Notes

Possible Intermediate Formation of Cyclic Nitrous Oxide, N_2O: Reaction of Oxygen Difluoride, OF_2, with Cesium Azide, CsN_3[†]

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Introduction

Recently the chemistry and the structures of several covalently bound azides of the type X−N_3 have been determined.[1,2a,b] These highly reactive compounds, often stable at low temperatures only, have been shown to decompose to form not X and N_3 through cleaving of the X−N bond (eq 1) but rather, the intermediate formation of XN and N_2 has been shown to occur despite being a spin-forbidden process (eq 2). Despite the relatively strong N1−N2 bond in covalent azides of the type X−N1−N2−N3 for HN_3, thermal fragmentation of this molecule is not induced by breaking the H−N_3 bond but rather by dissociation into HN and N_2. Since the electronic ground state of XN (X = H, halogen) is a triplet state ($^3\Sigma^-$), dissociation of XN_3 ($^1A'$) into XN ($^3\Sigma^-$) and N_2 ($^1\Sigma^+{}_g$) is spin-symmetry forbidden. Nevertheless, pyrolysis experiments have shown that HN_3 decomposes into N_2 and HN in the ground-state triplet ($^3\Sigma^-$) state.[2c] A theoretical study [2d] on the energetics of the dissociation reaction of HN_3 ($^1A'$) yielding N_2 ($^1\Sigma^+{}_g$) and HN ($^3\Sigma^-$) at a very high level of theory using CASSCF and MCSCF−CI techniques has shown that the singlet−triplet coupling occurs because the HN_3 wave function in the region of the transition state can be considered an equal mixture of N_2 (X)·NH($a^1\Delta$) and N_2 (X)·NH($b^1\Sigma^+$). The calculated barrier for the dissociation (35.7 kcal mol^{-1}) is in excellent agreement with the value of 36 kcal mol^{-1} estimated from thermal dissociation studies.[2e] This result suggests that the stabilities of XN_3 molecules may be determined by the activation barrier for breaking the XN−N_2 bond, which in turn involves singlet−triplet coupling along the reaction course. The accurate calculation of the dissociation barrier of XN_3 yielding XN and N_2 needs a very high level of theory that is not possible for larger atoms or substituent groups X at present time. However, Frenking et al.[2f] have shown that for covalently bound main-group azides the reaction energy of the dissociation reaction can be calculated at the electron-correlated MP2 level of theory.

$$XN_3 \rightarrow X + N_3 \tag{1}$$

$$XN_3 \rightarrow XN + N_2 \tag{2}$$

In this context, as well as the preparation of new binary azides, the investigation of their decomposition products has also been regarded as of equal importance. The often low thermal stability of binary azides which results in characterization difficulties led naturally to the use of other modern techniques such as high level quantum chemical calculations (which have been shown to exhibit a high degree of accuracy for such systems) to investigate the possible structure and decomposition pathways.[2] Moreover, we have for some time been interested in the elucidation of the bond properties, by high-level quantum chemical ab initio computations combined with modern spectroscopic methods.

In an earlier study we reported on the preparation and characterization of nitrosyl azide, N_4O, and its unimolecular fragmentation into N_2O and N_2. It was found through a combined quantum chemical study and experimentally observed gas-phase IR decomposition products that *trans-trans*-N_4O decomposes via rotation into the *cis-cis* isomer and cyclic N_4O to yield N_2O ($C_{\infty v}$) and N_2.[2−5] Through this combination of theory and experiment the formation of a new binary isomer of N_2O through this reaction was deemed highly unlikely. Therefore the ongoing quest for cyclic N_2O continued due to the observation of trans-cis isomerization of the N_4O moiety.

Results and Discussion

In the present study we now report about the reaction of oxygen difluoride, OF_2, with cesium azide, CsN_3, with the aim of investigating the decomposition pathway with respect to the formation of cyclic N_2O as the observation and characterization of a binary oxygen diazide, $O(N_3)_2$ would be expected only at extremely low temperatures. It was found that the reaction of OF_2 with NaN_3 or CsN_3 did indeed yield dinitrogen and nitrous oxide according to eq 3 in the molar ratio of roughly 1:2. Both gaseous products were unambiguously identified by IR spectroscopy (N_2O) and the typical gas discharge color of N_2 which is volatile at −196 °C.[6] Neither O_2 or NOF nor NO or NO_2 were detected as reaction products.

$$OF_2 + 2CsN_3 \xrightarrow{\Delta T} N_2O + 2N_2 + 2CsF \tag{3}$$

However, the undertaking of this experiment was hoped to show the formation of N_2O and N_2 which would then pose the interesting question of the decomposition pathway which was occurring.To explain the formation of nitrous oxide (NNO) from the reaction of OF_2 with CsN_3 we propose the intermediate

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[†] Part of this work has already been presented as a lecture at the ACS 14th Winter Fluorine Conference, St. Petersburg Beach, FL, January 17−22, 1999. [1 kcal mol^{-1} = 4.184 kJ mol^{-1}, 1 Å = 10^{-10} m (since these units are still used in computational chemistry we employed them throughout the paper).]

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Table 1. Structure, Energy, and Vibrational Frequencies of $O(N_3)_2$ Computed ab Initio at Various Levels of Theory

	HF[a]	HF[a]	MP2[a,c]	B3LYP[a]	CCD/D95V(d)[d]
symmetry	C_1	C_2	C_2	C_2	C_2
$-E$/au	401.353320	401.353320	402.594517	403.5792531	402.451087
NIMAG	0	0	0	0	0
zpe/kcal mol^{-1}	18.8	18.8	17.0	16.5	17.2
d(O1−N2)/Å	1.393	1.393	1.447	1.452	1.446
d(N2−N4)/Å	1.261	1.261	1.275	1.260	1.293
d(N4−N6)/Å	1.088	1.088	1.145	1.128	1.134
∠(N2−O1−N3)/deg	111.2	111.2	109.3	110.2	108.8
∠(O1−N2−N4)/deg	106.5	106.5	106.8	107.3	105.0
∠(N2−N4−N6)/deg	174.2	174.2	172.0	172.0	173.9
∠(N3−O1−N2−N4)/deg	88.7	88.7	82.5	89.8	86.8
∠(O1−N2−N4−N6)/deg	172.1	172.1	177.3	172.5	176.0
ν_1/cm^{-1} (rel. int.)[b]	50 (2)	50 (2)	47 (0.5)	46 (0.5)	45 (1)
ν_2/cm^{-1} (rel. int.)[b]	89 (2)	89 (2)	76 (0.5)	72 (14)	81 (1)
ν_3/cm^{-1} (rel. int.)[b]	226 (0)	226 (0)	183 (0)	190 (14)	196 (0)
ν_4/cm^{-1} (rel. int.)[b]	333 (6)	333 (6)	264 (3)	251 (5)	291 (5)
ν_5/cm^{-1} (rel. int.)[b]	499 (2)	499 (2)	423 (2)	416 (3)	440 (2)
ν_6/cm^{-1} (rel. int.)[b]	598 (7)	598 (7)	483 (2)	533 (3)	540 (2)
ν_7/cm^{-1} (rel. int.)[b]	610 (26)	610 (26)	508 (8)	547 (10)	550 (11)
ν_8/cm^{-1} (rel. int.)[b]	767 (1)	767 (1)	679 (31)	636 (54)	688 (0)
ν_9/cm^{-1} (rel. int.)[b]	827 (3)	827 (3)	698 (0.5)	666 (0.5)	726 (1)
ν_{10}/cm^{-1} (rel. int.)[b]	1034 (9)	1034 (9)	768 (16)	746 (2)	863 (14)
ν_{11}/cm^{-1} (rel. int.)[b]	1036 (355)	1036 (355)	859 (0.5)	862 (2)	917 (1)
ν_{12}/cm^{-1} (rel. int.)[b]	1097 (133)	1097 (133)	1101 (114)	1097 (229)	1068 (242)
ν_{13}/cm^{-1} (rel. int.)[b]	1124 (2)	1124 (2)	1125 (6)	1125 (4)	1100 (8)
ν_{14}/cm^{-1} (rel. int.)[b]	2421 (1194)	2421 (1194)	2327 (623)	2168 (861)	2256 (943)
ν_{15}/cm^{-1} (rel. int.)[b]	2446 (27)	2446 (27)	2347 (34)	2190 (16)	2282 (31)

[a] 6-311++G(d) basis. [b] Rel. IR int. in km mol^{-1}. [c] $-E$[MP4(SDTQ)//MP2][a] = 402.669763 au. [d] $-E$[CCSD(T)/D95V(d)//CCD/D95V(d)] = 402.522973 au.

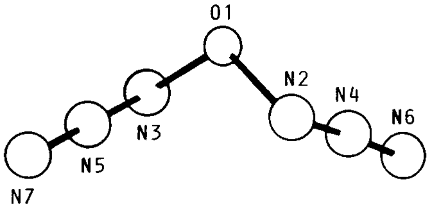

Figure 1. Ab initio computed C_2 structure of $O(N_3)_2$ (cf. Table 1).

formation of $O(N_3)_2$ which decomposes into N_2O and two equivalents of N_2. The structure, energy and vibrational frequencies of the hitherto unknown $O(N_3)_2$ were computed ab initio at various levels of theory (Table 1).[7] Initially calculations were performed without symmetry constraints but in all cases the structure was optimized to C_2 symmetry (Figure 1).[7] It can be stated that the molecule $O(N_3)_2$ in C_2 symmetry possesses a true minimum (*NIMAG* = 0) on its potential energy hypersurface and is vibrationally stable. Therefore $O(N_3)_2$ is an intrinsically stable but elusive molecule since the overall decomposition reaction according to eq 4 is thermodynamically highly favorable. The calculated total energies of $O(N_3)_2$, N_2O ($C_{\infty v}$), and N_2 can be used to predict theoretically the energy of reaction 4. After correction for zero point energies (*zpe*, $\Delta U^{\mathrm{vib}} = -4.2$ kcal mol^{-1}), rotational ($\Delta U^{\mathrm{rot}} = +{}^3/_2RT$), translational correction ($\Delta U^{\mathrm{tr}} = +3RT$) and the work term ($p\Delta V = +2RT$), the reaction

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(6) **Caution:** Covalent azides are usually highly explosive and often are very toxic. ClF_3, F_2, and OF_2 are strong oxidizers. Although no explosion was observed in our studies, all covalent azides and high oxidizers should be handled with respect and fully protective clothing should be worn at all times. A stainless steel (T316SS) reaction vessel was pre-passivated with ClF_3 (1 bar, 100 °C, 12 h) and loaded in the drybox with 1.05 g (6.0 mmol) of dry CsN_3 (Dynamite Nobel). The vessel was then cooled to −196 °C, all N_2 was pumped off and 0.11 g (2.0 mmol) OF_2 were condensed onto the CsN_3. The reaction vessel was then warmed to room temperature and heated for 15 min. to 250 °C. After this the reaction vessel was cooled to −196 °C and all products volatile at this temperature were pumped off and identified by their typical gas-discharge color. N_2 was identified as the only volatile reaction product at this temperature. Then the reaction vessel was allowed to warm to room-temperature again and a gas-phase IR spectrum was recorded [gas IR (2 Torr, 25 °C, 10 cm cell, ν in cm^{-1}): 3480 m (NNO), 2565 m (2 × ν_3, NNO), 2460 w, 2225 vs (ν_1, NNO), 1285 s (ν_3, NNO), 825 m (ν_3, FOF), 590 w (ν_2, NNO)]. Finally all volatile products were pumped off and the steel vessel was taken into the drybox and the remaining solid material identified as a mixture of unreacted CsN_3 (excess, see above) and CsF (F^- in CsF was detected after the residue was dissolved in water using a fluoride sensitive electrode). Qualitatively the same results were obtained when NaN_3 or Me_3SiN_3 were used as the azide compound.

(7) The structures of all compounds considered were "*pre*"-optimized using semiempirical calculations. All semiempirical calculations were carried out with the program package HyperChem[8] at the semiempirical PM3[9] level of theory using a VSTO-3G* basis set. Finally, the structures, energies, vibrational frequencies and zero point energies were computed ab initio with the program package Gaussian 94.[10] All structures were fully optimized at the HF and electron correlated MP2 and CCD (using double substitutions from the Hartree−Fock determinant)[11] as well as at the DFT hybrid B3LYP level of theory.[12] In addition, the energy of $O(N_3)_2$ at the MP2 structure was computed at the MP4(SDTQ) level of theory and in addition at the CCD structure at the CCSD(T) level. For all HF, MPn and B3LYP calculations a 6-311++G(d) basis set was used.[13] The coupled cluster calculations were performed with a Dunning/Huzinaga valence double-ζ basis with the addition of a set of d-type polarization functions to each atom (D95V(d))[14] whereas for computing the potential energy hypersurface at the MP2 level of theory a 6-31+G(d) basis set was used.[13]

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Table 2. Comparison of Different Isomers of N_2O, ab Initio Calculated at the MP2/6-311++G(d) Level of Theory

	linear NNO ($C_{\infty v}$)	linear NNO ($C_{\infty v}$), exptl	cyclic NON (C_{2v})	linear NON ($D_{\infty h}$)
$-E$/au	184.290030		184.169357	184.183851
$E_{rel.}$/kcal mol^{-1}	0.0		+75.7	+66.6
d (NN)/Å	1.163	1.126[15]	1.214	
d (NO)/Å	1.181	1.186[15]	1.511	1.342
∠(NON)/deg			47.4	
∠(ONN)/deg			66.4	
NIMAG [a]	0	0	0	0
zpe/kcal mol^{-1}	6.58	6.70	4.13	5.26
ν_1/cm^{-1} (IR int.)[b]	2243 (366)	2225 s[16]	966 (16)	2398 (2647)
ν_2/cm^{-1} (IR int.)[b]	538 (3)	590 w[16]	287 (3)	368 (11)
ν_3/cm^{-1} (IR int.)[b]	1286 (11)	1285 s[15,16]	1636 (3)	546 (0)

[a] *NIMAG* = number of imaginary frequencies. [b] IR intensities are given in km mol^{-1}.

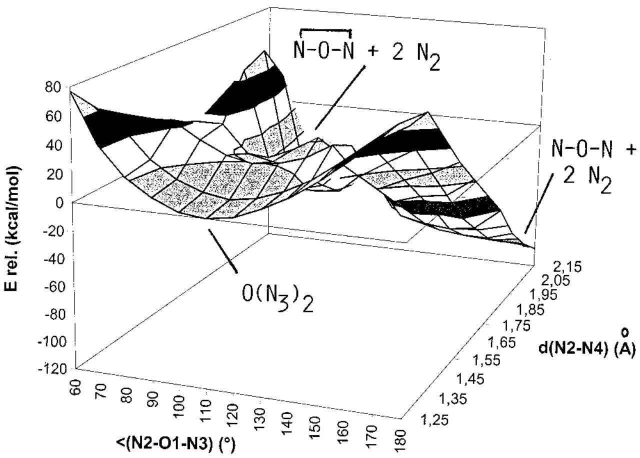

Figure 2. Two-dimensional potential energy hypersurface representing the unimolecular decay of $O(N_3)_2$ to yield cyclic N_2O and N_2 computed at MP2/6-31+G(d) level of theory.

enthalpy of the gas-phase reaction according to eq 4 was calculated at the optimized MP2/6-311++G(d) geometries to be $\Delta H^\circ{}_{298}(2) = -187.7$ kcal mol^{-1}.

$$O(N_3)_2\ (C_2) \rightarrow N_2O\ (C_{\infty v}) + 2N_2\ (D_{\infty h}) \qquad (4)$$

However, according to the gas-phase IR data[6] the experimentally observed nitrous oxide has undoubtedly a N−N−O ($C_{\infty v}$) (and not a N−O−N ($D_{\infty h}$)) connectivity. We therefore propose for the unimolecular decomposition in the gas phase a dissociation of $O(N_3)_2$ into 2 equiv of N_2 and initially formed cyclic N_2O (C_{2v}) which then rearranges to give the more stable linear isomer $N{=}N{=}O$ ($C_{\infty v}$) (Table 2). The energies of activation separating cyclic NON (C_{2v}) from (i) linear NON ($D_{\infty h}$) and (ii) linear NNO ($C_{\infty v}$) have also been calculated. At MP2/6-31+G(d) level the barrier for the reaction from cyclic NON (C_{2v}) to form linear NON ($D_{\infty h}$) is 53 kcal mol^{-1} whereas it is only 26 kcal mol^{-1} for the reaction from cyclic NON (C_{2v}) to form linear NNO ($C_{\infty v}$). However, it has to be stressed that these energy potentials have been calculated for the singlet state only and that the triplet state lies energetically very close, especially for the high energy regions on the reaction pathway for the interconversion of cyclic NON into linear NNO or NON, respectively.

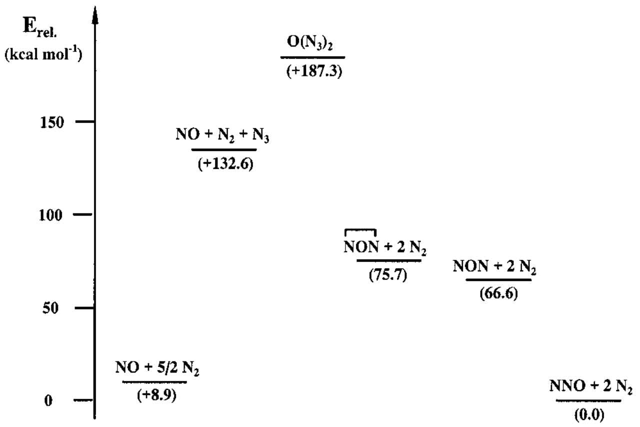

Figure 3. Relative stabilities of $O(N_3)_2$ with respect to N_2 and various oxides of nitrogen computed at MP2/6-311++G(d) level of theory. For comparison, the experimentally measured relative stabilities are $E^{rel}(NNO + 2N_2) = 0.00$ kcal mol^{-1}; $E^{rel}(NO + {}^5/_2N_2) = 1.97$ kcal mol^{-1}; and $E^{rel}(NO + N_2 + N_3) = 106.97$ kcal mol^{-1}.[17]

This proposition is an interesting and reasonable one when it is remembered that as was stated above that azides decompose initially into XN and N_2. Therefore, the proposed intermediately formed oxygen diazide would be expected to decompose according to eq 5. The formation of linear N_2O it was thought most likely to occur through a cyclization forming cyclic N_2O which would then from the more stable linear N_2O which was observed as the main reaction product along with N_2.

$$O(N_3)_2\ (C_2) \rightarrow NON\ (C_{2v}) + 2N_2 \qquad (5)$$

To account for the interconversion of $O(N_3)_2$ into N_2 and cyclic N_2O we calculated the corresponding two-dimensional energy hypersurface at MP2/6-31+G(d) level (Figure 2). Figure 2 clearly shows that the molecule $O(N_3)_2$ represents a local minimum at this hypersurface and that cyclic N_2O (C_{2v}) and two equivalents of N_2 are already 111.6 kcal mol^{-1} lower in energy (MP2/6-311++G(d), Figure 3). The experimentally observed products $2N_2$ and linear N_2O ($C_{\infty v}$), however, lie again 75.7 kcal mol^{-1} below cyclic N_2O (C_{2v}) and two equivalents of N_2 and therefore 187.3 kcal mol^{-1} below the initial compound $O(N_3)_2$. The relative stabilities of $O(N_3)_2$ with respect to N_2 and various oxides of nitrogen are summarized in Figure 3 (MP2/6-311++G(d)). It is noteworthy that the linear symmetric isomer of N_2O, i.e. NON ($D_{\infty h}$) has almost the same total energy as cyclic C_{2v} N_2O [ΔE(MP2/6-311++G(d)) = 9.1 kcal mol^{-1} in favor of linear NON in $D_{\infty h}$ symmetry] (Figure 3, Table 2). The intermediate formation of this isomer, however, would not explain the final formation of the stable NNO ($C_{\infty v}$).

From the present study the following conclusions can be drawn:

(i) OF_2 reacts with CsN_3 to yield the experimentally observed products dinitrogen (N_2) and nitrous oxide (linear N_2O, $C_{\infty v}$ symmetry).

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(ii) The formation of linear N_2O as the product of the reaction of OF_2 with CsN_3 can best be explained by the intermediate formation of $O(N_3)_2$ which then decomposes in an unimolecular reaction to yield N_2 and cyclic N_2O (C_{2v}) the latter of which then rearranges to form the more stable linear isomer of N_2O ($C_{\infty v}$).

(iii) The still elusive molecule $O(N_3)_2$ represents a true minimum in C_2 symmetry on its potential energy hypersurface at all levels of theory applied.

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