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Nitrosyl Isocyanate (ONNCO): Gas-Phase Generation and a HeI Photoelectron Spectroscopy Study

Xiaoqing Zeng,[†,‡] Maofa Ge,*[,†] Zheng Sun,[†] and Dianxun Wang*[,†]

State Key Laboratory for Structural Chemistry of Unstable and Stable Species,
Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China, and
Graduate School of Chinese Academy of Sciences, Beijing 100039, China

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The nitrosyl isocyanate (ONNCO) has been generated from a heterogeneous reaction of gaseous nitrosyl chloride with silver isocyanate and studied for the first time in the gas phase. This structurally and energetically novel transient specimen is characterized by HeI photoelectron spectroscopy combined with DFT calculations. Both the calculations and the spectroscopic results suggest that the molecule adopts an open-chain trans structure. The observed decomposition products indicate the formation of ONNCO and further confirm the previously reported decomposition pathway.

Introduction

As an important intermediate, nitrosyl isocyanate (ONNCO), although unstable, has received considerable attention in the reaction of NCO with NO (eq 1), because of its importance for the combustion of nitrogen-containing compounds.[1,2] Particularly, the reactions of NCO with NO*x* are key intermediate processes in the rapid reduction of nitrogen oxide (RAPRENO*x*)-effective removal of NO*x* from exhaust gases.[2] On the other hand, similar to other metastable molecules as OCN−NCO,[3] N−NCO,[4] ON−N_3,[5] and ON−NO,[6] ONNCO is also considered to be a potential high energy density material (HEDM), and several research methods have been devoted to it theoretically[7] and experimentally.[8]

The first attempt to prepare this novel compound was carried out by Klapötke et al.,[8] who have successfully isolated nitrosyl azide ON−N_3 at low temperature.[5a] They studied the reaction of AgOCN with NO, ClNO, and BrNO, according to the observed IR results after several seconds, a reaction mechanism involves the formation of neutral nitrosyl isocyanate, ONNCO was proposed as the initial step, and two possible decomposition pathways (eq 1) were discussed. However, no direct experimental data for this compound were obtained yet because of its instability.

$$\mathrm{NCO + NO \rightarrow OCNNO \rightarrow N_2O + CO} \qquad (1a)$$

$$\mathrm{\rightarrow N_2 + CO_2} \qquad (1b)$$

We have a long-standing interest in the generation, spectroscopy, and structure of small stable and unstable species.[9] Herein we present the first in situ generation of nitrosyl isocyanate ONNCO in the gas phase and the

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* Author to whom correspondence should be addressed. E-mail: gemaofa@iccas.ac.cn.

[†] Institute of Chemistry, Chinese Academy of Sciences.

[‡] Graduate School of Chinese Academy of Sciences.

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subsequent characterization by photoelectron spectroscopy (PE). The measured ionization energies have been assigned with the aid of OVGF calculations as well as in comparison to other nitrosyl and isocyanate containing molecules.

Experimental Section

(1) Reaction. As reported by Bartlett et al.,[7a] the most stable isomer *trans*-ONNCO is 113 kcal mol $^{-1}$ higher in energy than the most stable dissociation products N_2 and CO_2, but its 18 kcal mol^{-1} dissociation barrier is rather small for any but low-temperature gas phase or matrix observation. So, in the present study, we generated nitrosyl isocyanate similar to other unstable species such as ISeCN,[9a] $SO(N_3)_2$,[10] and NSCN,[11] by passing gaseous ClNO over finely powdered AgOCN. The reaction occurred spontaneously at room temperature, and the in situ photoelectron spectrum was recorded simultaneously. The reaction may be represented by the eq 2.

$$\text{AgOCN (s)} + \text{ClNO (g)} \rightarrow \text{ONNCO (g)} + \text{AgCl (s)} \qquad (2)$$

AgOCN (ACROS) was dried in a vacuum (10^{-4} Torr) for 2 h at 60 °C before the experiment. ClNO was prepared as reported,[12] and its PE spectra was checked to be the same with the literature.[13] An attempt to isolate nitrosyl isocyanate by dropping liquid ClNO over AgOCN at -45 °C resulted in a fierce explosion.

(2) Instrumentation. The PE spectrum was recorded on a double-Chamber UPS-II machine, which was designed specifically to detect transient species as described elsewhere[9,10] at a resolution of about 30 meV as indicated by the $Ar^+(^2P_{2/3})$ photoelectron band. Experimental vertical ionization energies (Iv in eV) are calibrated by simultaneous addition of a small amount of argon and methyl iodide to the sample.

(3) Computation. There have been many theoretical discussions on the isomers of CN_2O_2,[7,8,14] but here we only have to consider the two most stable isomers when taking into account the experiment:[8] *cis*-ONNCO and *trans*-ONNCO. The calculations were performed using the program package Gaussian 98.[15] All optimizations were done at the B3LYP/6-311++G(3d)level. The B3LYP is a hybrid functional method based on the Becke's three-parameter nonlocal exchange functional,[16] with the nonlocal correlation due to Lee, Yang, and Parr.[17] The vertical ionization energies (Ev) for cis and trans isomers were calculated at the ab initio level according to Cederbaum's outer valence Green's function (OVGF)[18] method at the 6-311++G(3d) basis set.

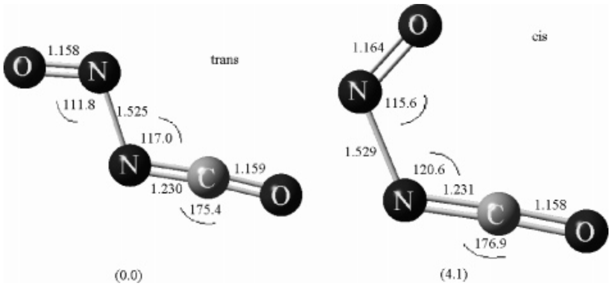

Figure 1. Geometries and relatives energies (kcal/mol) for cis and trans isomers of ONNCO at the B3LYP/ 6-311++G(3d) level of theory.

Results and Discussion

Calculated Structure. Due to the paucity of experimental data, theoretical calculations become important in providing information on structures and relative energies. As pointed out by Klapötke et al.,[8] two C_s isomers with trans and cis symmetry are located on the ONNCO potential energy hypersurface, the intermediate *trans*-ONNCO formed in the reaction of NO and OCN and then transformed to the cis isomer by surmounting 4.9 kcal mol^{-1} via a C_1-symmetry transient state. The structural parameters calculated at the B3LYP/6-311++G(3d) level are depicted in Figure 1, and the energy gap between two isomers is calculated to be 4.1 kcal mol^{-1} with the zero-point of energy corrections and coincides to the reported 4.0 kcal mol^{-1} (including ZPE) at the MP2/6-311+G(3df, 2p) level of theory.[14b] Recently, many theoretical research methods have been focused on some novel species which are composed of NO and pseudohalogen moieties such as NCO,[14] NC,[19] and N_3.[20] All calculations predict the trans open-chain isomer to be the most plausible candidate for the detectable neutral species in the gas phase, and this explains why the calculated ionization energies for the *trans*-ONNCO agree well with the experimental observed values (Table 1). Comparing the predicted O−N bond with the experimentally determined bond lengths of some similar molecules (there are no experimental results for ONNCO itself), we see that the predicted N−O bond of ONCNO (1.158 Å) lies between the diatomic NO (1.151 Å)[21] and N_2O (1.186 Å)[22] N−O bond lengths, favoring NO slightly. As for *trans*-ONNCO, the calculated N−N bond length is 1.525 Å, which is very close to that of *trans*-NNCO (1.498 Å)[4] and $ON-N_3$ (1.501 Å).[20]

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Table 1. PES Vertical Ionization Energies (IP in eV), Computed Vertical Ionization Energies (Ev in eV) by OVGF Calculation with 6-311++G(3d) Basis Sets, and Molecular Orbital Character for ONNCO

	calcd[a]			
exptl IP[b]	trans	cis	MO	character
10.71	10.57	11.05	15a′ (18)	$\pi_{nb\ (NO)}$, $\pi_{nb}{}^{c}{}_{(NCO)}$
11.59	11.50	11.53	3a″ (17)	$\pi_{nb}{}^{d}{}_{(NCO)}$, n_O
13.25	13.37	12.73	14a′ (16)	n_N, n_O
15.60	16.13	16.26	13a′ (15)	$\pi_b{}^{c}{}_{(NCO)}$, σ_{NO}
16.82	16.66	16.72	2a″ (14)	$\pi_b{}^{d}{}_{(NCO)}$, $\pi_{b\ (NO)}$
17.60	17.48	17.62	1a″ (13)	σ_{NO}

[a] ROVGF/6-311++G(3d). [b] Vertical ionization potentials. [c] In-plane orbital. [d] Out-of-plane orbital.

This prediction is longer than the experimental nitrogen−nitrogen bond length in hydrazine, N_2H_4 (1.449 Å),[23] but much shorter than the nitrogen−nitrogen bond length in the weakly bound dinitrogen tetraoxide, N_2O_4 (1.782 Å).[24] On considering the linearity from the point of the whole molecule, the participation of the oxygen atom in bonding with nitrogen causes the open-chain molecule in ONNCO ($\angle$=117.0°) to be just between NNCO ($\angle$=125.7°) and ON−N_3 ($\angle$=106.2°), owing to the similarities between the pseudohalogen moieties N_3 and NCO.

Photoelectron Spectrum. The HeI PE spectrum of the reaction products of gaseous ClNO and AgNCO at different temperatures is shown in Figure 2. Figure 2a depicts the recorded spectrum of the reaction at 55 °C. The sharp peaks marked with asterisks are characteristic bands for CO_2, while those marked with dots are for N_2.[25] Both compounds derive from the decomposition of ONNCO (eq 1b); however, no appreciable bands for N_2O and CO have been observed in the PE spectrum during the experiment. It confirms the reaction mechanism proposed for the formation of ONNCO in the initial step, because this short-lived intermediate is expected to decompose into N_2 and CO_2 via cleavage-rearrangement (eq 1b) or directly into N_2O and CO (eq 1a) or further react with ClNO, but as the transition state for this decomposition pathway is much higher in energy than the transition state for the second decomposition pathway (eq 1b).[7,8,14] Meanwhile, the in situ generation and characterization precludes its further reactions with ClNO, so no bands could be found for NO_2,[25] ClCN,[26] NCNCO,[27] and ClC(O)NCO,[28] which have been detected as final products by the IR spectrum after 10 s reaction time at room temperature.[8]

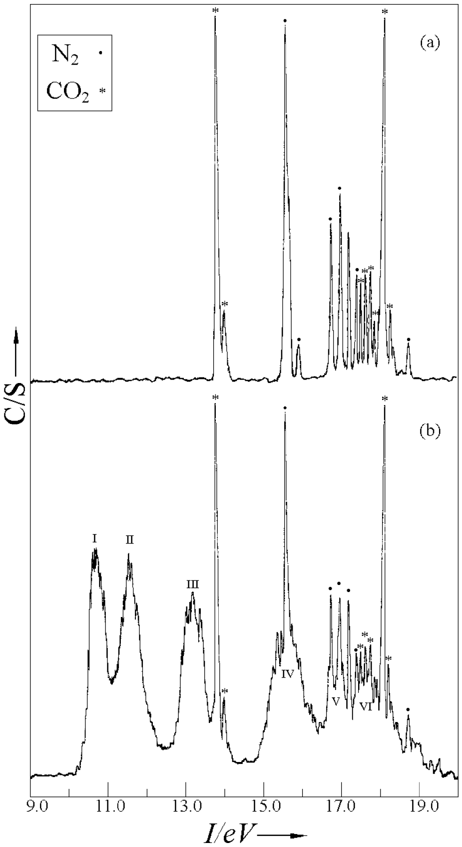

Figure 2. (a) HeI photoelectron spectrum of the gaseous products of reaction 2 at 55 °C. (b) HeI photoelectron spectrum of the gaseous products of reaction 2 at 20 °C.

Figure 2b illustrates the PE spectrum of the reaction at 20 °C. Several attempts were made to minimize the intensities of CO_2 or N_2 by lowering the reaction temperature but failed in the appearance of unreacted ClNO in PE spectrum.[13] On the whole, there are six distinct bands (I−VI) for ONNCO. The experimental and calculated vertical ionization energies using the ROVGF/6-311++G(3d) method (for both trans and cis isomers) are listed in Table 1. It can be seen clearly that the experimental results match well with the ionization potentials calculated for the energetically favorable trans isomer. Certainly, the theoretical results of the cis isomer are also close to the experimental IPs, and we could not exclude the existence of the relatively unstable cis isomer. In comparison with known PE spectra of HNCO[29] and CH_3-NO,[30] the assignment is relatively straightforward, especially since it is a planar open-chain molecule, there is almost complete π/σ separation. Similar to other nitrosyl pseudohalogen compounds ON−N_3[5] and ON−CN,[31] the ONNCO molecule can be described quite adequately as a loosely bound combination of a reorganized ON and a NCO radical. More specifically the ONNCO molecule orbitals (MOs) can be treated as MOs located on either the ON or the NCO

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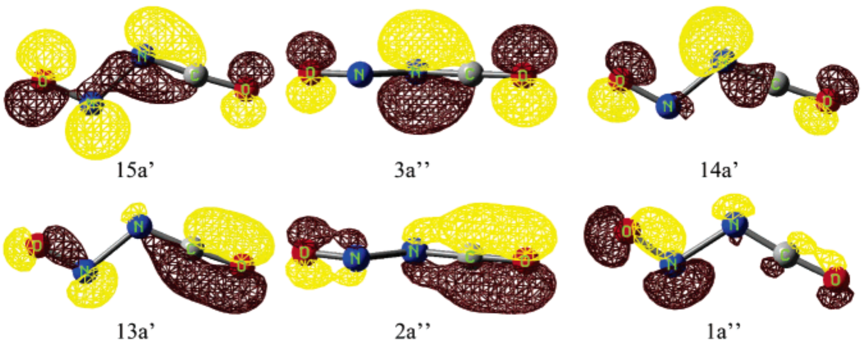

Figure 3. Characters of the first six highest occupied molecular orbitals for *trans*-ONNCO.

fragment of the molecule. Besides, within the HeI energy region (21.12 eV), the nonbonding and bonding π level (of the originally linear molecule) will give rise to four IPs in the linear molecule, viz. a″(n.b.), a′(n.b.) and a″(b), a′(b). These are partially localized on the pseudohalide group. Two additional IPs will arise from in-plane (a′) and out-of-plane (a″) π orbitals which are partly localized on the substituent group. As will become evident later there is considerable mixing between orbitals of the same symmetry. In addition, pσ type orbitals are also expected to occur within the 21.12 eV range.

First we compare the ONNCO PE spectrum with those of related molecules HNCO[29] and CH_3NO.[30] The first two bands (11.62 and 12.30 eV) for HNCO are assigned to the nonbonding out-of-plane (3a″) and the nonbonding in-plane (8a′) orbitals, respectively,[29] and the first band at 9.70 eV of monomer CH_3NO is attributed to the strong π_{NO} antibonding (combination of oxygen and nitrogen lone pairs) contributions.[30] By combining NO and NCO moieties and assuming a linear structure, the first two bands for ONNCO can be easily assigned. The vertical ionization potential for the first band I (Figure 2b) is 10.71 eV, and the calculated energy is 10.57 eV. This is a featureless band and can be compared to the first PE band of CH_3NO[30] at 9.70 eV and ONCN[31] at 11.50 eV. The HOMO (15a′) (Figure 3) for this ionization can be described as an in-plane combination of a strong antibonding π_{NO} and an in-plane nonbonding π_{NCO} with the same a′ symmetry. It indicates the interactions between the two moieties in the ONNCO molecule.

The second band II at 11.59 eV derives from the ionization of the 3a″ orbital and coincides to the calculated value 11.50 eV. This band is mainly ascribed to the nonbonding out-of-plane (perpendicular to the molecular plane) π_{NCO} orbital (Figure 3), and the participation of the oxygen lone pair of the NO moiety should also be included. However, the interference of NO on this 3a″ orbital seems to be negligible (Figure 3). The most recent experimental adiabatic ionization potential for the NCO radical was determined to be 11.759 ± 0.006 eV using photoionization mass spectrometry, and the computed vertical IP at the MRSD-CI level is 11.67 eV, which is very close to the value for this orbital in ONNCO (11.59 eV).[32] An interesting and important feature for the PE spectra of NCO containing compounds is that the energetic order of the first two highest occupied orbitals is out-of-plane $\pi_{nb(NCO)}$ < in-plane $\pi_{nb(NCO)}$, such as HNCO,[29] XNCO (X = Cl, Br, I),[33] CH_3NCO,[29] and NCNCO.[27] This trend is reversed in ONNCO by the extensive incorporation of the π_{NO} antibonding character into the HOMO 15a′. It is to be noted that the separations ΔE between the first two IPs of NCNCO[27] and ONNCO are 0.25 and 0.88 eV, respectively. This increase between the two components of the nonbonding orbitals is in accord with the approach to the deviation of linearity, that is $\angle$CNC = 140.0°, whereas $\angle$NNC in ONNCO is 117.0°. This smaller angle indicates larger off-axis twisted and less stabilized in ONNCO.

The experimental vertical ionization potential for the third band (Figure 2) is 13.25 eV and in well agreement with the calculated 13.37 eV, which is consistent with the corresponding band in NCNCO at 13.46 eV;[27] therefore, it can be unambiguously assigned to the nitrogen "lone-pair" orbital (n_N), mainly localized on the nitrogen atom of the NCO group (Figure 3) (14a′). The calculated character for this orbital also indicates the incorporation of the lone pair on the oxygen of the nitroso group. Beyond 15.0 eV it shows three additional bands similar to that of the other NCO containing molecules, which are hard to assign, since the π bonding and the pσ orbitals are predicted to lie close in energy, and most ionizations in this region (>15.0 eV) might be attributed to inner molecular orbitals with broad bands.[34] The bands with ionization energy at 15.60 and 16.82 eV, overlapped by N_2, involves the magnitude (and direction) of the separation of the $\pi_{(NCO)}$ bonding orbital (to give a′ and a″ levels), which is degenerate in unperturbed molecule HNCO,[29] because of the perturbation of the NO group on this orbital. The former is assigned to the 13a′, the primary characters are the bonding in-plane $\pi_{(NCO)}$ and σ_{NO}, and the latter is the out-of-plane bonding $\pi_{(NCO)}$ and π_{NO} (Figure 3). The $\pi_{(NCO)}$ bonding separation in ONNCO is 1.2 eV, in the range (1−2 eV) for the π bonding separations for isoelectronic analogues to parent acid HNCO[29] such as H_2CNN[35] and H_2CCO.[36] The last observable band VI (Figure 2b) below 18.0 eV is the ionization result of the 1a″ orbital superimposed at about

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17.60 eV, and it is overlapped by the typical bands of the decomposition product CO_2 in this region. The primary MO character is the σ_{NO} (Figure 3), and a similar band occurs in the PE spectrum of CH_3NO.[30]

Conclusion

The short-lived reactive specimen nitrosyl isocyanate ONNCO, containing only C, N, and O, can be generated in the gas phase by the heterogeneous reaction of gaseous ClNO with AgNCO. The electronic structure of this novel molecule is characterized by in situ photoelectron spectroscopy (PE), combined with DFT calculations. The agreement between the PES experiment and the OVGF calculations indicates the predominance of the trans isomer in the gas phase. The PE spectrum analysis provides a picture of the substantial interactions between the two halves of the molecule. The split of the degenerate nonbonding $\pi_{(NCO)}$ is indicated by the separation of the first two IPs at 10.71 eV (15a′) and 11.59 eV (3a″), respectively, in ONNCO, accompanied by the reversal of orbital ordering in comparison to the nonbonding π_{NCO} in other NCO containing molecules. The magnitude of separation ΔE is 0.88 eV, greater than that in another unstable molecule NCNCO ($\Delta E = 0.12$ eV), which indicates its less stability compared to NCNCO. This separation can be explained as the incorporation of the NO moiety. The observed decomposition products CO_2 and N_2 further confirm the formation and the theoretical predicted energetically favorable decomposition pathway of novel nitrosyl isocyanate ONNCO.

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Supporting Information Available: Optimized structures for isomers of ONNCO and the most stable conformer of ClC(O)NCO at B3LYP/6-311++G(3d) level of theory and tables of total energies of isomers of ONNCO at different levels of theory, relative energies at the B3LYP/6-311++G(3df) level of theory, and experimental and calculated vertical ionization energies by OVGF calculations with 6-311++G(3d) for isomers of ONNCO and ClC(O)NCO. This material is available free of charge via the Internet at http://pubs.acs.org.

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