J. Phys. Chem. A **1997,** *101,* 2709−2714 **2709**

Theoretical ab Initio Study of CN_2O_3 Structures: Prediction of New High-Energy Molecules

Anatoli A. Korkin,*,[1a] Alfred Lowrey,[1b] Jerzy Leszczynski,[1c] David B. Lempert,[1d] and Rodney J. Bartlett*,[1a]

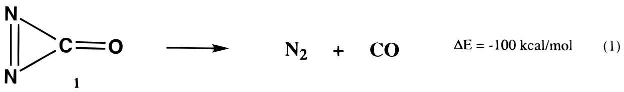
The Quantum Theory Project, University of Florida, Gainesville, Florida, 32611-8435, Naval Research Laboratory for the Structure of Matter, Washington, D.C. 20375, Department of Chemistry, Jackson State University, Jackson, Mississippi 39217, and Institute of Chemical Physics, Chernogolovka, Moscow Region 142432, Russia

Received: November 18, 1996; In Final Form: February 4, 1997⊗

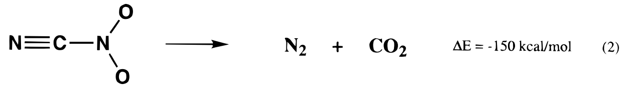
Structures and energies of CN_2O_3 isomers have been investigated theoretically at the ab initio CCSD(T)/TZ2P//MBPT(2)/6-31G* level in search of new high-energy molecules. The most energetically favorable isomer, five-membered cyclic nitrous carbonate, has only a 16 kcal/mol dissociation barrier toward decomposition into CO_2 and N_2O. Nitroisocyanate, $O_2N{-}NCO$, a collision complex in the gas-phase reaction of NCO and NO_2 radicals, is 29 kcal/mol higher in energy than nitrous carbonate and has a 11 kcal/mol barrier in the exothermic decomposition into CO_2 and N_2O, which involves formation of an intermediate four-membered cyclic form. Nitrofulminate has a higher CN bond dissociation energy and is expected to be a more stable molecule than the earlier studied nitrosofulminate (Korkin, A. A.; et al. *J. Phys. Chem.* **1996**, *100,* 19840). Regarding its high exothermicity in decomposition ($O_2N{-}CNO \rightarrow CO_2 + N_2 + 1/2O_2$; $\Delta E = -165$ kcal/mol), nitrofulminate is suggested as a potential energetic oxidizer. Another candidate is its six-membered cyclic trimer, 2,4,6-trinitro-1,2,3-triazine 1,2,3-trioxide. The estimated gaseous heats of formations of nitrofulminate and trinitrotriazine trioxide are 71 and 108 kcal/mol, respectively. Trinitrotriazine trioxide and two other cyclic trimers, trinitroisocyanurate and 2,4,6-tri(nitrosooxy)-1,3,5-triazine, have been optimized at the HF/6-31G* and at the MBPT(2)/6-31G* levels and characterized by HF analytical harmonic frequencies. Another CN_2O_3 isomer, dinitrosocarbonyl, $O{=}C(NO)_2$, has a low stability toward decomposition into CO and NO radicals.

Introduction

In our recent theoretical ab initio studies of CN_2O[2] and CN_2O_2[3] structures, we have predicted a series of new energetic molecules, which have sufficiently high barriers to unimolecular decomposition to be experimentally observed. Decomposition reactions of diazirinone (**1**) and nitryl cyanide (**2**) into nitrogen and carbon oxides are highly exothermic:



1



2

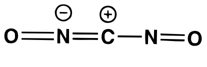
Other interesting molecules include the experimentally known nitrosocyanide (**3**)[4] and theoretically predicted nitrosoisocyanate (**4**),[3,5] nitrosofulminate (**5**),[3] and the bicyclic form (**6**)[3,6]

$$N{\equiv}C{-}N{=}O$$

3

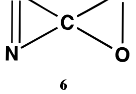
$$O{=}C{=}N{-}N{=}O$$

4



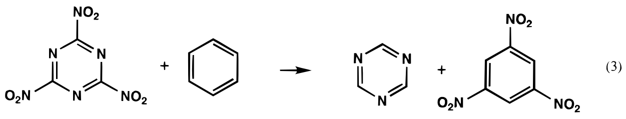
$$O{=}\overset{\ominus}{N}{=}\overset{\oplus}{C}{-}N{=}O$$

5



6

On the basis of the well-known tendency of cyano compounds toward self-aggregation,[7] we have predicted and characterized theoretically at the MBPT(2) level a trimer of $O_2N{-}CN$, 2,4,6-trinitro-1,3,5-triazine (**7**).[8] As estimated from the isodesmic eq 3, the heat of formation of **7** is 46 kcal/mol.



7

ΔE = -20.4 kcal/mol

Regarding balanced carbon−oxygen content (see eqs 1 and 2) CN_2O and CN_2O_2 species can be considered as potential monopropellants. The next species in the CN_2O_x series with an increased number of oxygen atoms ($x \geq 3$) can be oxidizers. Extending our previous work in the theoretical search and investigation of metastable energetic molecules,[2,3,8,9] we have performed a correlated ab initio study of CN_2O_3 structures, energies, and harmonic vibrational spectra, as well as some reference species, precursors and decomposition products, and complexes.[10]

Although none of the CN_2O_3 structures have been observed so far, formation of a collision complex in the gas-phase reaction of NCO and NO_2 (eq 4) has been suggested for explanation of a non-Arrhenius negative dependence of the total rate constant on temperature.[11] Carbon dioxide and nitrous oxide are major products in reaction 4, and only small amounts of CO and NO

⊗ Abstract published in *Advance ACS Abstracts,* March 1, 1997.

S1089-5639(96)03836-4 CCC: $14.00

were observed (k_{4a}:k_{4b} = 0.917:0.083).[12]

$$NCO + NO_2 \rightarrow N_2O + CO_2 \tag{4a}$$

$$\rightarrow 2NO + CO \tag{4b}$$

The rate constant of the reaction of NCO and NO (eq 5) also shows a non-Arrhenius behavior,[11] and it can be expected that similar types of collision complexes (e.g., OCN−NO_2 (**8**) vs OCN−NO (**4**)) are intermediates in both reactions

$$NCO + NO \rightarrow N_2O + CO \tag{5a}$$

$$\rightarrow N_2 + CO_2 \tag{5b}$$

A broad interest in experimental[11−14] and theoretical[5] studies of reactions of NCO with NO_x occurs because of their importance for the process of effective removal of NO_x from exhaust gases—the rapid reduction of nitrogen oxide (RAPRENO$_x$).[14]

In this study we raise the following questions. (1) What is the structure of possible intermediate(s) in the reaction of NCO and NO_2? (2) Can any CN_2O_3 isomer be observed as a metastable species? (3) Do they or their complexes (self-aggregates) have potential applications as high-energy molecules?

Computational Methods

Geometrical parameters of stationary structures, minima, and transition states (TS) for the CN_2O_3 potential energy surface (PES) and related molecules and radicals were optimized at the MBPT(2)/6-31G* level and then characterized by analytical calculations of harmonic vibrational frequencies.[15] More rigorous couple cluster methods[16] including single, double, and triple excitations (CCSD(T)) combined with larger TZ2P basis (11s,6p,2d/[5s,3p,2d])[17] sets have been employed for computations of single-point energies. The calculations were done with the ACES II[18] and Gaussian 94[19] program systems. The larger systems $(CHNO)_3$ and $(CN_2O_3)_3$ were optimized at the HF/6-31G* and at the MBPT(2)/6-31G* levels and characterized by analytical harmonic vibrational frequencies computed at the HF/6-31G* level. Energy and structure comparisons are discussed at the CCSD(T)/TZ2P//MBPT(2)/6-31G* + ZPE level[20] unless otherwise noted (see Table 1 and Figures 1 and 2).

Results and Discussion

The chemistry of nitroso and nitro compounds has numerous analogies,[21] and the similarity of structures and of relative (Δ*E*) and dissociation (DE) energies of the corresponding CN_2O_2 (XYZ−NO)[3] and CN_2O_3 (XYZ−NO_2) molecules has been anticipated:[22]

XYZ−NO/NO_2	*R*(XY)	*R*(YZ)	*R*(ZN)	∠YZN	Δ*E*	DE
OCN−	1.180	1.245	1.522	117.0	0.0	33.3
	1.173	1.253	1.451	115.4	0.0	35.4
NCO−	1.190	1.295	1.739	107.4	16.9	16.4
	1.195	1.280	1.796	105.6	27.3	8.1
ONC−	1.198	1.230	1.412	133.3	69.0	32.0
	1.198	1.215	1.419	139.6	63.0	39.7

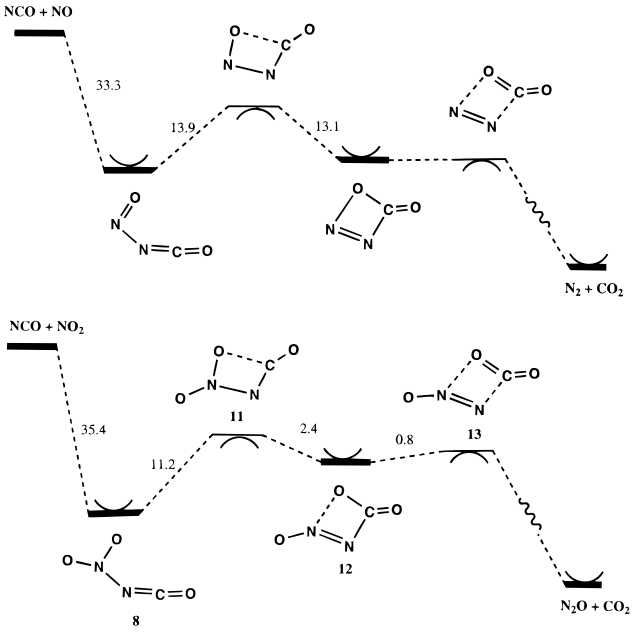
The relative energies (Δ*E*) of nitroso- and nitrocyanates, -isocyanates, and -fulminates are similar among themselves and to those of the corresponding acids, HNCO (0.0 kcal/mol), HOCN (25.1 kcal/mol), and HCNO (68.1 kcal/mol), computed at the MBPT(2)/TZ2P level.[23]

TABLE 1: Total (E_{tot} in au), Zero-Point (ZPE in kcal/mol), and Relative Energies (Δ*E* in kcal/mol) of CN_2O_3, OCNO, $(CN_2O_3)_3$, and $(CHNO)_3$ Structures and Reference Species[b]

	MBPT(2)/6-31G*// MBPT(2)/6-31G*			CCSD(T)/TZ2P// MBPT(2)/6-31G*	
	E_{tot}	ZPE	Δ*E*	E_{tot}	Δ*E*
	CN_2O_3 Structures				
8 (C_s)	−372.179 69	15.6 (0)	0.0	−372.511 06	0.0
9 (C_s)	−372.145 27	14.4 (0)	20.5	−372.465 79	27.3
10 (C_s)	−372.091 98	15.8 (0)	55.2	−372.410 20	63.0
11 (C_s)	−372.156 67	15.3 (1)	14.1	−372.492 72	11.2
12 (C_s)	-372.170 81	15.6 (0)	5.6	−372.496 93	8.8
13 (C_s)	−372.168 00	14.6 (1)	6.4	−372.494 35	9.6
20 (C_{2v})	−372.217 02	15.8 (0)	−23.2	−372.558 02	−29.3
21 (C_s)	−372.191 18	14.6 (1)	−8.1	−372.534 17	−13.6
24 (C_{2v})	−372.202 96	16.2 (0)	−14.0	−372.452 49	37.4
25 (C_{2v})	−372.185 93	16.5 (0)	−3.0	−372.429 44	52.1
27 (C_s)	−372.152 98	13.9 (0)	15.7	−372.490 01	11.5
	CNO_2 Structures				
28 (C_s)	−242.531 17	8.1 (0)	0.0	−242.762 89	0.0
29 (C_s)	−242.524 27	7.3 (1)	3.5	−242.757 64	2.5
	$(CN_2O_3)_3$ Structures				
14 (D_{3h})	−1116.60455	59.4 (0)[a]	0.0		
15 (C_3)	−1116.555 79	59.4 (0)[a]	30.6		
16 (D_{3h})	−1116.35383	57.2 (0)[a]	115.3		
	$(CHNO)_3$ Structures				
17 (D_{3h})	−504.75280	55.4 (0)[a]	0.0		
18 (C_{3h})	−504.698840	55.3 (0)[a]	34.0		
19 (D_{3h})	-504.42199	51.8 (0)[a]	204.4		

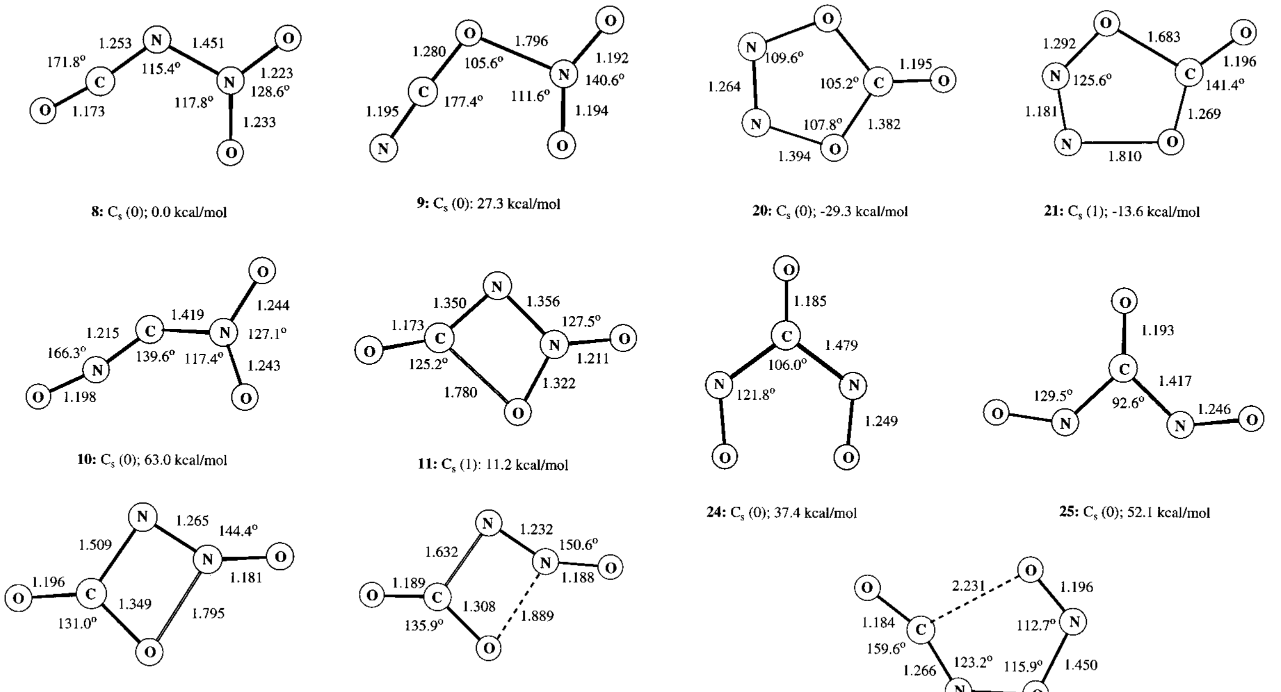
[a] At the HF/6-31G* level. [b] The number of imaginary frequencies is given in parentheses.

The dissociation energies of the isocyanates, OCN−NO and OCN−NO_2 (**8**), are within a 2 kcal/mol range. Nitrosoisocyanate and its nitro analogue, **8**, also have similar decomposition paths, which include the formation of four-membered cyclic intermediates:[3,24]



Decomposition barriers are low in both cases. The transition state (**11**) in the formation of the cyclic intermediate (**12**) is only 11 kcal/mol above **8**, and the following decomposition of **12** via TS **13** does not require any remarkable activation energy. These results are in good agreement with the experimentally known kinetics of reactions 4 and 5, e.g., with the role of a collision complex in the non-Arrhenius behavior of the rate constants for both reactions.[11]

Nitrocyanate (**9**) and nitrosocyanate are higher energy and more weakly bound complexes, which can only exist as very



8: C_s (0); 0.0 kcal/mol
9: C_s (0): 27.3 kcal/mol
20: C_s (0); -29.3 kcal/mol
21: C_s (1); -13.6 kcal/mol
10: C_s (0); 63.0 kcal/mol
11: C_s (1): 11.2 kcal/mol
24: C_s (0); 37.4 kcal/mol
25: C_s (0); 52.1 kcal/mol
12: C_s (0): 8.8 kcal/mol
13: C_s (1): 9.6 kcal/mol

Figure 1. Geometries and relative energies of CN_2O_3 structures at CCSD(T)/TZ2P//MBPT(2)/6-31G* + ZPE (MP2/6-31G*) level. The number of imaginary frequencies is given in parentheses.

short-lived intermediates, e.g., in the gas-phase reactions of CN with NO_3 and NO_2 radicals, respectively.

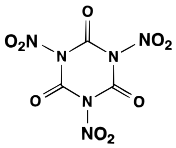
The 40 kcal/mol C−N bond dissociation energy in **10** is remarkably increased compared to the 32 kcal/mol value in its nitroso analogue. Assuming that other (e.g., bimolecular) reactions have higher barriers, an increased DE value in **10** can make this compound potentially observable in the gas phase or in a matrix and even available for application. A direct estimation of the energy release in the decomposition of nitrofulminate at the CCSD(T) level demonstrates **10** to be a very energetic oxidizer, remarkably superior to ammonium nitrate:

$$\mathrm{ONC{-}NO_2} \rightarrow \mathrm{N_2} + \mathrm{CO_2} + {}^1\!/_2\mathrm{O_2} \qquad \Delta E = -165.3 \text{ kcal/mol} \tag{6}$$

$$\mathrm{NH_4NO_3} \rightarrow \mathrm{N_2} + 2\mathrm{H_2O} + {}^1\!/_2\mathrm{O_2} \qquad \Delta E = -28.3 \text{ kcal/mol}^{25,26} \tag{7}$$

Although chemical stabilization of an energetic molecule by its complexing or polymerization will obviously reduce its performance (energy release in decomposition into stable compounds), a *moderate* loss in its energy content can be a *reasonable price* if its stability increases *significantly.* In our previous theoretical study[8] we have predicted an aromatic trimer of nitryl cyanide (**2**), trinitro-*s*-triazine (**7**), that can gain extra stability compared to **2** because of the cyclic electron delocalization in the six-membered ring. Exploring this idea further, we have computed the six-membered cyclic trimers of **8**, **9**, and **10**, which exhibit considerable stabilization compared to the corresponding monomers in eqs 8−10.[27]

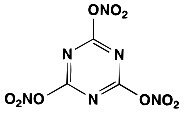
3 O_2N-NCO ⟶
8



14

ΔE = -32.1 kcal/mol (8)

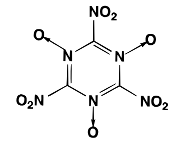
3 O_2N-OCN ⟶
9



15

ΔE = -62.8 kcal/mol (9)

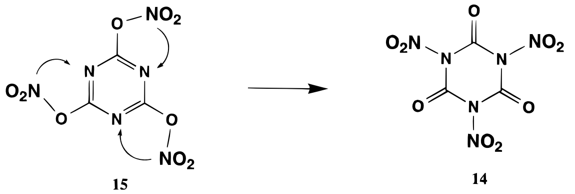
3 O_2N-CNO ⟶
10



16

ΔE = -42.1 kcal/mol (10)

Nitrocyanate (**9**) has the largest trimerization energy, as well as the shortest cyclic CN bond lengths in its trimer, 2,4,6-tri(nitrosooxy)-1,3,5-triazine (**15**). Although we have not computed the transition state between trinitroisocyanurate (**14**) and **15**, it can be expected that **15** can easily rearrange into the more stable **14** because the $(O_2)N{-}O(C)$ distance is long (for a normal NO single bond) and the $(O_2)N{-}N$(ring) distance is short (for a nonbonded atoms contact) in **15**. The electrostatic interaction in **15** is also in favor of such rearrangement, since the nitrogens of NO_2 groups have a positive charge and the ring nitrogens have a negative charge:



15 **14**

It is interesting to compare the trimerization energies of **8**, **9**, and **10** with those of the parent isocyanic, cyanic, and fulminic acids, respectively, as well as the corresponding structures and energies of the trimers (see Figure 2):

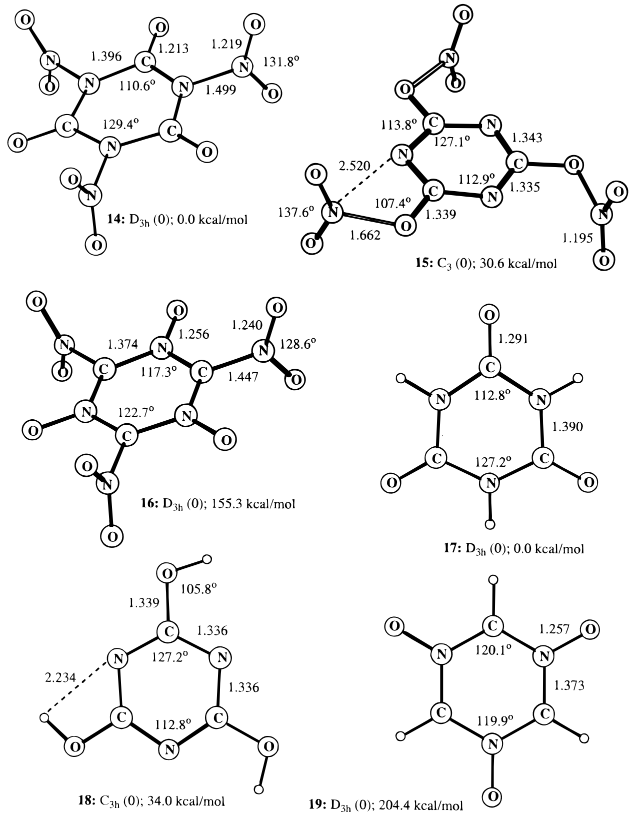
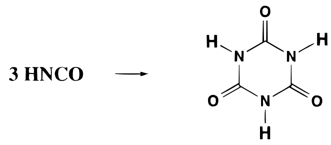
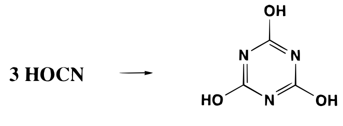


Figure 2. Geometries and relative energies of $(CN_2O_3)_3$ and $(CHNO)_3$ structures at MBPT(2)/6-31G*/MBPT(2)/6-31G* + ZPE (HF/6-31G*) level. The number of imaginary frequencies is given in parentheses.



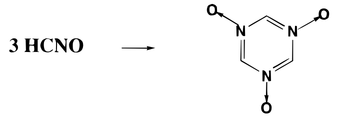
17

ΔE = -44.5 kcal/mol (11)



18

ΔE = -84.3 kcal/mol (12)



19

ΔE = -32.0 kcal/mol (13)

The substitution of H by the NO_2 group in HCNO increases the trimerization energy of **10** (eq 10) compared to that of HCNO (eq 13). As a result, the relative energy of 2,4,6-trinitro-1,3,5-triazine *N,N′,N″*-trioxide (**16**) to **14** is about 50 kcal/mol lower than the energy difference between *s*-triazine *N,N′,N″*-trioxide (**19**) and isocyanuric acid (**17**). Cyanic acid has a larger trimerization energy than **9** because of the hydrogen-bonding stabilization apparent in **18**.

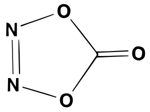
All three nitro substituted cyclic trimers, **14**, **15**, and **16**, have their NO_2 groups placed perpendicularly toward the ring plane.[28] The ring CN bond lengths are similar in the corresponding nonsubstituted and substituted trimers and increase in the following order: **17** (**14**) < **19** (**16**) < **18** (**15**). The CN bond lengths in **14** (1.396 Å) are slightly longer than in **17** (1.390 Å), and the latter bond lengths are very close to those in urea, $OC(NH_2)$ (1.389 Å in the C_2 symmetry minimum energy structure)[29] computed at the same MBPT(2)/6-31G* level. The CN bond in **15** (1.335 and 1.342 Å) and in **18** (1.336 Å) is similar to those in the parent *s*-triazine (1.341 Å at MBPT2/6-31G*,[8] 1.339 Å at MBPT(2)/6-31G**,[30] and 1.338 Å in an electron diffraction experiment[31]). The cyclic CN bond lengths in the triazine tri-*N*-oxides, **16** and **19**, are intermediate between these values in isomeric cyclic carbamides, **14** and **17**, and triazines, **15** and **18**.

TABLE 2: Total (in au) and Relative (in kcal/mol) Energies[a] of Four CN_2O_3 Isomers Computed at Different Levels of Theory Using TZ2P Basis Set and MBPT(2)/6-31G* Optimized Geometries

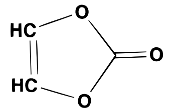
isomer	SCF	MBPT(2)	CCSD	CCSD(T)
8	−371.307 36	−372.475 16	−372.447 42	−372.511 06
	0.0	0.0	0.0	0.0
20	−371.361 94	−372.510 40	−372.498 50	−372.558 01
	−34.2	−22.1	−32.1	−29.5
24	−371.102 23	−372.494 25	−372.346 03	−372.452 49
	128.7	−12.0	63.6	36.8
25	−371.062 32	−372.480 79	−372.312 66	−372.429 44
	153.8	−3.5	84.6	51.2

[a] Without ZPE correction.

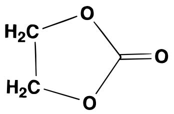
Among the CN_2O_3 structures investigated, nitrous carbonate (**20**) is energetically the most favorable CN_2O_3 isomer, but its stability toward decomposition into N_2O and CO_2 is rather low; the TS **21** in the decomposition reaction is only 16 kcal/mol above **20**. Vinylene carbonate[32,33] (**22**) and ethylene carbonate[34] (**23**) are the closest structural analogues of **20**, which have been studied experimentally and theoretically. The isoelectronic **20** and **22** are planar molecules with C_{2v} symmetry, and **23** has C_2 symmetry with a slightly folded five-membered ring.



20

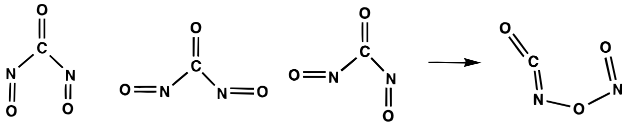


22



23

Two isomers of dinitrosocarbonyl, *trans,trans*- (**24**) and *cis,-cis*-forms (**25**), demonstrate the dramatic influence of electron correlation on their (relative) energies, which has been observed in other ab initio studies of the related molecule, chlorocarbonyl isocyanate, ClC(O)NCO.[35] The relative MBPT(2) and CCSD-(T) energies of all computed structures except **24** and **25** differ moderately, since they are within 7 kcal/mol. A detailed comparison of the energies at the four levels of theory, SCF, MBPT(2), CCSD, and CCSD(T), for the four selected structures is given in Table 2. The relative energies of **25** computed at the SCF and the MBPT(2) levels differ by more than 150 kcal/mol! At the same time the SCF and MBPT(2) energies of **20** vary by only 12 kcal/mol. The *cis,trans*-dinitrosocarbonyl (**26**) is unstable toward spontaneous rearrangement into nitrosooxy-isocyanate (**27**) at the MBPT(2) optimization:



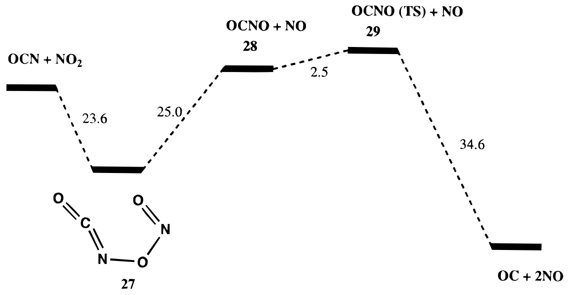
24 **25** **26** **27**

Both isomers of dinitrosocarbonyl, **24** and **25**, have negative (exothermic) dissociation energies in the decomposition into OCNO (**28**) and NO:

$$\mathbf{24} \rightarrow \mathbf{28} + NO \quad \Delta E = -12.4 \text{ kcal/mol} \qquad (14)$$

$$\mathbf{25} \rightarrow \mathbf{28} + NO \quad \Delta E = -27.1 \text{ kcal/mol} \qquad (15)$$

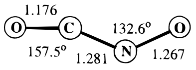
Similar to $O_2N{-}NCO$ (**8**) being an intermediate (collision complex) in reaction 5a (see scheme above and refs 3 and 5), ON−ONCO (**27**) is the most probable intermediate in reaction 5b:



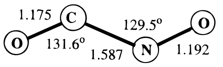
The *exothermic* formation of **27** from NCO and NO_2 and its subsequent *endothermic* decomposition into OCNO and NO have similar energies, resulting in almost thermoneutral oxygen atom exchange between two pairs of radicals:

$$NCO + NO_2 \rightarrow OCNO\ (\mathbf{28}) + NO \quad \Delta E = 1.4 \text{ kcal/mol} \qquad (16)$$

Although the nitrosoformyl radical (**28**) has a short CN bond length, its dissociation (via TS **29**) is 32 kcal/mol exothermic and it has a very low 2.5 kcal/mol barrier.



28



29

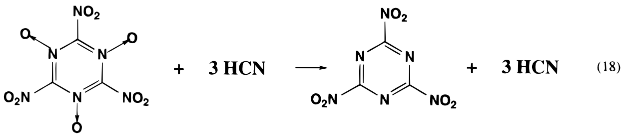
The overall reaction 5b is less exothermic than reaction 5a,[36] and its *effective* barrier (**27** → 28 + NO; $\Delta E = 25.0$ kcal/mol) is higher than the barrier in reaction 5a (**8** → **11**; $\Delta E = 11.2$ kcal/mol), which explains, qualitatively, the experimentally observed ratio between the rate constants of these two reactions.[12]

Heats of Formation. We consider two molecules, nitrofuliminate (**10**) and 2,4,6-trinitro-1,3,5-triazine *N,N′,N″*-trioxide (**16**), to be the most promising candidates as potential rocket oxidizers. Gaseous heats of formations ($\Delta H°_f$(g)) of **10** (71 kcal/mol) and **16** (108 kcal/mol) have been estimated from isodesmic eqs 17 and 18:[37]

$$O_2N\text{-}CNO + HCN \longrightarrow HCNO + O_2N\text{-}CN \qquad (17)$$

10

ΔE = -2.6 kcal/mol



(18)

16 **7**

ΔE = -28.1 kcal/mol

Among the molecules in eqs 17 and 18 only HCN is an experimentally well-known species. The heats of formation of HCN (31.9 kcal/mol) and HNCO (−27.5 kcal/mol) are available from an accurate theoretical coupled-cluster study,[38] and the heat of formation of HCNO (12.4 kcal/mol) has been computed using the 68.1 kcal/mol energy difference between HNCO and HCNO obtained at the MBPT(2)/TZ2P level.[23] The heats of formation of nitrocyanide O_2NCN (60 kcal/mol) and trinitrotriazine (46 kcal/mol) have been taken from our previous theoretical study.[3,8]

Since there are not many experimentally known compounds that are structurally similar to nitrofulminate, we can provide only tentative estimates of its heat of vaporization (~8 kcal/mol) and density (~1.8 g/cm^3) for further computations of energetic features of composite propellants.[39] We believe that our estimates of the heat of sublimation of trinitrotriazine trioxide (32 kcal/mol) and its density (1.82 g/cm^3) are more accurate, since some structural analogues and additive group increments are known from experimental studies.[40,41]

Conclusion

The mechanism of the gas-phase reaction between NCO and NO_2 radicals has been clarified by our theoretical study. Nitroisocyanate, $O_2N{-}NCO$ (**8**), and nitrosooxyisocyanate, ONONCO (**27**), are the most probable intermediates in reactions 5a and 5b, respectively. Both collision complexes, **8** and **27**, have low decomposition barriers. The mechanism of reaction 5a includes formation of a four-membered cyclic species (**12**), a structural analogue (*N*-oxide) of the four-membered intermediate in reaction 4a between NCO and NO radicals.[3,5] Both reactions are important processes in the rapid reduction of nitrogen oxide (RAPRENO$_x$)—effective removal of NO$_x$ from exhaust gases.[14] Nitrosooxyisocyanate (**27**) decomposes into OCNO (**28**) and NO radicals with the subsequent dissociation of **28** into CO and NO. The decomposition of **8** has a lower barrier than that of **27**, which results in CO_2 and N_2O being the major products. Two isomers of dinitrosocarbonyl, $OC(NO)_2$, *trans,trans* (**24**) and *cis,cis* (**25**) forms, are very highly correlated species, which have low stability and decompose into CO and NO. The *cis−trans* form rearranges spontenaously into **27** in the geometry optimization. Because of easy NO release, OC(NO)$_2$ could be toxic.

In search of more stable derivatives of CN_2O_3 isomers, and in relation to our previous study of nitrocyanide (**2**)[3] and trinitro-*s*-triazine (**7**),[8] we have computed the six-membered cyclic molecules, trinitroisocyanurate (**14**), 2,4,6-tri(nitrosooxy)-1,3,5-triazine (**15**), and 2,4,6,-trinitro-1,3,5-triazine 1,3,5-trioxide (**16**), the trimers of $O_2N{-}NCO$ (**8**), $O_2N{-}OCN$ (**9**), and $O_2N{-}CNO$ (**10**), respectively. Formation of all three $(CN_2O_3)_3$ complexes is *exothermic*, which gives them an additional stability compared to the corresponding monomers. Structures and energies of **14**, **15**, and **16** are compared with the corresponding nonsubstituted cyclic trimers, $(CHNO)_3$, **17**, **18**, and **19**.

Heats of formation and energetic features of nitrofulminate (NF) (**10**) ($\Delta H°_f(g) = 71$ kcal/mol) and 2,4,6-trinitro-1,2,3-triazine *N,N′,N″*-trioxide (TNTATO) (**19**) ($\Delta H°_f(g) = 108$ kcal/mol), as high-energetic oxidizers in composite liquid and solid propellants, were estimated and compared with the most energetic experimentally known oxidizers.

Acknowledgment. This work is supported by the AFOSR under Grant F49620-95-1-0130. We thank the Mississippi Center for Supercomputing Research for computer time.

References and Notes

(1) (a) University of Florida. (b) Naval Research Laboratory. (c) Jackson State University. (d) Institute of Chemical Physics.

(2) (a) Korkin, A. A.; Boyd, R. J.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1994**, *227*, 312. (b) Korkin, A. A.; Balkova, A.; Bartlett, R. J.; Boyd, R. J.; Schleyer, P. v. R. *J. Phys. Chem.* **1996**, *100*, 5702.

(3) Korkin, A. A.; Leszczynski, J.; Bartlett, R. J. *J. Phys. Chem.* **1996**, *100*, 19840.

(4) (a) Bak, B.; Nicolaisen, F. M.; Neilsen, O. J.; Skaarup, S. *J. Mol. Struct.* **1979**, *51*, 17. (b) Nadler, I.; Reisler, H.; Noble, M.; Wittig, C. *Chem.*

Phys. Lett. **1984**, *108*, 115. (c) Reisler, H.; Wittig, C. *Annu. Rev. Phys. Chem.* **1986**, *37*, 307. (d) Khundkar, L. R.; Knee, J. L.; Zewail, A. H. *J. Chem. Phys.* **1987**, *87*, 77.

(5) Lin, M. C.; He, Y.; Melius, C. F. *J. Phys. Chem.* **1993**, *97*, 9124.

(6) Averyanov, A. S.; Khait, Yu. G.; Puzanov, Yu. V. *J. Mol. Struct.: THEOCHEM.* **1996**, *367*, 87.

(7) Beyer, W. *Handbook of Organic Chemistry*; Prentice Hall: London, 1996.

(8) Korkin, A. A.; Bartlett, R. J. *J. Am. Chem. Soc.* **1993**, *118*, 12244.

(9) (a) Magers, D. H.; Salter, E. A.; Bartlett, R. J.; Salter, C.; Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1988**, *110*, 3435. (b) Lauderdale, W. J.; Myers, W. J.; Bernholdt, D. E.; Stanton, J. F.; Bartlett, R. J. Proceedings of the High Energy Density Materials Contractors Conference, Long Beach, CA, February 25−28, 1990; Phillips Laboratory, Edwards Air Force Base, 1990; p 121. (c) Lauderdale, W. J.; Stanton, J. F.; Bartlett, R. J. *J. Phys. Chem.* **1992**, *96*, 1174. (d) Ferris, K. F.; Bartlett, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 8302. (e) Stanton, J. F.; Gauss, J.; Bartlett, R. J.; Helgaker, T.; Jørgensen, P.; Jensen, H. J.; Taylor, P. R. *J. Chem. Phys.* **1992**, *97*, 1211. (f) Cernusak, I.; Beck, S.; Bartlett, R. J. *J. Phys. Chem.* **1992**, *96*, 10284. (g) Cernusak, I.; Urban, M.; Ertl, P.; Bartlett, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 10955.

(10) Fifth Conference on Current Trends in Computational Chemistry, Vicksburg, MS, November 1 and 2, 1996. See the conference abstracts book, pp 78−81.

(11) Juang, D. Y.; Lee, J.-S.; Wang, N. S. *Int. J. Chem. Kinet.* **1995**, *27*, 1111.

(12) Park, J.; Hershberger, J. F. *J. Chem. Phys.* **1993**, *99*, 3488.

(13) (a) Perry, R. A. *J. Chem. Phys.* **1985**, *82*, 5485. (b) Cookson, J. L.; Hancock, G.; McKendrick, K. G. *Ber. Bunsen-Ges. Phys. Chem.* **1985**, *89*, 335. (c) Hancock, G.; McKendrick, K. G. *Chem. Phys. Lett.* **1986**, *178*, 157. (d) Miller, J. A.; Bowman, C. T. *Prog. Energy Combust. Sci.* **1989**, *15*, 287. (e) Atakan, B.; Wolfrum, J. *Chem. Phys. Lett.* **1991**, *178*, 157. (f) Becker, K. H.; Kurtenbach, R.; Wiesen, P. *Chem. Phys. Lett.* **1992**, *198*, 424. (g) Cooper, W. F.; Hershberger, J. F. *J. Phys. Chem.* **1992**, *96*, 771. (h) Cooper, W. F.; Park, J.; Hershberger, J. F. *J. Phys. Chem.* **1993**, *97*, 3283. (i) Jones, W. E.; Wang, L. *Can. J. Appl. Chem.* **1993**, *38*, 32. (j) Wategaonkar, S.; Setser, D. W. *J. Phys. Chem.* **1993**, *97*, 10028.

(14) (a) Perry, R. A.; Siebers, D. L. *Nature* **1986**, *324*, 657. (b) Miller, J. A.; Bowman, C. T. *Int. J. Chem. Kinet.* **1991**, *23*, 289.

(15) Harmonic vibrational frequencies and their isotopic shifts for all studied structures (see Figures 1 and 2) can be obtained from the authors (korkin@qtp.ufl.edu) as supplementary materials.

(16) Bartlett, R. J.; Stanton, J. F. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH Publishers: New York, 1994; Vol. 5, Chapter 2.

(17) (a) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823. (b) Dunning, T. H. *J. Chem. Phys.* **1971**, *55*, 716.

(18) Stanton, J. F.; Gauss, J.; Watts, J. D.; Nooijen, M.; Oliphant, N.; Perera, S. A.; Szalay, P. G.; Lauderdale, W. J.; Gwaltney, S. R.; Beck, S.; Balkova, A.; Bernholdt, D. E.; Baeck, K.-K.; Rozyczko, P.; Sekino, H.; Huber, C.; Bartlett, R. J. *ACES II*; Quantum Theory Project, University of Florida: Gainsville, FL. Integral packages included are VMOL (Almlöf, J.; Taylor, P. R.), VPROPS (Taylor, P. R.), ABACUS (Helgaker, H. J.; Jensen, Aa.; JÌrgensen, P.; Taylor, P. R.).

(19) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision B.3.; Gaussian, Inc.: Pittsburgh, PA, 1995.

(20) Zero-point energies were scaled by 0.9 and by 0.95 at HF and at MBPT(2) levels, respectively, as recomended. Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(21) *Chemistry of Amino, Nitroso, and Nitro Compounds. Part 1 and 2*; Patai, S., Ed.; Wiley: New York, 1982.

(22) Bond lengths (R) are given in angströms, bond angles ($\angle$) in degrees, and energies (ΔE and DE) in kcal/mol.

(23) Pinnavaia, N.; Bramley, M. J.; Su, M.-D.; Green, W. H.; Handy, N. C. *Mol. Phys.* **1993**, *78*, 319.

(24) Relative energies in the chemical schemes are given in kcal/mol.

(25) Benson, S. W. *Thermochemical Kinetics*; John Wiley & Sons: New York, 1976.

(26) Meyer, R. *Explosives*, 3rd ed.; VCH: Weinheim, 1987; p 71.

(27) Energies in eqs 8−13 are computed at the MBPT(2) level.

(28) Nitro groups in C_3 **15** are rotated by 2° from the exact perpendicular arrangment with respect to the ring plane.

(29) Meier, R. J.; Coussens, B. *J. Mol. Struct.: THEOCHEM.* **1992**, *85*, 25.

(30) Creuzet, S.; Langlet, J. *Chem. Phys. Lett.* **1993**, *208*, 511.

(31) Pyckhout, W.; Callaerts, I.; Van Anselnoy, C.; Rae, A. I. M.; Pawley, G. S. *J. Mol. Struct.* **1986**, *147*, 321.

(32) Banhegyi, G.; Angyan, J.; Poirier, R. *J. Phys. Chem.* **1986**, *90*, 6420.

(33) (a) Dorris, K. L.; Boggs, J. E.; Danti, A.; Altpeter, L. L., Jr. *J. Chem. Phys.* **1967**, *46*, 119. (b) Durig, J. R.; Clark, J. W.; Casper, J. M. *J. Mol. Struct.* **1970**, *5*, 67.

(34) (a) Matias, P. M.; Jeffrey, G. A.; Wingert, L. M.; Ruble, J. R. *J. Mol. Struct.: THEOCHEM* **1989**, *53*, 247. (b) Degli, E. A.; Lister, D. G.; Palmieri, P. *J. Mol. Struct.* **1990**, *223*, 325.

(35) Mack, H.-G.; Oberhammer, H. *J. Mol. Struct.: THEOCHEM.* **1992**, *258*, 197, and references therein.

(36) The theoretical energies of reactions 4a and 4b, computed at the CCSD(T) level (see Table 1 in ref 3), are −111.3 and −22.8 kcal/mol, respectively, and the corresponding experimental values are −119 and −27 kcal/mol computed from the heats of formations in the following reference. Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. Gas-Phase Ion and Neutral Thermochemistry. *J. Phys. Chem. Ref. Data, Suppl. 1* **1988**, *17*.

(37) The energies in eqs 17 and 18 have been computed at the CCSD(T)/TZ2P//MBPT(2) and at the MBPT(2)/6-31G*//MBPT(2)/6-31G* levels, respectively, with ZPE corrections.

(38) East, A. L. L.; Allen, W. D. *J. Chem. Phys.* **1993**, *99*, 4638.

(39) The estimated propulsion characteristics of the propellants based on our theoretical predictions will be published separately.

(40) Lebedev, Yu. A.; Miroshnichenko, E. A. *Thermochemistry of Vaporization of Organic Substances*; Nauka: Moscow, 1981. In Russian.

(41) Immirzi, A.; Perini, B. *Acta Crystallogr.* **1977**, *A33*, 216.