new C−O bond, angular momentum contraints force the system to produce NH in its excited $a^1\Delta$ state.

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This behavior can partly be attributed to the much lower boiling point of NO (−152 °C) compared to that of NO_2.[51] Therefore, in contrast to the reaction with NO_2, one would not expect a liquid phase to be present in the reaction of NO with AgOCN. Alternatively, the different reactivity of NO_2 and NO can be explained by the fact that the E_A of NO_2 greatly exceeds that of NO.[35] One could expect the initial formation of the radial anion salt, $Ag^+(NO_2{}^{\bullet}OCN)^-$, which then collapses by electron transfer, while the analogous $Ag^+(NO^{\bullet}OCN)^-$ salt would be much less stable. On the other hand, NO reacts rapidly with other free radicals or halogens (forming nitrosyl halides) while it is not very reactive toward most stable molecules.[36]

In contrast to NO, nitrosyl chloride and nitrosyl bromide react with silver cyanate spontaneously. The IR spectrum obtained after a 10 s reaction time at room temperature clearly showed in both cases (Cl−NO and Br−NO) the presence of NO, NO_2, X−CN (X = Cl, Br), NC−NCO, X(CO)NCO, and small amounts of CO_2 and N_2O (Table 1). The difference in band shapes and band widths was indicative for the presence of at least two different NCO- and CN-containing molecules (in the region 2000−2300 cm^{-1}). Cyanogen isocyanate, NC−NCO,[1f,7] was unequivocally identified from the bands at 1775 ($\nu_3 + \nu_8$), 1743 ($\nu_2 - \nu_7$), 1430 (ν_3), and 1070 cm^{-1} (ν_4). The halogencarbonyl isocyanate, X(CO)NCO (X = Cl,[24] Br[23]), was deduced from the bands at 1820 (ν_2) and 990 cm^{-1} (ν_4) for Cl(CO)-NCO and 1815 (ν_2) and 980 cm^{-1} (ν_4) for Br(CO)NCO (Table 1). By noting and comparing differences in the relative intensities of the bands as well as band shapes and band widths in duplicate experiments but after different reaction times, it was possible to determine the infrared bands arising from each molecule. While after a 3 min reaction time the amount of CO_2 and N_2O had increased the amount of X(CO)NCO and the amount of NO_2 had decreased; neither ClCN nor BrNC could be detected. After 10 min, no halogencarbonyl isocyanate, X(CO)NCO (X = Cl, Br), remained, while increasing amounts of CO_2 and N_2O were observed. The volume of NO, NO_2, and NC−NCO decreased slowly. Eventually, after 24 h only CO_2 and N_2O remained as IR-active gaseous compounds. Furthermore, analysis of the nonvolatile solid revealed, beside unreacted AgOCN, the presence of AgX (X = Cl, Br), elemental silver, and oligomeric NCO compounds.

The initial step of the nitrosyl halide/silver cyanate reaction seems to be the exothermic formation [$\Delta_R H$(298K,X=Cl) = −1.6 kcal mol^{-1}; $\Delta_R H°$(298K,X=Br) = −2.8 kcal mol^{-1}; Table 2][37] of the intermediate OCN−NO (eq 10) Since the highly polarized OCN−NO molecule is very reactive,[38] this short-lived intermediate is expected to react immediately with XNO (X = Cl, Br) or decompose into either molecular N_2 and CO_2 via cleavage−rearrangement (eq 11) or into N_2O and CO (eq 12).

$$\mathrm{AgOCN(s) + X{-}NO(g) \rightarrow AgX(s) + OCN{-}NO(g)} \qquad \mathrm{X = Cl, Br} \tag{10}$$

$$\mathrm{OCN{-}NO(g) \rightarrow CO_2(g) + N_2(g)} \tag{11}$$

$$\mathrm{OCN{-}NO(g) \rightarrow CO(g) + N_2O(g)} \tag{12}$$

Combining the exothermicities of reactions 11 and 12 suggests that oxygen transfer from N_2O to CO is 85.8 kcal mol^{-1} exothermic. The experimental value of 87.1 kcal mol^{-1} is nicely in agreement with this calculation.[29d] Both dissociation reactions are exothermic [$\Delta_R H$(298K,eq11) = −115.6 kcal mol^{-1}; $\Delta_R H$(298K,eq12) = −29.8 kcal mol^{-1}; Table 2], but as the transition state for the decomposition according to eq 12 is much higher in energy than the transition state for the decomposition into CO_2 and N_2 (see Computations, Table 6) only the products for reaction 11 were observed (small amounts of N_2)[39] as well as those of the more likely reaction with XNO.

The formation of X−CN, NO_2, and NO can best be explained by the following mechanism (eq 13, Figure 1).

$$\mathrm{OCN{-}NO(g) + X{-}NO(g) \rightarrow \{X{-}CN{-}NO^{\bullet}\}(g) + {}^{\bullet}NO_2(g)} \tag{13}$$

Due to the polarity of the O−N moiety in OCN−NO and Cl−N in Cl−NO (Figure 1), nitrogen dioxide is formed as well as $X{-}CN{-}NO^{\bullet}$ radicals which can decompose rapidly to give X−CN and $^{\bullet}NO$ (eq 14).[40] The thermodynamic driving force

$$\mathrm{\{X{-}CN{-}NO^{\bullet}\} \rightarrow X{-}CN(g) + {}^{\bullet}NO(g)} \tag{14}$$

for both reactions (eqs 13 and 14), the formation of the unstable radical $X{-}CN{-}NO^{\bullet}$ (which does not represent a minimum on the PES) and the decomposition into the experimentally observed X−CN and NO, is the formation of CO_2 and N_2O. The formation of CO_2 and N_2O can easily be explained by the reaction of nitrogen dioxide with an excess of silver cyanate as described before (eqs 7 and 8). The experimental result (formation of NO_2 and NO) suggests that the stability of the OCN−NO molecule may be determined by the activation barrier for breaking the OCN−NO bond.

The reaction of cyanogen chloride, ClCN, with silver cyanate has been known for a long time, yielding monomeric NCNCO ([$\Delta_R H$(298K, eq15, X=Cl) = −14.9 kcal mol^{-1}; $\Delta_R H$(298K, eq15, X=Br) = −21.0 kcal mol^{-1}; Table 2)] (eq 15) which is in equilibrium with polymeric cyanogen isocyanate (eq 16).[7,41] The polymerization as well as its slow decomposition explains the disappearance of NC−NCO after 24 h.

$$\mathrm{X{-}CN(g) + AgOCN(s) \rightarrow AgX(s) + NC{-}NCO(g)} \tag{15}$$

$$n\mathrm{NC{-}NCO \rightleftarrows (C_2N_2O)_n} \tag{16}$$

The explanation for the formation of the halogencarbonyl isocyanate is not as straightforward as with NC−NCO. We assume it is formed in a much more complex reaction of NC−NCO with X−NC (X = Cl, Br) and solid AgOCN similar to the formation of carbonyl diisocyanate (eq 1). The corresponding halogencarbonyl isocyanate is not stable in the mixture of NC−NCO, NO_2, NO, CO_2, N_2O, and solid AgOCN and could not be observed anymore after 10 min.

(3) Computations. Structural parameters obtained from MP2/6-31G* calculations for isocyanates, nitryl, and nitrosyl compounds as well as azides are in good agreement with those obtained from experimental studies.[42,43] It is generally agreed that this level is sufficient to predict the relative stabilities of

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(35) I_p(NO) = 215.0 kcal mol^{-1};[29b] $\Delta_R H$(298K,eq19) = −172.9 kcal mol^{-1} (see Table 2).

(36) (a) Czapski, G.; Holcman, J.; Bielski, B. H. *J. Am. Chem. Soc.* **1994**, *116*, 11465. (b) Stamler, J. S.; Singel, D. J.; Loscalzo, J. *Science* **1992**, *258*, 1898. (c) Blough, N.; Zafiriou, O. C. *Inorg. Chem.* **1985**, *24*, 3502.

(37) $\Delta_R H$ was calculated for the following reaction: OCN^-(g) + XNO(g) → Cl^-(g) + OCN−NO(g).

(38) The N−N bond of OCN−NO is about as weak (d(NN) = 1.522 Å) as the weak halogen−nitrogen bond in nitrosyl halides.

(39) The formation of N_2 was established by gas discharge.

(40) XCN is more stable than XNC, X = Cl, Br: Schulz, A.; Klapötke, T. M., unpublished results.

(41) $\Delta_R H$ was calculated for the following reaction: X−CN(g) + OCN^-(g) → X^-(g) + NC−NCO(g).

(42) (a) Otto, M.; Lotz, S. D.; Frenking, G. *Inorg. Chem.* **1992**, *31*, 3647. (b) Schulz, A.; Tornieporth-Oetting, I. C.; Klapötke, T. *Inorg. Chem.* **1995**, *34*, 4343. (c) Cradock, S.; Durig, J. R.; Sullivan, J. F. *J. Mol. Struct.* **1985**, *131*, 121. (d) Durig, J. R.; Little, T. S. Gounev, T. K.;

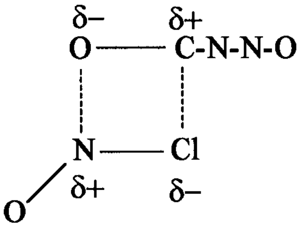

Figure 1. Polarity of the O−N moiety in OCN−NO and Cl−N in Cl−NO.

the isomers and will give reasonably reliable results for the equilibrium structures.[44,45]

Table 7 shows the calculated structures at MP2/6-31G* level as well as the total energies and zero point vibrational energies for all discussed species. The theoretically predicted vibrational frequencies for all species have been calculated with the harmonic approximation. The deviation from experimentally obtained frequencies may partly be compensated by using scaling factors. They may also be different for various vibrational modes present in the molecule.[42a,46] Some of the calculated molecules were calculated before by other groups at different levels so that we want to focus only on the OCN−NO_2 and OCN−NO molecules.[47]

OCN−NO_2. We discussed two possibilities of the formation of OCN−NO_2: (i) the reaction of $OCN^{\bullet}$ radicals with $^{\bullet}NO_2$ radicals according to eq 6 and (ii) the reaction of $ClNO_2$ with AgOCN (eq 9). Both reactions are exothermic; however, for the radical reaction the energy liberated is much higher (Table 2). Another possible mechanism would involve the ionic reaction of NO_2^+ cations (e.g., NO_2BF_4) with OCN^- anions (e.g., NaOCN) in solution. The reaction of the ions in the gas phase has been estimated to be strongly exothermic [$\Delta_R H$(298K,eq 17) = −175.6 kcal mol^{-1}; Table 2].

$$OCN^- \ (g) + NO_2^{\ +}(g) \rightarrow OCN{-}NO_2(g) \qquad (17)$$

To answer the question *why* nitryl isocyanate, OCN−NO_2, and not nitryl cyanate, NCO−NO_2, is formed as a short-lived intermediate by the reaction of AgOCN with NO_2 (as well as AgOCN and Cl−NO_2), we carried out ab initio computations at a correlated level. Only for the N−N bound species was a minimum ground state structure found whereas for the O−N bound species neither a singlet nor a triplet ground state exists at the applied level of theory. At this point, the question of whether there is a minimum for the O−N bound species must still be regarded as being open. It is not unreasonable to assume that with even larger basis sets and applying higher levels of theory NCO−NO_2 may possess a minimum. In any case, one would expect the N−O bound species to be less stable than the N−N bound species because of a strong intramolecular σ(ON)/π(CN) interaction which weakens the N−O single bond in NCO−NO_2.

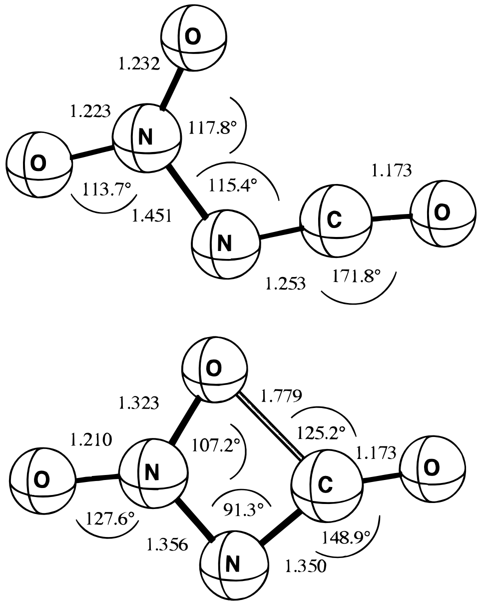

Figure 2. MP2/6-31G* optimized minimum structure of OCN−NO_2 (C_s symmetry) and the structure of the transition state (C_s symmetry) for the intrinsic decomposition into CO_2 and N_2O (bond distances in Å, angles in deg).

Table 3. MP2/6-31G* Level Fully Optimized Structures (Distances in Å, Angles in deg) of Y−NO_2 and Y−NO (Y = OCN, NNN)

	OCN−NO_2	$N_aN_bN_c$−N_dO_2	OCN−NO	$N_aN_bN_c$−N_dO
d(NO)				
trans	1.226	1.223	1.191	1.204
cis	1.235	1.232		
d(NN), *d*(N_cN_d)	1.462	1.451	1.522	1.484
d(CN), *d*(N_bN_c)	1.274	1.253	1.245	1.270
d(OC), *d*(N_aN_b)	1.151	1.173	1.181	1.154
∠(OCN), ∠($N_aN_bN_c$)	172.7	171.8	173.4	174.3
∠(ONN)				
trans	112.5	113.7	110.9	110.5
cis	118.5	117.8		
∠(CNN), ∠($N_bN_cN_d$)	108.0	115.4	117.0	107.1
∠(ONO)	129.0	128.5		

Nicely in agreement with this, the MO computations for the $^{\bullet}NCO$ radical clearly indicate much larger odd-electron density for nitrogen (0.6477) than for oxygen (0.0994).[48] Similarly, it can be expected that also for $^{\bullet}NO_2$ the odd electron is more localized on the nitrogen so that for a radical mechanism the formation of the N−N bound species should be favored.

Table 3 summarizes the computed structural parameters of OCN−NO_2. The molecular structure of OCN−NO_2 was fully optimized at the MP2/6-31G* level and is shown in Figure 2. All structural parameters are in good agreement with those of other covalent isocyanates and nitryl compounds.[9,10,12,23,24,42c,d,44,49] Therefore, the interpretation of OCN−NO_2 as *nitryl isocyanate* seems to be justified. As expected for covalently bound isocyanates, OCN−NO_2 displays a bent configuration with an N−C−O bond angle of 171.8°. The calculated structure reminds one of the situation for the isoelectronic nitryl azide, NNN−NO_2 (Table 3).[10] The computed N−O bond distances in OCN−NO_2 of 1.232 and 1.223 Å are slightly longer than in N_2O (1.186 Å)[50] and in $ClNO_2$ (1.21 Å),[51] corresponding to a bond order slightly less than 2. The N−N bond is rather long

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Gardner, J. K.; Sullivan, J. F. *J. Mol. Struct.* **1996**, *375*, 83. (e) Durig, J. R.; Guirgis, K. A.; Krutules, Phan, H. V.; Stidham, H. D. *J. Raman Spectrosc.* **1994**, *25*, 221. (f) Klatt, G.; Willetts, A.; Handy, N. C.; Esposti, C. D. *Chem. Phys. Lett.* **1995**, *237*, 273.

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(45) MP2 calculations with a 6-31G* basis set give bond length of ∼0.01 Å, generally too long, especially for multiple bonds, and angles in the range 1−2°.[46]

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Table 4. Computed NPA Partial Charges (e) of $Y-N_dO_2$ and $Y-N_dO$ ($Y = O_aC_bN_c$, $N_aN_bN_c$)

	N_a/O_a	N_b/C_b	N_c/N_c	N_d/N_d	*trans* O	*cis* O
$NNN-NO_2$	+0.17	+0.29	−0.32	+0.76	−0.40	−0.49
$OCN-NO_2$	−0.51	+1.12	−0.56	+0.77	−0.37	−0.45
NNN−NO	+0.07	+0.25	−0.34	+0.34	−0.30	
OCN−NO	−0.54	+1.09	−0.62	+0.35	−0.28	

Table 5. Computed IR Data (MP2/6-31G*); Harmonic Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km mol^{-1}) of $^1A'$ $OCN-NO_2$ and $^1A'$ OCN−NO[a]

	$OCN-NO_2$	approx assignment	OCN−NO	approx assignment
ω_1	2285(692)	ν_{as}(OCN)	2280(941)	ν_{as}(OCN)
ω_2	1843(150)	$\nu_{as}(NO_2)$	1614(398)	ν(NO)
ω_3	1319(20)	$\nu(OCNNO_2)$	1296(206)	ν_s(OCN)
ω_4	1299(442)	$\nu(OCNNO_2)$	768(196)	ν(OCN−NO)
ω_5	858(192)	$\nu(OCN-NO_2)$	640(18)	δ(OCN)
ω_6	750(19)	$\delta(OCNNO_2)$	591(20)	γ(OCN)
ω_7	731(11)	$\gamma(OCNNO_2)$	359(378)	δ(OCNNO)
ω_8	563(22)	$\gamma(OCNNO_2)$	159(4)	δ(OCNNO)
ω_9	535(16)	$\delta(OCNNO_2)$	110(0)	γ(OCNNO)
ω_{10}	515(8)	$\delta(OCNNO_2)$		
ω_{11}	144(1)	$\delta(OCNNO_2)$		
ω_{12}	70(0)	$\gamma(OCNNO_2)$		

[a] Unscaled.

with 1.451 Å, comparable to 1.462 Å in $NNN-NO_2$ (Table 3). The value of the N−N distance corresponds to a bond order less than 1 (typical values: N−N single bond, 1.447 Å in N_2H_4,[52] N=N double bond, 1.252 Å in N_2H_2).[53] As indicated by NBO analysis,[54] there is a significant interaction of the lone pairs on both oxygen atoms with the unoccupied, antibonding σ^* orbital of the N−N bond. This LP(O) → σ^*(N−N) donor−acceptor interaction (hyperconjugation)[46b] accounts for the rather long N−N bond [LP(*cis*-O) $E^2 = 29.9$ kcal mol^{-1}; LP(*trans*-O) $E^2 = 32.5$ kcal mol^{-1}].[55] Moreover, the N−N bond has a polarity $OCN^{\delta-}-N^{\delta+}O_2$ that resembles the situation of the polarized halogen isocyanates and covalent azides with the N−N moiety being even more polarized than in $NNN-NO_2$ (Table 4).

The theoretically predicted harmonic vibrational frequencies and IR intensities of $OCN-NO_2$ are presented in Table 5. According to Table 5, ω_1 is almost purely an asymmetric stretching mode of the OCN moiety, while ω_2 represents the asymmetric stretch for the NO_2 group. The assignments of ω_3 and ω_4 are not as straightforward as with ω_1 and ω_2. The ω_3 and ω_4 motions can be described as a mixture of both symmetric stretch of the OCN and the NO_2 units, whereas ω_5 represents an N−N stretching along with O−N−O and O−C−N bending. The remaining normal modes are either in-plane deformation or out-of-plane deformation vibrations.

The dissociation of isolated, gaseous $OCN-NO_2$ molecules into the experimentally observed products, CO_2 and N_2O, according to eq 7 was calculated to be strongly exothermic [$\Delta_RH(298K) = -82.9$ kcal mol^{-1}, Table 2]. The decomposition of the short-lived $OCN-NO_2$ could go either in an unimolecular process via cleavage−rearrangement to give N_2O and CO_2 (cf. $NNN-NO_2$ decomposes intrinsically into two N_2O)[10] or in a bimolecular process. Exploration of the PES led to the C_s symmetry transition state (TS) for the intrinsic decomposition (Figure 2). The transition structure (Figure 2) is basically a distorted O−N−N−C ring with a rather long O−C bond distance of 1.779 Å and still resembles more the nitryl isocyanate structure than the decomposition products. This is in agreement with Hammond's postulates that the TS lies more toward the higher energy side.[56] Mechanistically, this cleavage−rearrangement is thought to be driven by a nucleophilic attack of one of the nitryl oxygens on the carbon of the OCN chain. Energetically, the barrier to dissociation is at 14.4 kcal mol^{-1}, indicating that the $OCN-NO_2$ is intrinsically stable, but this small barrier could severely impede further attempts to isolate $OCN-NO_2$.

OCN−NO. Recently, the heavier analogues, XCN(NY) [X, Y = S,O; X ≠ Y], have been investigated by using ab initio MP2/6-31G* methods.[44] This study indicates that the NS−NCO isomer is more stable than the SN−NCO isomer and that the ON−SCN isomer is more stable than the ON−NCS isomer. In contrast to the sulfur analogues but in agreement with the nitrosyl azide, the ab initio computation shows a planar *trans trans* structure for (C_s) OCN−NO (Figure 3, Table 3) as the most likely minimum structure in the gas phase (N.B. The O−N bound species, NCO−NO, is higher in energy and possesses a rather weak and long N−O bond of 1.69 Å at MP2/6-31+G* level). The remarkable difference to the bond situation in nitrosyl azide and nitryl isocyanate is the fact that the N−N bond of 1.522 Å is rather long and comparable with 1.49 Å in F_2N-NF_2.[57] The predicted bond length is longer than the experimental nitrogen−nitrogen bond length in hydrazine H_2N-NH_2 (1.449 Å)[52] but much shorter than the nitrogen−nitrogen bond length in the weakly bound dinitrogen tetraoxide O_2N-NO_2 (1.782 Å)[58] and resembles the weak halogen−nitrogen bond situation in XNO molecules. It has been known for a long time that all species of the form XNO (X = F, Cl, Br) have a bent structure (C_s) with tight N−O bonds and weak bonds between the halogen and the NO moiety.[59] The weak halogen−nitrogen bond in nitrosyl halides stems from an unfavorable overlap of a singly-occupied halogen valence p orbital with a singly occupied antibonding 2π orbital of NO.[21,59d] In addition, the heavier halides are better electron donors and therefore contribute more electron density to the NO π^* orbital,[59d] a trend that is consistent with the decreased X−N bond strength from F to Cl to Br. Since the OCN unit can be regarded as a pseudohalogen, these rather special bonding situations can be rationalized in the picture of localized bond orbitals (NBO) by strong noncovalent contributions (donor−acceptor interaction). There is one strong p-LP(O) → σ^*(N−N) intramolecular donor−acceptor interaction (besides π electron density delocalization) which weakens the N−N bond and therefore also explains the fairly long N−N distance ($E^2 = 42.3$ kcal mol^{-1}).[55] There are several possible ways of drawing reasonable Lewis structures for the *trans*-chain nitrosyl isocyanate, a few of which are represented in Figure 4 with structure A corresponding to the most likely one due to NBO analysis.

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(55) NBO analysis: The second-order pertubative energy was computed according to $E^2 = -2(\langle\phi|h^F\phi^*\rangle)^2/E_{\phi^*} - E_\phi)$, with h^F being the Fock operator.

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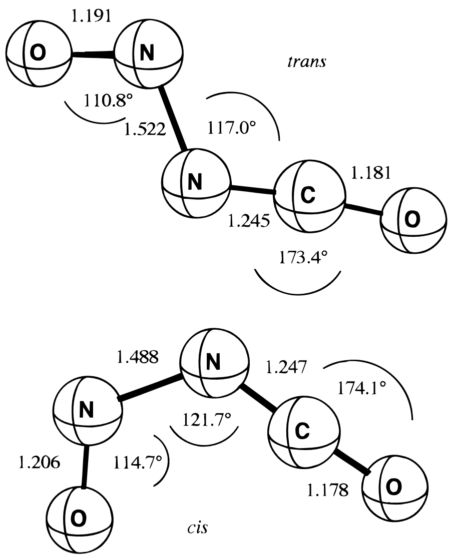

Figure 3. MP2/6-31G* optimized minimum structure (bond distances in Å, angles in deg) of *trans*- and *cis*-OCN−NO$_2$ (C_s symmetry).

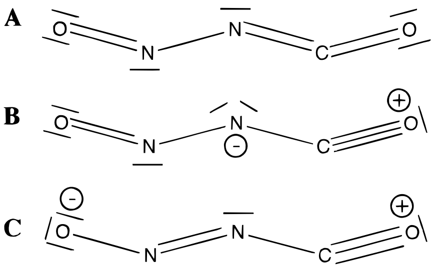

Figure 4. Lewis structures for OCN−NO.

Table 5 shows the calculated unscaled MP2 frequencies for the nitrosyl isocyanate. Analogous to OCN−NO$_2$, ω_1 is almost purely an asymmetric stretching mode of the OCN moiety, whereas ω_2 represents the N-O stretch. The ω_3 motion can be described as the asymmetric O−C−N stretch, and ω_4 is best described as an N−N stretching along with O−N−O and O−C−N bending. The remaining normal modes correspond either to in-plane or to out-of-plane deformation vibrations.

Nitrosyl isocyanate can be formed in three different reactions: (i) in a radical reaction (eq 18), (ii) in an ionic process

$$^{\bullet}\mathrm{NO(g)} + \mathrm{OCN}^{\bullet}\mathrm{(g)} \rightarrow \mathrm{OCN{-}NO(g)}, \quad \Delta_{\mathrm{R}}H(298\mathrm{K}) = -38.2\ \mathrm{kcal\ mol^{-1}} \quad (18)$$

(eq 19), and (iii) in the reaction of MOCN and XNO (M = Na,

$$\mathrm{NO^{+}(g)} + \mathrm{OCN^{-}(g)} \rightarrow \mathrm{OCN{-}NO(g)}, \quad \Delta_{\mathrm{R}}H(298\mathrm{K}) = -172.9\ \mathrm{kcal\ mol^{-1}} \quad (19)$$

Ag; X = Cl, Br; eq 10). While all these reactions were predicted to be exothermic, the reaction of the ions is the most exothermic one. These $\Delta_{\mathrm{R}}H(298\mathrm{K})$ values are estimates for the gas phase reactions (lattice or solvation energies were not included). Combining the data used in the reactions 18 and 19 suggests an electron affinity for OCN of $E_{\mathrm{A}}(\mathrm{OCN}) = 65.8$ kcal mol^{-1} and an ionization potential for NO of $I_{\mathrm{p}}(\mathrm{NO}) = 201.2$ kcal mol^{-1} (cf. Table 7). These values are in reasonable agreement with the experimental data of $\mathrm{E_A(OCN)} = 83.0$ kcal mol^{-1} and an ionization potential for NO of $\mathrm{I_p(NO)} = 215.0$ kcal mol^{-1}.[29b,62]

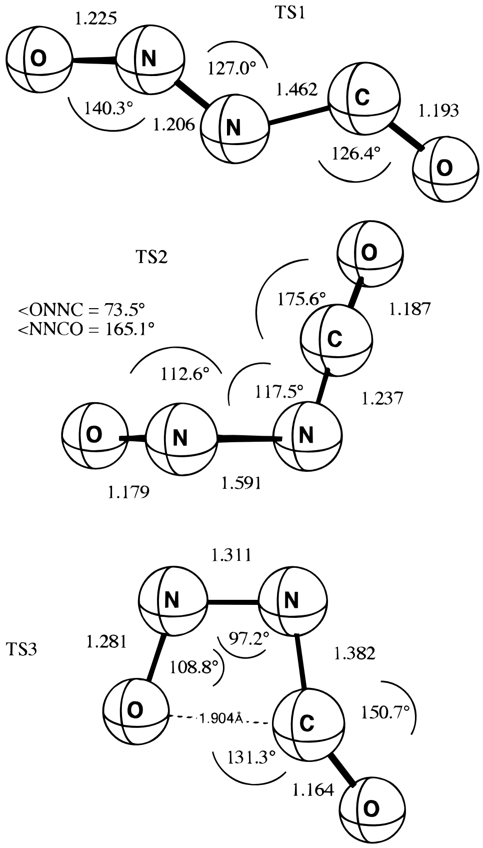

Figure 5. MP2/6-31G* optimized transition state structures (bond distances in Å, angles in deg) of OCN−NO; TS1 (→ CO + N$_2$O); TS2 (rotation → *cis*-isomer), TS3 (ring → CO$_2$ + N$_2$).

Table 6. Energies (kcal mol^{-1}) Relative to CO$_2$ + N$_2$ of the Stationary Points on the OCN−NO PES and the Likely Decomposition Products

	trans	*cis*	TS1[a]	TS2[b]	TS3[c]	CO + N$_2$O	CO$_2$ + N$_2$
MP2	116.5	119.8	175.3	121.1	136.1	86.4	0.0
MP2 + zpe	115.6	118.9	175.1	120.5	135.1	87.0	0.0

[a] TS1 (→ CO + N$_2$O). [b] TS2 (rotation → *cis*-isomer). [c] TS3 (ring → CO$_2$ + N$_2$).

According to our experiments, presumably OCN−NO is initially formed in the reaction of anhydrous silver isocyanate with XNO (X = Cl, Br) but is not stable in the presence of either XNO and AgOCN. On the other hand, there are two possible ways for an intrinsic decomposition (eqs 9 and 10). The driving force is the formation of the much more thermodynamically stable CO$_2$ and N$_2$ or CO and N$_2$O.

Similar to the decomposition of *trans*-N$_4$O, the direct decomposition into CO and N$_2$O (eq 12) is impeded since the barrier to overcome is ~58.1 kcal mol^{-1} (breaking of the strong N−C bond, C_s-TS1, Figure 5), and in accordance with this, CO was not observed in the experiment. On the other hand, the reaction via rotation (C_1-TS2, Figure 5) to *cis*-OCN−NO (Figure 3)[60] followed by intrinsic decomposition via a four-membered-ring transition state structure into CO$_2$ and N$_2$ is favored (eq 11, Table 6). This is in contrast to the decomposition of *cis*-N$_4$O, where first a cyclic N$_4$O isomer is formed which then dissociates. No minimum structure for a five-membered OCN−NO ring was found. Energetically, the breaking of the extended

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(60) 2266(773), 1555(107), 1269(274), 802(172), 716(177), 595(24), 358-(228), 132(1), and 114(0) cm^{-1}.

(61) $d(\mathrm{N_aC_b}) = 1.136$ Å, $d(\mathrm{C_cN_d}) = 1.315$ Å, $d(\mathrm{N_eC_f}) = 1.206$ Å, and $d(\mathrm{C_fO}) = 1.136$ Å; $\angle(\mathrm{NCN}) = 177.3°$, $\angle(\mathrm{CNC}) = 133.8°$, and $\angle(\mathrm{NCO}) = 173.7°$.

(62) Ziegler, T.; Gutsev, G. L. *J. Comput. Chem.* **1992**, *13*, 70.

Table 7. Calculated Total Energies E_{tot}^{MP2} (au), Interatomic Distances (Å) and Angles (deg), and Zero-Point Vibrational Energies zpe (kcal mol^{-1})

species		E_{tot}^{MP2}	$\langle S^2 \rangle$	E_{tot}^{PMP2a}	structural data[b]	zpe
BrCN	($^1\Sigma$)	−2662.56668			d(BrC) = 1.791 d(CN) = 1.185	4.9
BrNO	($^1A'$)	−2699.56541			d(BrN) = 2.211, d(NO) = 1.157, ∠BrNO = 114.5[59d]	3.8
ClCN	($^1\Sigma$)	-552.17622			d(ClC) = 1.638, d(CN) = 1.185	5.2
ClNO	($^1A'$)	−589.16773			d(ClN)=2.033, d(NO) = 1.156, ∠(ClNO = 114.0[59d]	3.9
Cl-NO$_2$)	($^1A_1$)	−664.16328			d(NO) = 1.207, ∠(ONCl) = 113.4[22]	7.7
CO	($^1\Sigma$)	−113.02122			d(CO = 1.151	3.0
CO$_2$	($^1\Sigma_g$)	−188.10775			d(CO) = 1.180[43]	7.2
NC−NCO	($^1A'$)	−260.20812			ref 61	13.1
NN	($^1\Sigma_g$)	−109.25528			d(NN) = 1.131	3.1
N$_2$O	($^1\Sigma$)	−184.20414			d(NN) = 1.172, d(NO) = 1.193	6.7
NO$^+$	($^1\Sigma$)	−129.24259			d(NO) = 1.103	3.0
•NO	($^2\Pi$)	−129.55890	0.78 (0.75)	−129.56321	d(NO) = 1.143	2.58
NO$_2^+$	($^1\Sigma_g$)	−204.23933			d(NO) = 1.156	7.2
•NO$_2$	($^2A_1$)	−204.56025	0.771 (0.75)	−204.56420	d(NO) = 1.217,[43,62] ∠(ONO) = 133.7	6.3
OCN$^-$	($^1\Sigma$)	−167.65908			d(CO) = 1.242, d(CN) = 1.211[43]	6.6
OCN•	($^2A_1$)	−167.54486	0.833 (0.75)	−167.55333	d(CN) = 1.255, d(CO) = 1.167[43,62]	7.1
tt-OCN−NO	($^1A'$)	−297.17740			Figure 3	11.2
ct-OCN−NO	($^1A'$)[60]	−297.17209			Figure 3	11.2
TS1-OCN−NO	($^1A'$)[64]	−297.08359			Figure 5	10.5
TS2-OCN−NO	($^1A'$)[65]	−297.17010			Figure 5	10.9
TS3-OCN−NO	($^1A'$)[66]	−297.14621			Figure 5	11.3
OCN−NO$_2$	($^1A'$)	−372.17969			Figure 2	15.6
TS-OCN−NO$_2$	($^1A'$)[67]	−372.15667			Figure 2	

[a] Spin-projected energies. [b] Structural data at MP2/6-31G* level; references concerning different levels of theory.

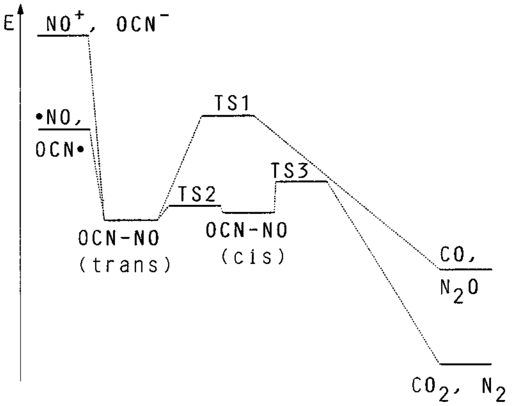

Figure 6. Qualitative description of the OCN−NO potential energy hypersurface.

π system by rotation about the C−N bond is accompanied by a smaller energy barrier (4.6 kcal mol^{-1}) and cyclic decomposition transition state (19.6 kcal mol^{-1}, Table 6). Moreover, the rotation into the *cis* structure results in an increase in the O−N and N−C bond lengths and a decrease in the N−N and C−O bond lengths (Figure 5, Table 6). With the molecule again contained in a single plane, delocalized π interaction over the entire molecule is possible and the energy of the *cis* chain isomer (Figure 3) drops to near that of the *trans* chain isomer (Table 6). A qualitative description of the OCN−NO PES is shown in Figure 6.

Conclusions

We have carried out a combined theoretical and experimental study and investigated the reaction behavior of silver cyanate toward NO$_2$, NO, ClNO$_2$, BrNO, and ClNO. On the basis of the observed decomposition products, we propose nitryl isocyanate, OCN−NO$_2$, as a likely intermediate for the NO$_2$/ClNO$_2$ reaction, which decomposes at room temperature forming CO$_2$ and N$_2$O. The AgOCN/XNO reaction (X = Cl, Br) is a highly complex reaction where X−CN and X(CO)NCO were experimentally observed as long-lived intermediates, in addition to NO, NO$_2$, N$_2$O, and CO$_2$.

Moreover, the OCN−NO$_2$ and the OCN−NO singlet potential energy hypersurfaces have been studied in detail using ab initio techniques and have been compared with the results previously published for the isoelectronic azides, NNN−NO$_2$ and NNN−NO. For both molecules, OCN−NO$_2$ and OCN−NO, the structural parameters and vibrational frequencies have been characterized in order to aid future experimental attempts at isolation. The intrinsic decomposition of OCN−NO was calculated to be different from that of NNN−NO since no cyclic isomer was found and the decomposition products CO$_2$ and N$_2$ are more likely than N$_2$O and CO (the latter would correspond to the decomposition products N$_2$O and N$_2$ for N$_4$O).

Both molecules, nitryl isocyanate and nitrosyl cyanate, are intrinsically stable. Although their intramolecular dissociation is accompanied by a release of −82.9 (OCN−NO$_2$, eq 7) and −115.6 kcal mol^{-1} (OCN−NO, eq 11), it should be possible to isolate these molecules using low-temperature techniques as their barriers to decomposition are high enough (for OCN−NO$_2$ 14.4 kcal mol^{-1}; for OCN−NO 19.6 kcal mol^{-1}).

Note Added in Proof. While this paper was with the referees, in an independent theoretical and experimental study G. Maier et al. could for the first time isolate the predicted NCO−OCN molecule from the photolysis reaction of carbolyl azide isocyanate (eq 20) in an argon matrix at 10 K.[63]

$$N_3{-}C(O){-}N{=}C{=}O \xrightarrow{H\nu,\ 10\ K} O{=}C{=}N{-}N{=}C{=}O + N_2 \qquad (20)$$

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(63) Maier, G.; Naumann, M.; Reisenauer, H. P.; Eckwert, J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1696.

(64) 1969, 1752, 1241, 850, 559, 493, 311, 150, and −i1172 cm^{-1}.

(65) 2293, 1662, 1301, 726, 642, 551, 276, 153, and −i102 cm^{-1}.

(66) 2120, 1418, 1293,1038, 777, 711, 324, 233, and −i568 cm^{-1}.

(67) 2144, 1734, 1360, 1082, 1049, 770, 759, 639, 609, 391, 179, and −i459 cm^{-1}.