

Mechanism of Formation of Hydrogen Trioxide (HOOH) in the Ozonation of 1,2-Diphenylhydrazine and 1,2-Dimethylhydrazine: An Experimental and Theoretical Investigation

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Abstract: Low-temperature ($-78\text{ }^{\circ}\text{C}$) ozonation of 1,2-diphenylhydrazine in various oxygen bases as solvents (acetone- d_6 , methyl acetate, *tert*-butyl methyl ether) produced hydrogen trioxide (HOOH), 1,2-diphenyldiazene, 1,2-diphenyldiazene-*N*-oxide, and hydrogen peroxide. Ozonation of 1,2-dimethylhydrazine produced besides HOOH, 1,2-dimethyldiazene, 1,2-dimethyldiazene-*N*-oxide and hydrogen peroxide, also formic acid and nitromethane. Kinetic and activation parameters for the decomposition of the HOOH produced in this way, and identified by ^1H , ^2H , and ^{17}O NMR spectroscopy, are in agreement with our previous proposal that water participates in this reaction as a bifunctional catalyst in a polar decomposition process to produce water and singlet oxygen (O_2 , $^1\Delta_g$). The possibility that hydrogen peroxide is, besides water, also involved in the decomposition of hydrogen trioxide is also considered. The half-life of HOOH at room temperature ($20\text{ }^{\circ}\text{C}$) is 16 ± 1 min in all solvents investigated. Using a variety of DFT methods (restricted, broken-symmetry unrestricted, self-interaction corrected) in connection with the B3LYP functional, a stepwise mechanism involving the hydrotrioxyl (HOOO^{\bullet}) radical is proposed for the ozonation of hydrazines (RNHNHR , $\text{R} = \text{H, Ph, Me}$) that involves the abstraction of the N-hydrogen atom by ozone to form a radical pair, $\text{RNNHR}^{\bullet} \cdot \text{OOO}^{\bullet}$. The hydrotrioxyl radical can then either abstract the remaining N(H) hydrogen atom from the RNNHR^{\bullet} radical to form the corresponding diazene ($\text{RN}=\text{NR}$), or recombines with RNNHR^{\bullet} in a solvent cage to form the hydrotrioxide, $\text{RN}(\text{OOH})\text{NHR}$. The decomposition of these very labile hydrotrioxides involves the homolytic scission of the $\text{RO}-\text{OOH}$ bond with subsequent "in cage" formation of the diazene-*N*-oxide and hydrogen peroxide. Although 1,2-diphenyldiazene is unreactive toward ozone under conditions investigated, 1,2-dimethyldiazene reacts with relative ease to yield 1,2-dimethyldiazene-*N*-oxide and singlet oxygen (O_2 , $^1\Delta_g$). The subsequent reaction sequence between these two components to yield nitromethane as the final product is discussed. The formation of formic acid and nitromethane in the ozonolysis of 1,2-dimethylhydrazine is explained as being due to the abstraction of a methyl H atom of the $\text{CH}_3\text{NNHCH}_3^{\bullet}$ radical by HOOO^{\bullet} in the solvent cage. The possible mechanism of the reaction of the initially formed formaldehyde methylhydrazone (and HOOH) with ozone/oxygen mixtures to produce formic acid and nitromethane is also discussed.

Introduction

Reactions of saturated organic compounds with ozone are at the focus of current research.¹ Among the various less explored topics of research in this field are the reactions of substituted hydrazines with ozone. Although the oxidation of both aliphatic and aromatic hydrazines with various oxidants has been extensively studied,^{2,3} there are only a few reports on the

ozonation of these compounds, which date back to the early 20th century. Molinari^{4a} as well as Strecker and Baltes^{4b} studied the ozonation of 1,2-diphenylhydrazine (hydrazobenzene) and reported 1,2-diphenyldiazene (azobenzene) to be the only reaction product (for a summary of these studies, see ref 2).

Hydrazines occur in the environment,^{5,5c} and it is by now well established that humans exposed to these compounds by drinking contaminated water and by inhaling contaminated air may develop adverse systemic health effects or cancer.⁵ It is,

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therefore, obvious that detailed knowledge about the oxidation pathways of these hazardous compounds is of the utmost importance.

We have already reported in a preliminary form that the reaction of 1,2-diphenylhydrazine with ozone is more complex than originally believed, and that hydrogen trioxide (HOOH) is an important intermediate formed in these reactions.⁶ The hydrazine-ozone reaction appears to be currently the most reliable and efficient procedure for the production of relatively highly concentrated solutions of HOOH in various organic solvents without the interfering presence of other organic hydrotrioxides (ROOOH).^{7,8} Recent evidence even indicates that HOOH is formed as an intermediate in H₂O₂ and ozone production from water and singlet oxygen by antibodies.⁹ Therefore, we report here the results of detailed experimental and theoretical studies of the ozonation of 1,2-diphenylhydrazine and 1,2-dimethylhydrazine.

Experimental Section

Instrumentation. Low-temperature ¹H, ²H, ¹³C, and ¹⁷O NMR spectra were recorded on a Bruker Avance 300 DPX (¹H NMR, 300.3 MHz; ²H NMR, 46.07 MHz; ¹³C NMR, 75.48 MHz; ¹⁷O NMR, 40.70 MHz) and on Varian Unity Inova-600 spectrometers (¹H NMR, 600.09 MHz; ¹⁷O NMR, 81.37 MHz) with TMS (¹H and ¹³C NMR), acetone-*d*₆ (²H NMR), and H₂¹⁷O (¹⁷O NMR) as internal standards. GC/MS was performed on a Hewlett-Packard 6890 chromatograph (HP-5MS column). Near-IR spectra were recorded on Perkin-Elmer UV/VIS/NIR Lambda 19 spectrometer.

Materials. All solvents were the purest commercially available products and were (except of acetone-*d*₆) rigorously dried and distilled according to the literature methods. The purity was checked by GC/MS. 1,2-Diphenyldiazene (99%, Aldrich), nitrobenzene (99+%, Aldrich), 1,2-dimethylhydrazine dihydrochloride (99+%, Aldrich), nitromethane (99+%, Aldrich), 9,10-dimethylanthracene (99%, Aldrich), and 3-chloroperoxybenzoic acid (77%, Aldrich) were used as received. 1,2-

Diphenylhydrazine (Aldrich) was crystallized from methanol before use.^{10a} 1,2-Dideutero-1,2-diphenylhydrazine was synthesized by Zn/ND₄Cl reduction of 1,2-dipenyldiazene.^{10b} 1,2-Dipenyldiazene-*N*-oxide was prepared by oxidation of 1,2-dipenyldiazene with 3-chloroperoxybenzoic acid in dichloromethane,¹¹ and from reductive coupling of nitrobenzene with Zn/glucose.^{10a} 4-Methoxy-1,2-diphenylhydrazine,^{10b} 4-methoxy-1,2-dipenyldiazene-*N*-oxide, and 4-methoxy-1,2-dipenyldiazene-*N'*-oxide were prepared according to the literature procedures.¹¹ 1,2-Dimethylhydrazine was obtained by neutralization of its dihydrochloride with sodium hydroxide,¹² and 1,2-dimethylhydrazine by HgO oxidation of 1,2-dimethylhydrazine dihydrochloride.¹³

Ozonation Procedure. Ozone-oxygen mixtures were produced by flowing oxygen through a Welsbach T-816 ozonator.⁶ Ozone-nitrogen mixtures were obtained as already reported. The concentration of ozone in the gas stream was measured according to the literature procedure.¹⁷ ¹⁷O-enriched ozone was generated by flowing ¹⁷O-enriched oxygen (58% ¹⁷O₂, ISOTEC) through a semimicro ozonator.^{6d}

WARNING: Although we have not had any accidents in handling solutions of peroxides and polyoxides formed in the ozonation of hydrazines, care should be exercised in handling dried and concentrated solutions of these potentially hazardous compounds.

Product Analysis. Reaction products of the ozonation of 1,2-diphenylhydrazine and 1,2-dimethylhydrazine were determined by a combination of methods.^{6d} All products, except hydrogen peroxide, were determined by GC/MS, by using calibrated internal standards and known reference materials. All products were also collected and identified by NMR. Hydrogen peroxide was determined by ¹H NMR (and ¹⁷O NMR) and by other analytical methods that have been described previously.^{6d}

Kinetic Studies. Kinetics of the decomposition of hydrogen trioxide was performed by following the decay of the OOOH absorption by ¹H NMR, using TMS as the internal standard. Kinetic and activation parameters were obtained by standard procedures.⁶

Computational Methods. Different reaction paths of the ozonation of hydrazine (**1a**), 1,2-dimethylhydrazine (**1b**), and 1,2-diphenylhydrazine (**1c**) were investigated. In view of the large amount of calculations to be carried out in this connection, we used standard density functional theory (DFT)¹⁴ and employed the B3LYP hybrid functional¹⁵ because the latter provides an acceptable cost-efficiency ratio. However, there were several intermediates and transition states (TS) with

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significant multireference character that are difficult to describe with restricted or unrestricted DFT (RDFT and UDFT). Therefore, we routinely carried out stability tests¹⁶ and used broken-symmetry UDFT (BS-UDFT) when needed (i.e., in case of negative eigenvalues of the stability matrix). BS-UDFT implicitly provides a two-configurational description and leads to reasonable results provided the splitting between the low-spin state in question and the associated high-spin state is relatively small.^{17,18} In this connection it has to be mentioned that standard functionals based on the generalized gradient approximation (GGA) account for a significant amount of long-range correlation,¹⁹ but lead to a double-counting of correlation effects when used in connection with BS-UDFT.²⁰ This was another reason why B3LYP rather than BLYP was used in this work.²⁰

The fact that DFT with the exchange functionals presently in use accounts for unspecified nondynamic electron correlation is closely connected with the self-interaction error (SIE) of these functionals.^{19,21} The SIE is often the reason for the good performance of DFT in cases where other single determinant methods fail.^{19,21} However, the SIE also results in a serious failure of DFT when odd-electron situations occur in a chemical reaction.^{19–22} For example, H abstraction by a radical (three-electron situation) is wrongly described by any exchange functional based on either the local density approximation or GGA.²³ The TS of the reaction is severely underestimated thus leading often to reactions without barrier. We use in these situations self-interaction corrected DFT (SIC-DFT) based on the Perdew–Zunger approach²⁴ and programmed in a perturbational (PSIC) and a self-consistent version (SCF-SIC).^{19–21} For details, see ref 25.

TS energies were determined by SIC-DFT using the following procedure. The geometry of the DFT calculation was used for PSIC and SCF-SIC single point calculations. In this way an estimate of the improved barrier was found. If a TS geometry could not be determined, that found for a derivative was used to obtain by single point calculation a SIC-DFT barrier. Alternatively, increments were used determined for a homologue. Calculations showed that in this way consistent reaction barriers could be obtained. The corresponding activation enthalpies were determined by using vibrational corrections from the DFT calculation or estimating the latter from values obtained for another hydrazine.

For all calculations, Pople's 6-31G(d,p) basis set^{26a} was used, however in several cases the 6-311++G(3df,3pd) basis^{26b} was employed to verify 6-31G(d,p) results. Geometry optimizations

were carried out with standard procedures based on analytical energy gradients. Frequency calculations were performed to characterize the optimized structures as minima or transition states, where the transition states were found to each have a single imaginary frequency. In addition, the vibrational frequencies were used to obtain temperature corrected energies, enthalpies, entropies, and free energies. For the purpose of modeling the effects of solvation, the PISA continuum model²⁷ was applied using acetone as a solvent (dielectric constant $\epsilon = 20.728$).

van der Waals complexes are difficult to calculate with DFT.²⁹ However, if complexes are stabilized by H-bonding, which include both electrostatic and some covalent bonding, DFT performs better.³⁰ For the purpose of getting reasonable complex binding energies, we apply the counterpoise method³¹ to reduce the basis set superposition error (BSSE).

In some cases, cyclic transition states were optimized using the ring puckering coordinates of Cremer and Pople.³² These coordinates make it possible to freeze individual puckering parameters and to carry out constrained optimizations. For this purpose the program PUCKER³³ was used, which is part of the quantum chemical package COLOGNE 2003.³⁴ All calculations were performed with the quantum chemical program packages COLOGNE 2003³⁴ and Gaussian 98.³⁵

Results and Discussion

In the following we will discuss first the ozonation of 1,2-diphenylhydrazine, then that of 1,2-dimethylhydrazine. Calcula-

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tions have also been carried out for the ozonation of hydrazine itself to have a suitable reference for assessing substituent effects.

1,2-Diphenylhydrazine (1c). Ozonation of 1,2-diphenylhydrazine with ozone-nitrogen or ozone-oxygen mixtures in acetone-*d*₆ or methyl acetate (0.1–0.5 M) at –78 °C produced an oxygen-rich intermediate with the OOOH ¹H NMR absorption at 13.3 ± 0.3 ppm downfield from Me₄Si. Furthermore, ozonation of 1,2-dideutero-1,2-diphenylhydrazine in acetone at –78 °C produced a somewhat broader OOOD ²H NMR absorption at 13 ppm (11 ppm relative to acetone-*d*₆ absorption). This polyoxide with exchangeable protons (fast exchange with D₂O and CH₃OD at –60 °C) was assigned to HOOOH (DOOOD) using ¹⁷O NMR spectroscopy for a highly ¹⁷O-enriched species. This assignment was confirmed by ¹⁷O NMR chemical shift calculations using either GIAO/MP2/6-311++G-(d,p)^{36,6c} or GIAO/CCSD(T)³⁷ with a (11s7p2d/7s2p)[6s4p2d/4s2p] basis.³⁸ Results of both sets of calculations are in good agreement with the experimental values (see Figure 1).³⁹ The yield of HOOOH was estimated to be 45 ± 10% (at –60 °C).

A detailed investigation of other products of ozonation of **1c** (at –60 °C) by GC/MS and NMR revealed the presence of 1,2-diphenyldiazene (trans isomer, 65 ± 5%, mol %), 1,2-diphenyldiazene-*N*-oxide (azoxybenzene)(35 ± 5%), hydrogen peroxide (30 ± 10%), and water. Ozonation of 1,2-dideutero-1,2-diphenylhydrazine yielded deuterated hydrogen peroxide and water.

Ozonation of an asymmetric hydrazine, i.e., 4-methoxy-1,2-diphenylhydrazine produced, besides 4-methoxy-1,2-diphenyldiazene, also 4-methoxy-1,2-diphenyldiazene-*N*'-oxide (MeOC₆H₄N=N(O)C₆H₅).

Similar results were also obtained in *tert*-butyl methyl ether as solvent, i.e., HOOOH (30 ± 10%), 1,2-diphenyldiazene (75 ± 5%), 1,2-diphenyldiazene-*N*-oxide (25 ± 5%), hydrogen peroxide (10 ± 5%), and water. Control experiments showed that in the ozonation of 1,2-diphenyldiazene in acetone-*d*₆ or *tert*-butyl methyl ether at low temperatures, no 1,2-diphenyldiazene-*N*-oxide could be detected and 1,2-diphenyldiazene was recovered quantitatively.

The proposed mechanisms of the ozonation of 1,2-diphenylhydrazine is illustrated in Scheme 1.

The presence of both 1,2-diphenyldiazene and 1,2-diphenyldiazene-*N*-oxide suggests that two different competitive reaction mechanisms are operative in the ozonation of 1,2-diphenylhydrazine (path A and B in Scheme 1). Path A implies the stepwise H abstraction from hydrazine by ozone thus yielding via a H-bonded hydrazine-ozone complex **2**, an intermediate RNHN••OOH radical pair **3**, the diazene-hydrogen trioxide complex **4**, which can dissociate to the separated products diazene and hydrogen trioxide (**5**).⁴⁰ Alternatively, the intermediate radical

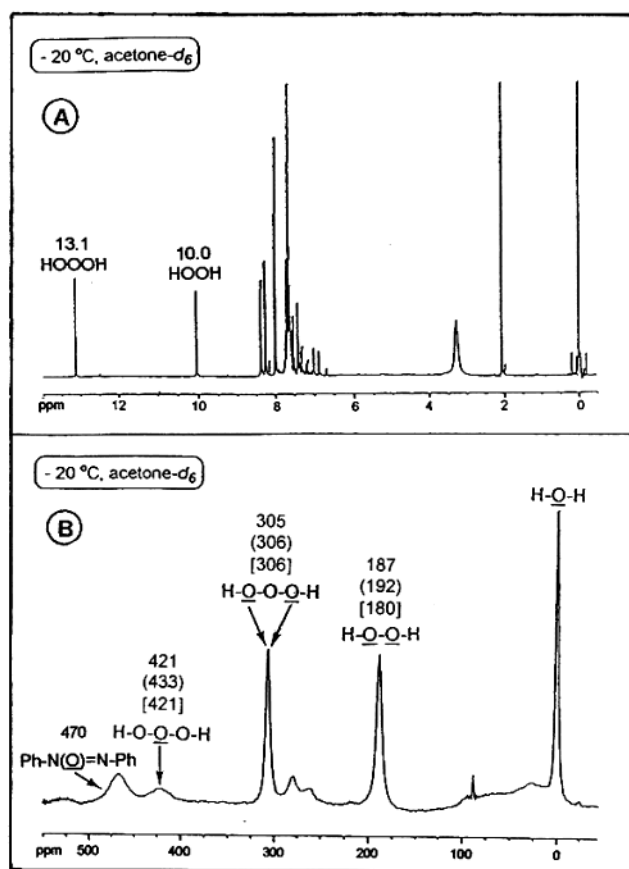


Figure 1. (A) ¹H and (B) ¹⁷O NMR spectra of hydrogen trioxide generated by the low-temperature ozonation of 1,2-diphenylhydrazine in acetone-*d*₆ at –20 °C. All absorptions of hydrogen trioxide completely disappeared at +20 °C. (B) ¹⁷O NMR chemical shifts in parentheses refer to GIAO/MP2/6-311++G** values^{6c} those in brackets to GIAO/CCSD(T)/qz2p values.³⁸

pair **3** can recombine to form hydrazine hydrotrioxide **6**, which can dissociate to radicals **7** and then form diazene-*N*-oxide and HOOH (**8**).

Calculated energies, enthalpies, and entropies for structures **1–8** are summarized in Table 1.

In Figure 2, calculated enthalpies for path A are shown for R = Ph, R = Me, and R = H, those for path B are given in Figure 3 for the case R = Ph. Ozone and hydrazine form a H-bonded complex with a binding energy of 8 kcal/mol (6-311++G(3df,3pd): Δ*H*(298) = –3.2 kcal/mol, Table 1). In the case of 1,2-dimethylhydrazine one NH and one CH bond are involved in H-bonding thus increasing the complex stability to 9 kcal/mol (for structural details, see Figure 4 and the Supporting Information). Neither of these arrangements is possible in the case of 1,2-diphenylhydrazine so that the complex stability is reduced to 7.4 kcal/mol.

The activation enthalpy for H abstraction could only be estimated to be close to 14 kcal/mol for the parent system, i.e., **TS(2a-3a)**, using PSIC/B3LYP (just 5 kcal/mol at B3LYP/6-311G++G(3df,3pd)). DFT severely underestimates the barrier

(36) (a) Gauss, J. *Chem. Phys. Lett.* **1992**, *191*, 614. (b) Gauss, J. *J. Chem. Phys.* **1993**, *99*, 3629.

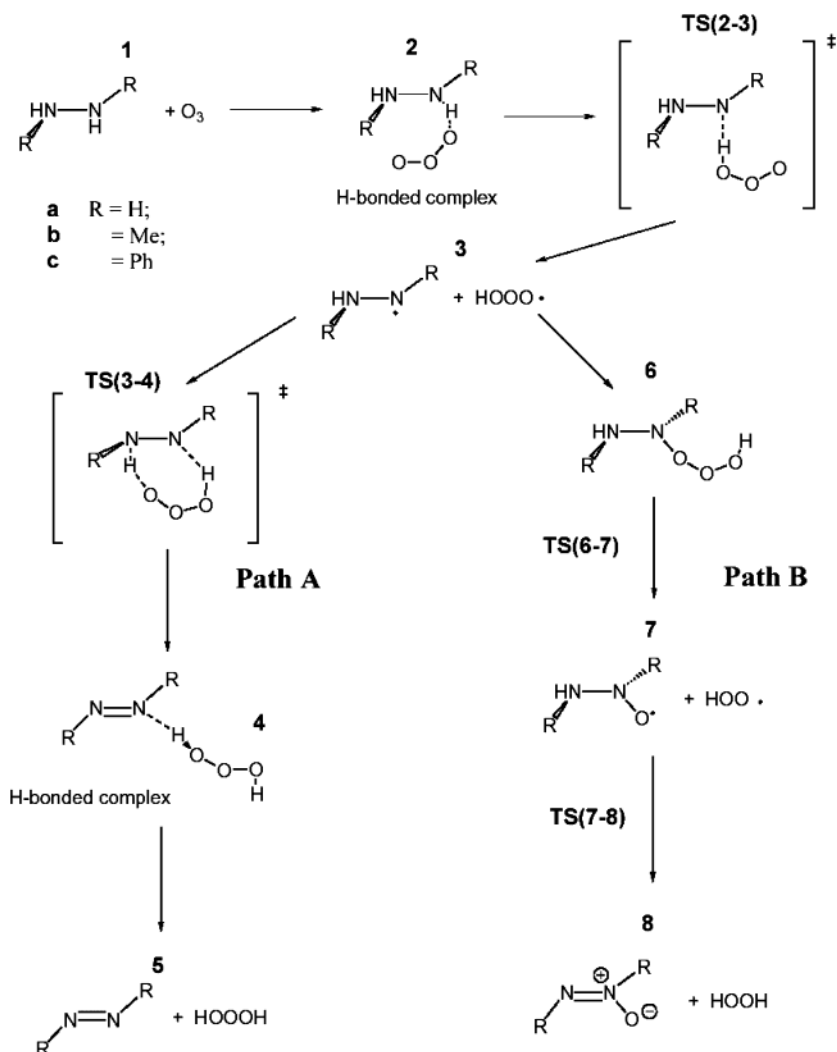
(37) Gauss, J.; Stanton, J. F. *J. Chem. Phys.* **1996**, *104*, 2574.

(38) Wu, A.; Cremer, D.; Gauss, J., in press.

(39) Our preliminary experiments by using low-temperature (–40 °C) FT IR immersion probe (Mettler Toledo React IR 1000) revealed a typical O–H stretching vibration at 3209 ± 15 cm^{–1}, which disappeared upon warming of the reaction mixture to room temperature. This vibration was tentatively assigned to HOOOH (0.3–0.5 M in acetone). For comparison, the OH stretching vibration for H₂O₂, also present in the reaction mixture, was 3350 ± 15 cm^{–1} under the same conditions. (Lendero, N.; Cerkovnik, J.; Plesničar, B. In preparation.)

(40) Pryor et al. considered in the ozonation of saturated hydrocarbons, alcohols, and ethers the H abstraction and the hydride abstraction as two extremes between which the initial reaction complex could choose according to solvent, temperature, and other reaction conditions. Giamalva, D. H.; Church, D. F.; Pryor, W. A. *J. Am. Chem. Soc.* **1986**, *108*, 7678. Giamalva, D. H.; Church, D. F.; Pryor, W. A. *J. Org. Chem.* **1988**, *53*, 3429. See also: Hellman, T. M.; Hamilton, G. A. *J. Am. Chem. Soc.* **1974**, *96*, 1530. Nangia, P. S.; Benson, S. W. *J. Am. Chem. Soc.* **1980**, *102*, 3105.

Scheme 1



due to the three-electron situation in the TS (ozone acts as a biradical thus leading to $O\cdot H\cdot N$ and the resulting large SIE lowers the energy) yielding for **TS(2b-3b)** and **TS(2c-3c)** even energies below that of **2**. The methyl and the phenyl group facilitate H abstraction considerably because the hydrazine radical **3** formed is stabilized by either hyperconjugation or π -conjugation with a phenyl ring. This stabilizing nature of phenyl substituents for the radical intermediate has been observed experimentally by Zhao and co-workers⁴¹ in the measurement of bond dissociation energies.

The $HO_2O\cdot$ radical formed in the first step can abstract a second H atom of hydrazine directly in the solvent cage and form a rather stable H-bonded complex between diazene and HO_2OH (**4**), which is 7 to 8 kcal/mol more stable than the separated products (**5**, Figure 2). The formation of **4** from **2** is exothermic by 35.1 (**2a** \rightarrow **4a**), 44.9 (**2b** \rightarrow **4b**), and 41.6 kcal/mol (**2c** \rightarrow **4c**) thus reflecting the increased stabilization possibilities of the substituents in the diazene (hyperconjugation and π -conjugation). The kinetics of the reaction should be determined by the first reaction step, which should be fast considering the low barriers and the energy gained by the formation of complex **2**.⁴²

The second H-abstraction is also a rapid reaction (estimated activation enthalpies, see Figure 2), in particular if it takes place in the solvent cage and if the second terminal O atom is already oriented toward the second NH bond as in the case of **2a** (Figure 4). A previous investigation by Ingemann and co-workers⁴³ concluded that the abstraction of the H(N) atoms from the 1,2-diphenylhydrazine requires a larger energy than the subsequent H abstraction from the resulting radical, based on an analysis of the relative N–H bond energies of the two species. In the case of hydrazine, the first bond dissociation energy is 87.5 kcal/mol, whereas the second leading to diazene requires just 42.6 kcal/mol.⁴⁴

For both the methyl and the phenyl derivative a reorientation of the $HO_2O\cdot$ radical in the solvent cage is required to initiate the second H abstraction (the second terminal O atom is oriented in **2b** toward a methyl hydrogen or away from the hydrazine frame, see Figure 4). Such a reorientation can easily lead to a radical recombination reaction and the formation of hydrotri-

(41) Zhao, Y.; Bordwell, F. G.; Cheng, J.-P.; Wang, D. *J. Am. Chem. Soc.* **1997**, *119*, 9125.

(42) Although no detailed experimental studies on the ozonation of the parent hydrazine were undertaken, it was obvious from our preliminary experiments that HO_2OH was formed in good yields in all the solvents investigated.

(43) Ingemann, S.; Fokkens, R. H.; Nibbering, N. M. M. *J. Org. Chem.* **1991**, *56*, 607.

(44) Luo, Y.-R. *Handbook of Bond Dissociation Energies in Organic Compounds*; CRC Press: Boca Raton, 2003.

Table 1. Energies, Enthalpies, Entropies, and Dipole Moments of Structures 1–8 with R = H, R = Me, and R = Ph Calculated at B3LYP/6-31G(d,p)^a

system	sym	ΔE	ΣZPE	$\Delta H(298)$	ΣS	$\Delta G(298)$	μ
R = H							
1a	<i>C</i> ₂	0.0	38.1	0.0	113.4	0.0	2.14, 0.61
	<i>C</i> ₂	0.0	38.1	0.0	113.4	0.0	1.98, 0.65
2a	<i>C</i> ₁	-8.7	39.2	-8.0	79.9	2.0	0.01
	<i>C</i> ₁	-4.0	39.2	-3.2	79.9	6.8	0.27
TS(2a-3a)	<i>C</i> ₁	-0.8	36.2	-3.3	74.6	8.3	2.3
	<i>C</i> ₁	-4.6	36.2	-7.1	74.6	4.5	2.56
3a	<i>C</i> ₁	-9.8	36.0	-11.5	119.5	-13.3	2.61, 1.22
	<i>C</i> ₁	-8.1	36.0	-9.8	119.5	-11.6	2.54, 1.15
4a	<i>C</i> ₁	-43.7	38.5	-43.1	85.4	-34.8	1.65
	<i>C</i> ₁	-39.9	38.5	-39.3	85.4	-31.0	1.55
5a	<i>C</i> _{2h}	-35.0	36.8	-36.1	112.9	-35.9	0, 1.12
	<i>C</i> _{2h}	-34.5	36.8	-35.6	112.9	-35.4	0, 1.15
6a	<i>C</i> ₁	-33.8	40.4	-32.3	75.7	-21.1	2.38
	<i>C</i> ₁	-29.6	40.4	-28.1	75.7	-26.9	2.42
7a	<i>C</i> ₁	-32.5	36.8	-33.4	119.7	-35.3	1.67, 2.26
	<i>C</i> ₁	-32.5	36.8	-33.4	119.7	-35.3	1.83, 2.22
8a	<i>C</i> _s	-65.4	38.4	-65.0	114.7	-65.4	1.17, 1.76
	<i>C</i> _s	-67.6	38.4	-67.2	114.7	-67.6	1.22, 1.64
R = Me							
1b	<i>C</i> ₂	0.0	73.5	0.0	128.5	0.0	1.54, 0.61
2b	<i>C</i> ₁	-9.4	74.1	-9.0	92.1	1.8	2.66
3b	<i>C</i> ₁	-14.3	71.3	-16.0	136.6	-18.4	2.05, 1.22
4b	<i>C</i> ₁	-54.4	73.8	-53.9	85.4	-45.9	1.89
5b	<i>C</i> _{2h}	-44.5	72.1	-45.6	136.6	-46.2	0, 1.13
6b	<i>C</i> ₁	-35.0	75.1	-33.8	89.7	-22.3	2.62
7b	<i>C</i> ₁	-35.3	72.3	-35.9	135.8	-38.1	1.83, 2.26
8b	<i>C</i> _s	-73.9	73.4	-73.7	129.9	-74.1	1.58, 1.76
R = Ph							
1c	<i>C</i> ₂	0.0	139.6	0.0	164.6	0.0	1.91, 0.61
2c	<i>C</i> ₁	-8.4	140.4	-7.4	129.2	3.2	2.52
3c	<i>C</i> ₁	-19.3	138.0	-20.5	170.4	-22.2	1.68, 1.23
4c	<i>C</i> ₁	-50.1	140.2	-49.0	134.1	-39.9	1.54
5c	<i>C</i> _{2h}	-41.4	138.9	-41.9	166.5	-42.5	0, 1.13
6c	<i>C</i> ₁	-27.3	140.9	-26.2	125.7	-14.6	2.15
7c	<i>C</i> ₁	-32.3	138.5	-32.8	169.4	-34.3	1.85, 2.26
8c	<i>C</i> _s	-64.5	139.8	-65.0	164.7	-65.0	1.75, 1.76

^a For a definition of structures see Scheme 1. Relative energies (ΔE), zero point energies (ZPE), relative enthalpies ($\Delta H(298)$), and relative Gibbs free energies ($\Delta G(298)$) in kcal/mol, dipole moments (μ) in Debye, entropies (S) in cal mol/deg. – The symmetry in column Sym is given with regard to the first molecule in a system of two molecules; the same holds for the dipole moment. Data in italics has been calculated with the 6-311++G(3df,3pd) basis in conjunction with the B3LYP functional.

oxide **6**. Although the formation of **6c** is just exothermic by 5.7 kcal/mol ($\Delta H(298)$, Figure 3), the hydrotrioxide should possess so much excess energy to surmount directly a small barrier (both DFT and SIC-DFT calculations could not locate **TS(6c-7c)**) and to decompose to a hydrazine-*N*-oxyl radical and the HOO• radical (**7**, Figure 3) in another exothermic reaction ($\Delta H(298) = -6.6$ kcal/mol, (Table 1). H-abstraction by the HOO• radical leads to an diazene-*N*-oxide zwitterion and HOOH (**8**).

The relative abundance of the 1,2-diphenyldiazene measured experimentally suggests that path A is the preferred mechanism, which seems to imply that a reorientation of the HOOO• radical in the solvent cage for the recombination reaction is more difficult than the H abstraction reaction. The required movement (a head–tail exchange of the HOOO• radical) might only be possible outside the solvent cage and therefore less frequent than the H-abstraction reaction in mechanism A.

The experimental yield of the hydrogen trioxide generated via Path A ($30 \pm 10\%$) is ca. 45% lower than the corresponding yield of the 1,2-diphenyldiazene ($75 \pm 5\%$). Also, the yield of

1,2-diphenyldiazene-*N*-oxide ($25 \pm 5\%$) produced via path B is larger than that of HOOH ($10 \pm 5\%$). The loss of hydrogen trioxide can result from its decomposition into O₂ (¹ Δ_g) catalyzed by either water or hydrogen peroxide molecules (reactions I-1 and I-2, in Scheme 2) as previously suggested by us.^{6,9b} The decomposition of HOOOH was investigated at higher temperatures. The yield of singlet oxygen was determined with the use of a typical O₂ (¹ Δ_g) acceptor, i.e., 9,10-dimethylanthracene, to be $20 \pm 10\%$ (9,10-dimethylanthracene endoperoxide)⁴⁵ in acetone-*d*₆ and methyl acetate. The formation of O₂ (¹ Δ_g) in the decomposition of HOOOH was also confirmed by chemiluminescence in the infrared region with a maximum at 1272 nm (acetone-*d*₆, -10 °C). The kinetic and activation parameters for the decomposition of this simplest of polyoxides (Table 2) are in accord with the mechanism shown in Scheme 2 (reactions I-1 and I-2) and our previous proposal^{6,9b} although the calculated activation enthalpies (18.8 and 17.3 kcal/mol, Scheme 2) are 2–3 kcal/mol higher than the measured Arrhenius energies (15.3–16.7 kcal/mol, Table 2). This difference is obviously the result of the effect that in a solvent and with additional water molecules present the catalytic effect is more efficient. In any case, water or hydrogen peroxide can participate in the decomposition of HOOOH as a bifunctional catalyst in a “polar” decomposition process to yielding O₂ (¹ Δ_g).

It should be pointed out that in all cases under investigation sufficient water was present after the ozonation of 1,2-diphenylhydrazine to complex all the HOOOH present in solutions (see Figure 3.) Because water was found to be labeled with ¹⁷O (by ¹⁷O NMR), it was most likely formed, at least in large part, during the ozonation by the decomposition of hydrogen trioxide as described in Scheme 2.^{46,47}

Xu, Muller, and Goddard^{9b} investigated reactions between simple polyoxides using similar methods (B3LYP calculations with 6-31G(d,p) and cc-pVTZ basis sets) as those employed in this work. Their reaction and activation enthalpy for reaction I-1 are close to what we obtain. In addition, these authors suggest two other decomposition paths of hydrogen trioxide (reactions II and III in Scheme 2). In the case that local concentrations make the formation of a hydrogen trioxide dimer possible (one HOOOH adopts the 3.5 kcal/mol less stable *C*_s-symmetrical *cis* conformation by flip-flop rotation⁴⁸), this can initiate the decomposition to O₂ (¹ Δ_g) (or O₂ (³ Σ_g^-)) and two HOOH molecules via intermediate O₃ and H₂O₄ complexes.^{9b} The rate determining activation enthalpy of this process was calculated to be 19.7 kcal/mol. Alternatively, O₂ (¹ Δ_g) formed in the solution reacts directly with hydrogen trioxide (activation enthalpy: 12.0 kcal/mol, reaction III in Scheme 2) thus leading to ozone and HOOH.

(45) (a) Corey, E. J.; Mehrotra, M. M.; Khan, A. U. *J. Am. Chem. Soc.* **1986**, *108*, 2472. (b) Clennan, E. L.; Foote, C. S. In *Organic Peroxides*; Ando, W. Ed.; Wiley: New York, 1992; p 255.

(46) Lerner et al. have reported a surprising observation that ozone is formed (besides hydrogen peroxide) in biological systems and that the first step of its formation most likely involves the antibody catalyzed conversion of molecular singlet oxygen and water to HOOOH (see ref 9).

(47) Water is most probably also formed in the reaction of ozone with hydrogen trioxide and hydrogen peroxide (Xu, X.; Goddard, W. A., III. *Proc. Natl. Acad. Sci. USA*, **2002**, *99*, 15 308). However, control experiments (-78 °C) showed that these processes are rather slow under experimental conditions investigated.

(48) MP2/6-31G(d) calculations: D. Cremer, *J. Chem. Phys.*, **1978**, *69*, 4456. – The flip-flop rotation of HOOOH from its most stable *C*₂-symmetrical conformation into the mirror image of this conformation proceeds via the *C*_s-symmetrical form and resembles the pseudorotation of a five-membered ring.

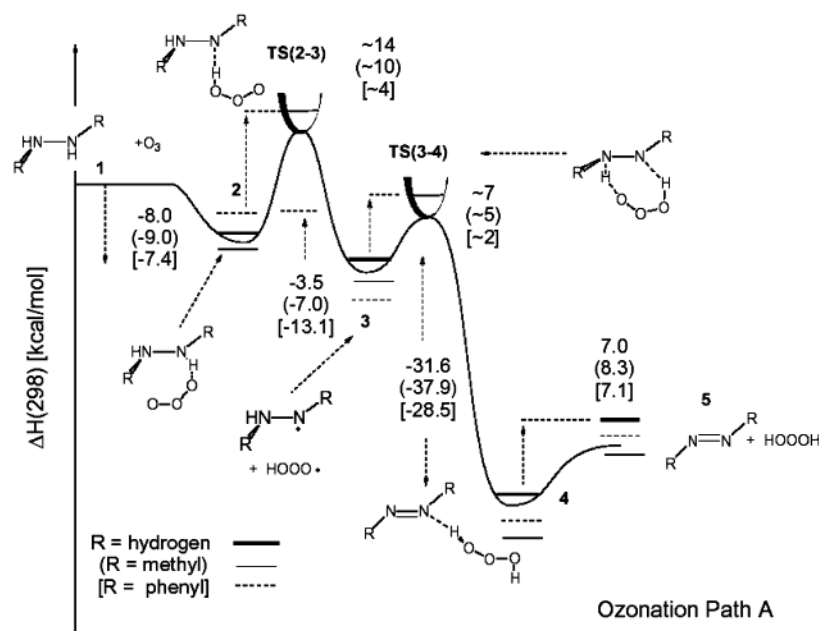


Figure 2. Enthalpy profile for the ozonation of hydrazine (normal numbers), 1,2-dimethylhydrazine (numbers in parentheses), and 1,2-diphenylhydrazine (numbers in brackets) according to path A (see Scheme 1). B3LYP/6-31G(d,p) calculations using RDFT, BS-UDFT, and SIC-DFT.

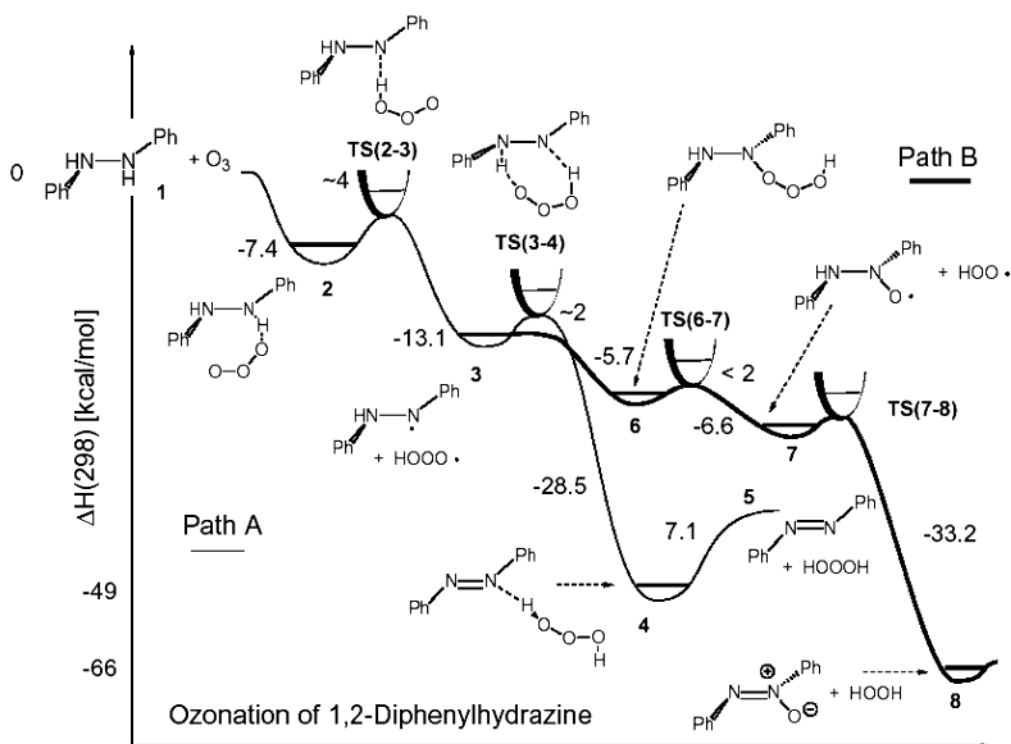


Figure 3. Enthalpy profile for the ozonation of 1,2-diphenylhydrazine according to paths A and B (see Scheme 1). B3LYP/6-31G(d,p) calculations using RDFT, BS-UDFT, and SIC-DFT.

Hence, there are several decomposition possibilities for HOOOH, which explains the relatively high loss (45%) of this polyoxide in the reaction mixture. For HOOH, a low energy decomposition path according to reaction Ia in Scheme 2 does not exist. The most likely decomposition reaction (observed for concentrated hydrogen peroxide solutions and also investigated by Xu, Muller, and Goddard^{9b}) starts from a dimer and yields two water and a O₂ (¹Δ_g) molecule. The activation enthalpy is 26.9 kcal/mol,^{9b} but can be somewhat lowered by the inclusion of two water molecules in the reaction mechanism. In any case,

the decomposition of hydrogen peroxide is slower than that of hydrogen trioxide and can proceed via essentially one mechanism (in solutions free of acids and metal ions, which also can act as catalysts). This seems to explain the smaller degree of decomposition of HOOH as compared to that found for HOOOH.

1,2-Dimethylhydrazine (1b). Ozonation of 1,2-dimethylhydrazine with ozone-oxygen or ozone-nitrogen mixtures in acetone-*d*₆ (0.01–0.1 M) at –78 °C yielded 1,2-dimethyldiazene (trans isomer, 20 ± 10%, mol %), 1,2-dimethyldiazene-*N*-oxide

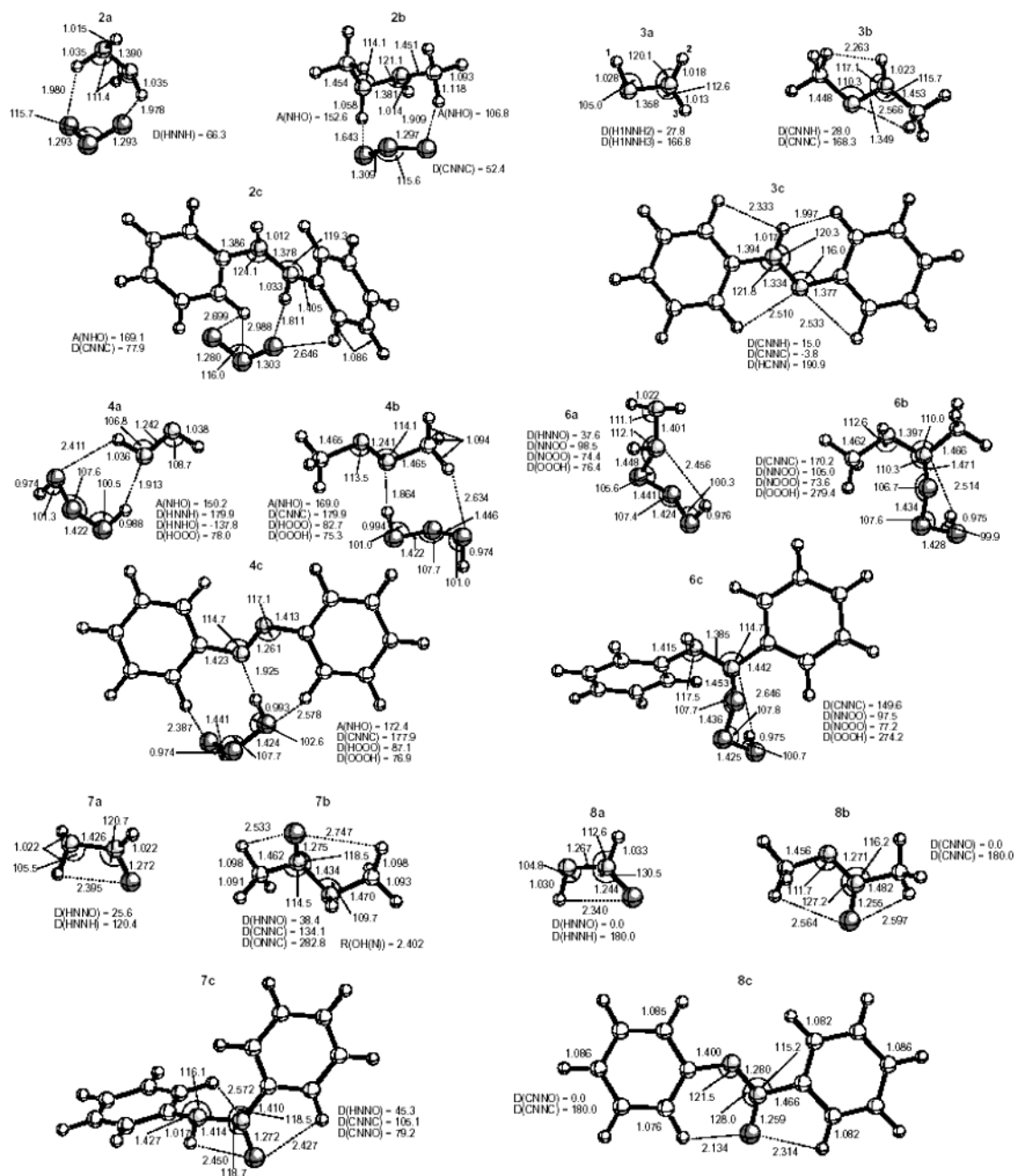


Figure 4. B3LYP/6-31G(d,p) geometries for selected structures. Distances in Å, angles in deg. For other geometries, see the Supporting Information.

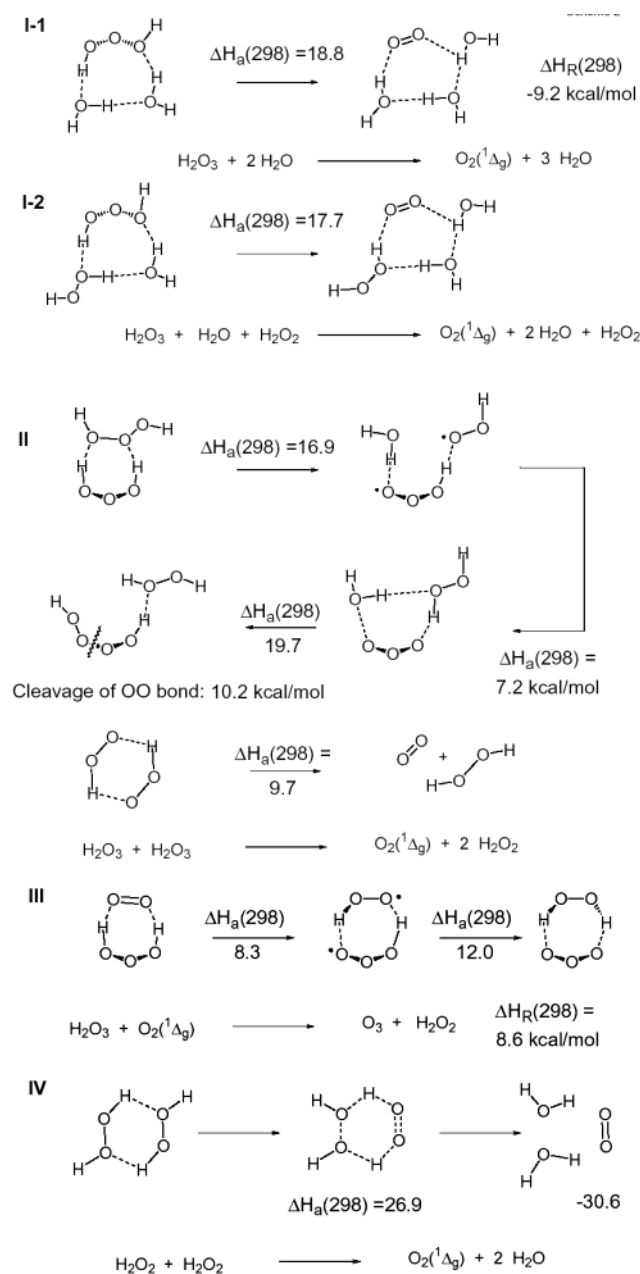
($50 \pm 10\%$), formic acid ($15 \pm 5\%$), nitromethane ($10 \pm 5\%$), hydrogen trioxide ($45 \pm 10\%$), hydrogen peroxide ($55 \pm 10\%$), and water. The increased yield of 1,2-dimethyldiazene-*N*-oxide relative to the phenyl system is most likely due to subsequent oxidation of the dimethyldiazene. Control experiments showed that 1,2-dimethyldiazene reacted slowly with ozone ($-78\text{ }^\circ\text{C}$) to form 1,2-dimethyldiazene-*N*-oxide (90 mol %) and nitromethane (10%) as the main reaction products. The proposed mechanism of this oxidation is illustrated in Scheme 3.

Oxidation of the diazene with ozone was originally thought to occur in a concerted symmetry-allowed $[4\pi + 2\pi]$ reaction via the generation of a primary ozonide. However, neither the corresponding TS nor the ozonide ring could be located on the potential energy surface. When performing constrained optimizations with the help of the puckering coordinates³² (freezing, e.g., the phase angle³³) structures were found (testing both cis-

and trans-diazenes) that correspond to the breaking off of a singlet oxygen molecule and that are already in the exit channel of an O-transfer reaction from ozone to diazene (Scheme 3 and Figure 5). The instability of the ozonide ring system results from strong destabilizing lone pair–lone pair (lp–lp) repulsion (a planar diazoazoxide would be a 10π system with two occupied antibonding π^* MOs). The nature of lp–lp repulsion implies that such a system will not be significantly stabilized regardless of the degree of puckering or the substituents of the diazene system. The formation of 1,2-dimethyldiazene-*N*-oxide can only occur via a stepwise process involving an in-plane attack of the electrophilic ozone molecule at an electron lp of one of the diazene N atoms and the O transfer from the ozone molecule to the diazene.

This conclusion implies an important corollary: If the in-plane attack of ozone is sterically hindered as in the case of

Scheme 2



1,2-diphenyldiazene (the ortho-H atoms of the phenyl rings in the planar molecule block the entrance to the bay-region, in which the N atoms are located; see the Supporting Information) then ozonation products of the diazene can no longer be observed. However, 1,2-dimethyldiazene reacts with relative ease (activation enthalpy of 13.6 kcal/mol) to yield the 1,2-dimethyldiazene-*N*-oxide and singlet oxygen (**10**) in a strongly exothermic reaction ($\Delta_R H(298) = -42.0$ kcal/mol).

If the reaction takes place in the solvent cage, then molecular singlet oxygen oxidizes the diazene-*N*-oxide and **11** is formed (Figure 5). The activation enthalpy is 41.2 kcal/mol ($\Delta_R H(298) = 29.3$ kcal/mol), which in view of an excess energy of 55.6 kcal/mol from the first step is available for some of the molecules (dissipation determines the yield of **11**). Nitrosomethane and nitrosomethane oxide can recombine to form nitromethane and nitrosomethane. Nitrosomethane can then easily be oxidized by ozone to nitromethane. We investigated

Table 2. Proton Chemical Shifts, Rate Constants, Frequency Factors, and Activation Energies for the Decomposition of Hydrogen Trioxide (HOOOH) Formed in the Ozonation of 1,2-Diphenylhydrazine (**1a**) and 1,2-Dimethylhydrazine (**1b**) in Various Solvents^a

	solvent	<i>T</i> (°C)	δ (ppm)	$10^4 k(T), s^{-1}$	E_a (kcal mol ⁻¹)	log <i>A</i>		
1a	acetone- <i>d</i> ₆	-30	13.24	(0.16) ^b				
		-20	13.11	0.1				
			13.19	(0.55) ^b				
		-10	13.02	0.25				
			13.10	(1.58) ^b				
			13.09	[1.5] ^c				
		0	12.93	1.4	16.7 ± 1.5	9.4 ± 1.0		
			13.00	(5.0) ^b	(15.9 ± 1.4) ^b	(9.5 ± 1.0) ^b		
			13.00	[4.6] ^c	[16.0 ± 1.4] ^c	[9.5 ± 1.0] ^c		
		10	12.84	2.5				
			12.90	(14.5) ^b				
			12.88	[13.1] ^c				
			20	12.75	6.8			
			30	12.67	17.4			
methyl acetate		-10	12.47	0.4				
		0	12.38	1.43	16.5 ± 1.5	9.5 ± 1.1		
		10	12.29	4.3				
		15	12.25	7.2				
		20	12.21	12.4				
		30	12.14	29.0				
		<i>tert</i> -butyl methyl ether		-10	12.62	0.38		
				0	12.55	0.95		
				5	12.54	1.37		
				10	12.50	2.4	15.3 ± 1.3	8.3 ± 0.9
15	12.46			5.1				
20	12.41			5.7				
1b	acetone- <i>d</i> ₆	-10	13.10	0.26				
		-5	13.05	0.35				
		0	12.99	0.81				
		5	12.95	1.76	17.0 ± 1.6	9.6 ± 1.1		
		10	12.91	2.28				
		15	12.86	4.04				
		20	12.81	6.50				
		methyl acetate		-5	12.55	0.63		
				0	12.47	1.35		
				5	12.42	2.45	16.7 ± 1.6	9.5 ± 1.0
				10	12.38	4.05		
				15	12.34	5.51		
				20	12.28	10.5		

^a *c*(HOOOH) = 0.002–0.01 M. Standard deviations $\leq \pm 10\%$. By following the decay of the HOOOH absorption. ^b *c*(HOOOH) = 0.01–0.1 M. ^c Runs as in footnote *b* in the presence of the radical inhibitor 2,6-di-*tert*-butyl-4-methylphenol (BMP). Molar ratio HOOOH:BMP = 1.5.

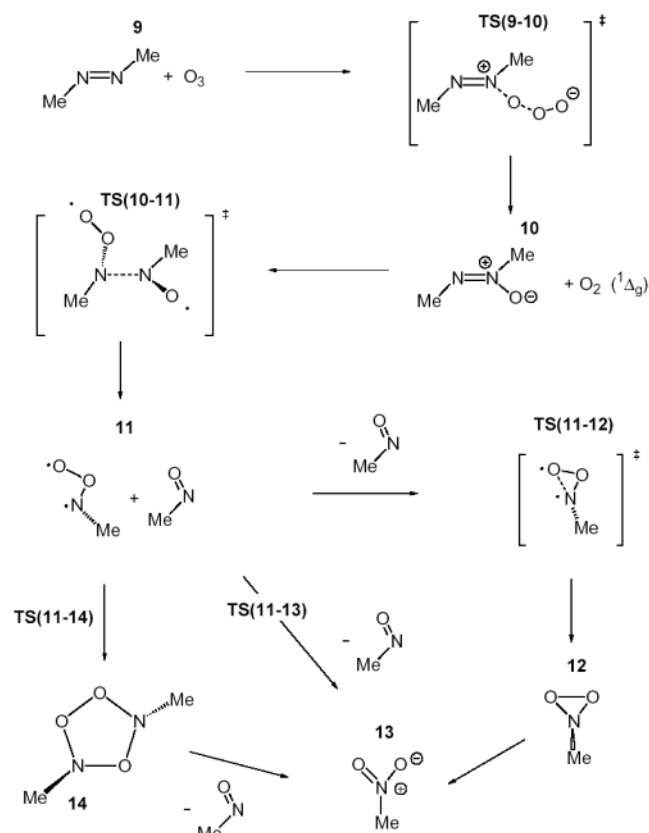
three possible mechanistic alternatives for the formation of nitromethane (see Scheme 3): (a) Ring closure of the nitroso oxide to an azadioxirane, which can open to the nitromethane. This reaction is similar to the isomerization of carbonyl oxide to dioxirane and the opening of dioxirane to the methylene-(bis)oxy biradical.⁴⁹

(b) Cycloaddition of the nitroso oxide biradical to the N=O double bond of nitrosomethane and formation of a 1,3-diaz-2,4,5-trioxolane, which by cycloreversion can yield nitrosomethane and nitromethane.

(c) O-transfer from the nitroso oxide to nitrosomethane thus yielding nitromethane and nitrosomethane.

Possibility (a) is unlikely due to the fact that the activation enthalpy for ring closure is 46.1 kcal/mol, which leads to an enthalpy 33.4 kcal/mol above that of the reactants **9** (see Figure 5). For the cycloaddition reaction (b) a TS and the ozonide **14** (Scheme 3) were not found for reasons similar as in the case of the diazene-ozone cycloaddition reaction (see above). Reaction

Scheme 3



(c) requires an activation enthalpy of just 29 kcal/mol. Considering that in the formation of **10** 55.6 kcal/mol excess energy is generated, of which just 29.3 kcal/mol are reused in the decomposition of **10** to **11**, there are still 26.3 kcal/mol left (in the best case considering dissipation) for the O-transfer reaction and the formation of nitromethane and nitrosomethane (**13**, Figure 5). Therefore, possibility (c) represents the most likely mechanism for nitromethane formation, which was found in the reaction mixture.

A further point of note in the reaction of the 1,2-dimethylhydrazine is the production of formic acid. This observation suggests a third competing pathway for the reaction of the 1,2-dimethylhydrazine radical (Scheme 4) to those outlined in Scheme 1. In this mechanism the 1,2-dimethylhydrazine radical reacts with the $\text{HOOO}\cdot$ radical (**3**) to produce formaldehyde methylhydrazone and HOOOH (**15**), which can be ozonolyzed⁵⁰ to yield formic acid and nitromethane via **16** and **17** (Scheme 4).

Although neither formaldehyde methylhydrazone^{51a} nor *N*-methyl-*N*-nitrosoamine,^{51b} already proposed before as the products of the ozonation of hydrazones,⁵⁰ were detected in the reaction mixture, control experiments showed that ozonation of formaldehyde methylhydrazone (0.1 M in acetone, at -78°C) actually produced nitromethane and formic acid as the main products. The proposed mechanism shown in Scheme 4 is based on the fact that both the NH and a CH hydrogen should be prone to abstraction by the $\text{HOOO}\cdot$ radical (Schemes 1 and 4). The corresponding **TS(3–15)** represents again a three-electron situation with a large self-interaction error. It could not be found, which suggests that the corresponding barrier is rather low thus yielding at the DFT level a “negative” TS energy.

The C=N double bond of the hydrazone formed reacts with ozone similarly as the N=N double bond of the diazene does (Scheme 3), i.e., in an O-transfer step rather than a cycloaddition step. The activation enthalpy is 25.2 kcal/mol (B3LYP/6-31G-(d,p) calculations, Table 3), almost twice as large as in the diazene reaction (13.6 kcal/mol, Figure 5). The O_2 ($^1\Delta_g$) formed can react with the hydrazone *N*-oxide to give *N*-methyl-*N*-nitrosoamine and carbonyl oxide (**17**, Scheme 4) in an exothermic reaction ($\Delta H(298) = -11.7$ kcal/mol, Table 4) analogue to the corresponding reaction of the diazene *N*-oxide (Scheme 3). Carbonyl oxide is known⁴⁹ to proceed via isomerization to dioxirane (activation enthalpy 20.4 kcal/mol, $\Delta H(298) = -23.4$ kcal/mol), which rearranges easily to formic acid (activation enthalpy 21.7 kcal/mol, $\Delta H(298) = -89.4$ kcal/mol) by H-migration and OO-cleavage. *N*-methyl-*N*-nitrosoamine can

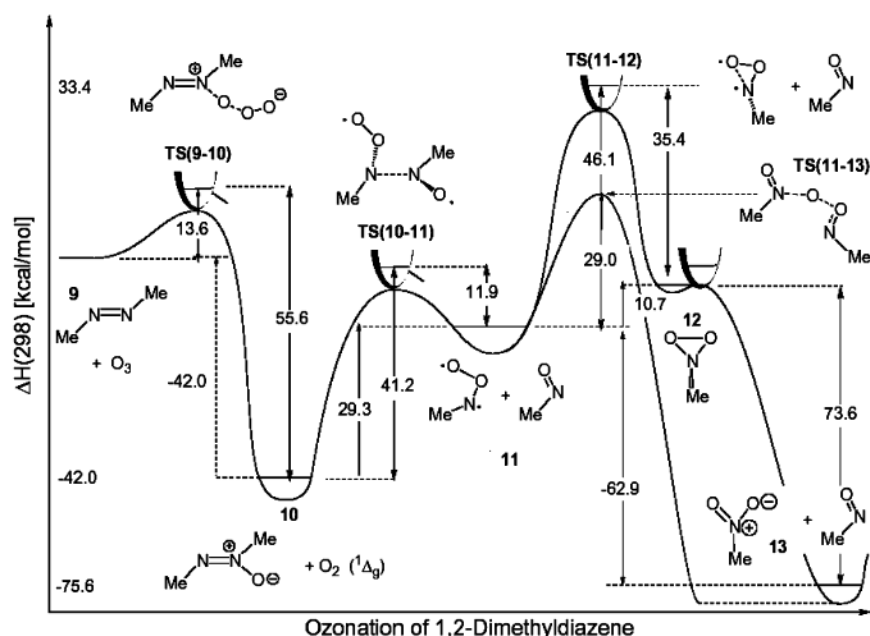


Figure 5. Enthalpy profile for the ozonation of 1,2-dimethyldiazene (see Scheme 3). B3LYP/6-31G(d,p) calculations using RDFT, BS-UDFT, and SIC-DFT.

Scheme 4

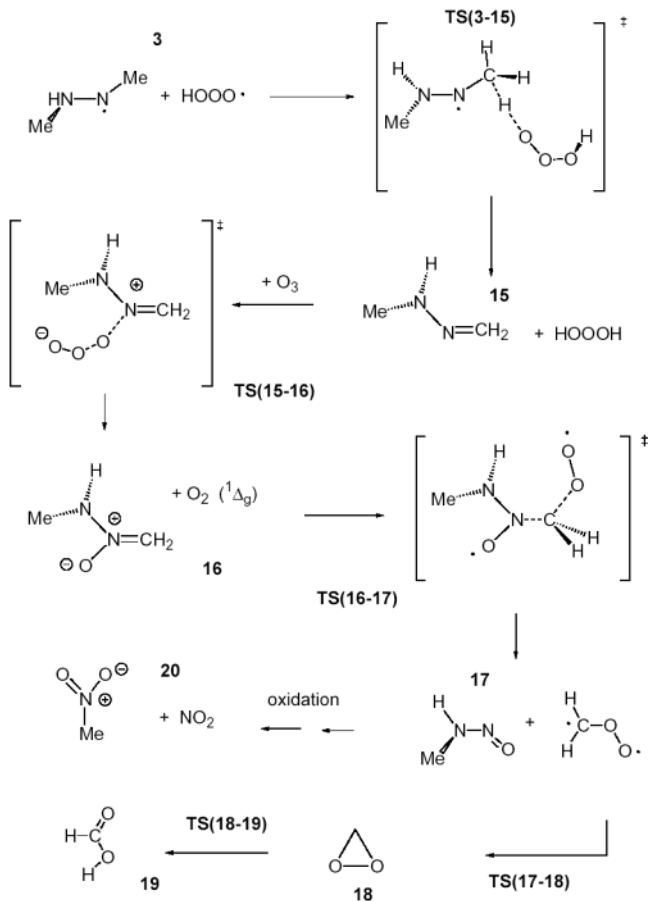


Table 3. Energies, Enthalpies, Entropies, and Dipole Moments of Structures Involved in the Ozonation of 1,2-Dimethyldiazene as Calculated at B3LYP/6-31G(d,p)^a

system	sym	ΔE	ZPE	$\Delta H(298)$	S	$\Delta G(298)$	μ
9	C_{2h}	0.0	57.7	0.0	126.5	0.0	0, 0.61
TS(9–10)	C_1	13.6	58.4	13.6	86.9	25.4	5.58
10	C_s	-43.4	59.3	-41.9	123.1	-40.8	1.58, 0
TS(10–11)	C_1	-1.1	59.0	-0.8	83.9	11.9	3.39
11	C_s	-12.1	57.3	-12.7	127.5	-13.0	2.37, 2.39
TS(11–12)	C_1	35.7	28.5	33.4	65.3	33.2	2.90
TS(11–13)	C_1	16.5	58.1	16.3	87.7	27.8	4.01
12	C_s	-1.4	60.1	-2.0	131.0	-2.3	2.54, 2.39
13	C_s	-76.6	61.4	-75.7	136.6	-77.6	3.48, 2.39
3b	C_1	0.0	60.1	0.0	73.7	0.0	2.05
15	C_1	-28.2	53.6	-27.3	69.0	-25.3	1.82
TS(15–16)	C_1	-2.8	58.2	-2.1	90.2	10.6	7.16
16	C_1	-54.9	59.0	-53.0	124.1	-50.6	3.21, 0
17	C_s	-65.7	58.1	-64.7	129.0	-63.6	3.90, 3.96
TS(17–18)	C_1	-44.2	38.3	-44.3	118.8	-43.1	3.90, 3.68
18	C_{2v}	-89.8	40.0	-88.1	118.5	-86.8	3.90, 2.53
TS(18–19)^b	C_{2v}	-66.6	38.6	-66.4			3.90, 2.30
19	C_s	-180.1	40.9	-177.5	118.9	-176.3	3.90, 1.44
20	C_s	-147.3	45.1	-144.7	129.4	-144.5	3.48, 2.59

^a For a definition of structures see Scheme 3 and Scheme 4. Relative energies (ΔE), zero point energies (ZPE), relative enthalpies ($\Delta H(298)$) and relative Gibb's free energies ($\Delta G(298)$) in kcal/mol, dipole moments (μ) in Debye, entropies (S) in cal mol/deg. – The symmetry in column Sym is given with regard to the first molecule in a system of two molecules; where two molecules form a system the sum of their zero point energies and the sum of their entropies are reported. ^b Data for the reaction of **18** to **19** via **TS(18–19)** from ref 49.

be oxidized to nitromethane and NO_2 , however, no attempt was made at present to explore experimentally these mechanistic

Table 4. Comparison of Relative Energies, and Free Energies of Structures **1a–8a** Calculated for the Solvent Phase (Acetone) and the Gas Phase at B3LYP/6-31G(d,p)^a

system	sym	ΔE	$\Delta G(298)$	μ
1a	C_2	0.0 (0.0)	0.0 (0.0)	2.38
2a	C_1	-7.5 (-8.7)	-7.0 (2.0)	0.12 (0.01)
TS(2a–3a)	C_1	-1.1 (-0.8)	-0.8 (8.3)	3.11 (2.30)
3a	C_1	-13.0 (-9.8)	-12.8 (-13.3)	3.03 (2.61)
4a	C_1	-44.8 (-43.7)	-43.8 (-34.8)	1.85 (1.65)
5a	C_{2h}	-38.8 (-35.0)	-38.5 (-35.9)	0 (0)
6a	C_1	-35.8 (-33.8)	-35.9 (-21.1)	2.83 (2.38)
7a	C_1	-36.8 (-32.5)	-36.4 (-35.3)	1.98 (1.67)
8a	C_s	-71.1 (-65.4)	-70.8 (-65.4)	1.38 (1.17)

^a For a definition of structures see Scheme 1. Relative energies (ΔE) and relative Gibb's free energies ($\Delta G(298)$) in kcal/mol, dipole moments (μ) in Debye. The symmetry in column Sym is given with regard to the first molecule in a system of two molecules. The values in parentheses correspond to the gas-phase values.

steps further. We consider the mechanism shown in Scheme 4 as reasonable to explain the ozonation products of hydrazones.

The mechanism of the ozonation of the hydrazines **1a**, **1b**, and **1c** has been explored quantum chemically in the gas phase while experimental investigations were performed in solution. For the purpose of assessing possible solvent effects on the reaction mechanism, we calculated electrostatic effects caused by acetone in the case of the ozonation of **1a**. Some selected data are summarized in Table 4. They reveal that the solvent acetone should favor reaction path B somewhat more (reactions become more exothermic), although the mechanisms discussed above will not change. However, a solvent, which can establish H-bonds to the reaction partners can have a significant effect on the mechanism. For example, water is generated in the reaction, which may form H-bonded complexes with reaction partners and intermediates thus influencing reaction barriers and reaction enthalpies. Further studies will have to be carried out to investigate these effects.

Conclusions

In the present investigation we have shown that several mechanisms are involved in the oxidation of substituted hydrazines by ozone where the preferred reaction path depends on the nature of the substituent (alkyl or aryl). In any case, the ozonation reaction leads to a major production of hydrogen trioxide (HOOOH), and represents insofar the best method for the preparation of this polyoxide in significant amounts without the interfering presence of organic hydrotrioxides (ROOOH).

(1) Ozonation is initialized by the formation of an ozone-hydrazone complex, followed by stepwise H-abstraction and the generation of a diazene-hydrogen trioxide complex, which is 49 kcal/mol more stable than the reactants.

(2) Alternatively, radical recombination can lead to a hydrazone hydrotrioxide, (R_2NOOOH), which decomposes quickly even at low temperatures to diazene-*N*-oxide and HOOH . But the yield of these products is smaller because, the radical recombination requires either diffusion out of the solvent cage or an overall rotation of $\text{HOOO}\cdot$ in the solvent cage.

- (49) See, for example, Cremer, D.; Kraka, E.; Szalay, P. G. *Chem. Phys. Lett.*, **1998**, 292, 97, and references therein.
 (50) For previous studies on the ozonation of carbon–nitrogen double bonds, see: (a) Erickson, R. E.; Andrusis, P. J., Jr.; Collins, J. C.; Lungle, M. L.; Merger, G. D. *J. Org. Chem.* **1969**, 34, 2961. (b) Enders, D.; Wortmann, L.; Peters, R. *Acc. Chem. Res.* **2000**, 33, 157.
 (51) (a) Begtrup, M.; Nytoft, H. P. *J. Chem. Soc., Perkin Trans. 1*, **1985**, 81. (b) Castro, A.; Leis, J. R.; Pena, M. E. *J. Chem. Soc., Perkin Trans. 2*, **1989**, 1861.

(3) A new mechanism for the decomposition of hydrogen trioxide involving both hydrogen peroxide and water in a pericyclic process (via the hydrogen-bonded HOOOH–HOOH–HOH complex) is proposed thus lowering the yield of HOOOH in the ozonation of hydrazines.

(4) For alkyl hydrazines, H can be abstracted from the CH₃ group in α -position to the N thus leading to a hydrazone. In the case of 1,2-dimethylhydrazine, the corresponding hydrazone is ozonolyzed further yielding nitromethane and formic acid.

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Supporting Information Available: Geometries and energy data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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