# Energetics and Mechanisms for Reactions Involving Nitrosamide, Hydroxydiazenes, and Diimide *N*-Oxides

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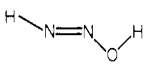
**Abstract**: Using ab initio techniques, we have solved for the geometries and energies of nine isomers of $N_2H_2O$ including hydroxy-1,1- and hydroxy-1,2-diazenes[1] (e.g., HN=NOH), nitrosamide ($H_2N$—NO), and diimide *N*-oxides (HN=N(→O)H). The heats of formation obtained from these calculations are used to examine several chemical processes including (i) the reaction $H_2N + NO \rightarrow N_2 + H_2O$, postulated to be a key step in the thermal $DeNO_x$ process for reducing NO to $N_2$ in stationary power plants, (ii) deoxygenation of *N*-nitroso compounds and azoxy compounds, and (iii) nitrosation of amines.

## I. Introduction

This paper describes GVB-CI studies on the thermochemistry of several isomers of $N_2H_2O$ (I–IX). Although none of these molecules has been isolated or characterized, several are likely intermediates in processes involving the reduction of oxides of nitrogen to molecular nitrogen and water.[2-4] For example, the postulated key step[2-4]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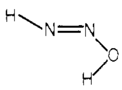
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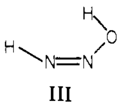
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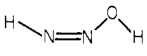
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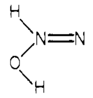
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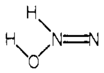
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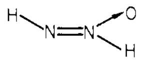
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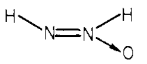
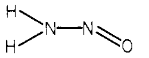

VIII


IX

$$NH_2 + NO \rightarrow \ \rightarrow N_2 + H_2O$$

in the thermal $DeNO_x$ process using ammonia or primary amines to reduce NO to $N_2$ is thought[4] to involve several of species I–IX.

In addition, thermochemical studies of I–IX provide information useful in making estimates for substituted compounds known to exist but for which extremely limited thermochemical data are available. Several ab initio calculations on $N_2H_2O$ isomers have previously been reported.[5] Pople and co-workers[5a] and Thomson and co-workers[5b] have studied the hydroxy diimides (I–IV) and nitrosamide (IX) at the Hartree–Fock level using the 4-31G and STO-4G bases, respectively. Cimiraglia and co-workers[5c] have carried out CI calculations (STO-3G + sp) on diimide *N*-oxides (VII, VIII). Large basis set calculations on $N_2H_2O$ including electron correlation have not yet been reported.

Table I. Calculated Heats of Formation (kcal/mol) for Various Isomers of $N_2H_2O$

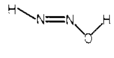
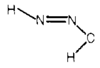
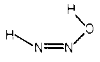
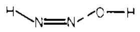
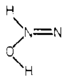
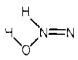
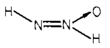
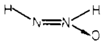
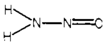
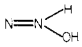
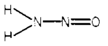
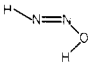
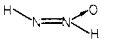
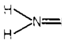
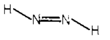
| molecule | $\Delta H_{f(0K)}$ | $\Delta H_{f(298K)}$ | relative enthalpy (298 K) |
|---|---|---|---|
|  I | 36.2 | 33.7 | 1.3 |
|  II | 35.3 | 32.8 | 0.4 |
|  III | 43.3 | 40.8 | 8.4 |
|  IV | 34.9 | 32.4 | 0.0 |
|  V | 59.2 | 56.7 | 24.3 |
|  VI | 68.1 | 65.7 | 33.3 |
|  VII | 51.3 | 48.6 | 16.2 |
|  VIII | 61.0 | 58.4 | 26.0 |
|  IX | 37.6 | 35.4 | 3.0 |

Table II. Relative Enthalpies (at 298 K) Useful in Analyzing Reaction 57

| | | | |
|---|---|---|---|
| $NH_2$ + NO | 0 |  | −9.3 |
|  | −30.6 | $N_2$ + $H_2O$ | −123.8 |
|  | −33.2 | $N_2O$ + $H_2$ | −46.4 |
|  | −17.4 | HNO + NH | +42.1 |
| NNH + OH | +12.0 |  + O | +71.7 |
| $N_2$ + H + OH | −4.4 |  + O | +44.3 |

The results of our calculations are summarized in section II and applied to considerations of such reactions as (i) the N–O homolytic fission of the coupling product of aryldiazonium salts with oxy anions (section IIA), (ii) deoxygenation of *N*-nitroso compounds (section IIB), (iii) nitrosation of aliphatic and aromatic amines (section IIC), (iv) reaction of nitrosobenzene with hy-

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[1] In this paper, the names 1,1- and 1,2-diazene are used in a nonsystematic fashion. More appropriate names would be 1λ⁵-diazyne (or isodiazene) and diazene, respectively. The hydroxy derivatives would then be hydroxy-1λ⁵-diazyne and hydroxydiazene.

[2] Lyon, R. K. *Int. J. Chem. Kinet.* **1976**, *8*, 315.

[3] Lyon, R. K.; Benn, D. J. "Seventeenth Symposium (International) on Combustion"; The Combustion Institute: Pittsburgh, Pa., 1977; p 199.

[4] Miller, J. A.; Branch, M. C.; Kee, R. J. *Combust. Flame*, to be submitted for publication. Salimian, S.; Hanson, R. K. *Combust. Sci. Technol.* **1980**, *23*, 225.

[5] (a) Random, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 289–300. (b) Thomson, C.; Provan, D.; Clark, S. *Int. J. Quantum Chem., Quantum Biol. Symp.* **1977**, *4*, 205–215. (c) Cimiraglia, R.; Persico, M.; Tomasi, J. *J. Phys. Chem.* **1977**, *81*, 1876–1881.

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Table III. Total Energies (hartrees) for $N_2H_2O$

| | HF (4-31G) | HF[a] | GVB-PP[a] | GVB-CI[a] |
|---|---|---|---|---|
| I | −184.525 77 | −184.860 83 | −185.008 85 | −185.122 61 |
| II | −184.527 16 | −184.863 58 | −185.009 40 | −185.123 98 |
| III | −184.510 04 | −184.847 86 | −184.994 96 | −185.110 93 |
| IV | −184.528 97 | −184.860 02 | −185.009 48 | −185.124 62 |
| V | −184.506 03 | −184.826 71 | −184.963 83 | −185.084 76 |
| VI | −184.492 36 | −184.813 46 | −184.949 58 | −185.070 62 |
| VII | −184.502 42 | −184.838 99 | −184.976 62 | −185.100 35 |
| VIII | −184.486 05 | −184.826 52 | −184.963.41 | −185.084 40 |
| IX | −184.538 65 | −184.865 97 | −185.001 74 | −185.118 31 |
| $N_2$ | | −108.957 64 | −109.044 80 | −109.119 16 |
| $H_2O$ | | −76.034 20 | −76.092 94 | −76.145 86 |

[a] Double-ζ basis plus d polarization functions.

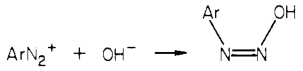
drazoic acid (section IIF), and (v) the mechanisms for the reduction of NO by $NH_2$ postulated as the key step in the thermal $DeNO_x$ process (section IIG). Calculational details are presented in section III.

## II. Results and Discussion

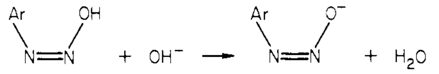
From the theoretical studies described in section III, we find the heats of formation and relative energies listed in Table I. Some implications of these results are as follows.

**A. Hydroxydiimide (I–IV).** Hydroxydiimide has never been isolated although it is thought to be involved in the reaction of ammonium salts with nitrous acid[6] (eq 1). Substituted hydroxydiimides can be formed by coupling aryldiazonium salts with hydroxide ion (eq 2). The first formed *cis*-arylazo hydroxide is, however, rapidly deprotonated to the aryldiazotate (eq 3).[7] Thus, because the concentration of arylazo hydroxide is never more than a few percent, it is difficult to experimentally study these compounds.

$$NH_3 + HONO \xrightarrow{-H_2O} H_2N\text{—}NO \rightarrow HNNOH \rightarrow N_2 + H_2O \quad (1)$$

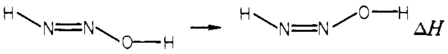


(2)



(3)

Generalized valence bond–configuration interaction (GVB-CI) calculations indicate that the cis and trans isomers I and IV are essentially equivalent in energy, with cis lower (eq 4). This is in contrast to the 4.7-kcal calculated energy difference between trans and *cis*-diimide[8] with trans lower (eq 5). The cis geometry is apparently favored by diimides with electronegative substituents. The reasons for this preference will be discussed in section IIH.

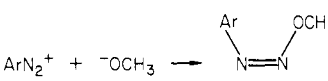


$\Delta H = -1.3$ kcal/mol (4)

I IV

$\Delta H = 4.7$ kcal/mol (5)

Arylazo ethers formed in the reaction of alkoxides with aryldiazonium salts are, in some cases, isolable[9] (eq 6). The *cis*-arylazo ether is formed faster than the trans, although the trans isomer is thermodynamically more stable.[9] The electronic effects favoring a cis geometry are apparently overcome by steric effects favoring a trans structure. Interestingly, the fact that the *cis*-arylazo ether is formed faster than the trans indicates that electronic rather than steric factors determine the energy of the transition state.



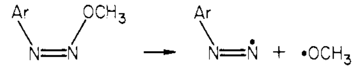
(6)

The homolytic dediazoniation of aryldiazonium salts by methoxide ion gives products consistent with the formation of aryl radicals.[9] It has been suggested by Szele and Zollinger[10] that this decomposition occurs via the homolytic fission of the N–O bond in the first formed *cis*-aryldiazo ether (eq 7). We can use the N–O bond energy of hydroxydiimide to model this N–O cleavage. Using the thermochemistry developed in this paper plus the values in Table IV leads to a $\Delta H$ for the N–O bond cleavage of 45.6 kcal (eq 9). The N–O bond energy of IV may be used to give an estimate of the N–O bond energy of an arylazo methyl ether. Correcting the N–O bond energy of IV by the energy difference between an $N\text{–}OCH_3$ and N–OH bond (8.6 kcal),[12] we predict that (10) is endothermic by 33.0 kcal.

Table IV. Heats of Formation Used in This Paper[a]

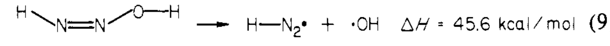
| | 0 K (in kcal) | 298 K (in kcal) |
|---|---|---|
| H | 51.634 | 52.103 |
| N | 112.5 | 113.0 |
| NH | 84.3[b] | 84.3[b] |
| $NH_2$ | 45.1[c] | 44.4[c] |
| $NH_3$ | −9.3 | −10.97 |
| OH | 9.35 | 9.49 |
| $H_2O$ | −57.103 | −57.798 |
| $H_2O_2$ | | −32.5 |
| $HO_2$ | | 5 |
| NO | 21.46 | 21.58 |
| $N_2O$ | 20.43 | 19.61 |
| $NO_2$ | 8.59 | 7.91 |
| HNO | 24.5 | 23.8 |
| *cis*-$HNO_2$ | −16.85 | −18.34 |
| *trans*-$HNO_2$ | −17.37 | −18.84 |
| *trans*-HNNH | 52.4[d] | 50.7[d] |
| *cis*-HNNH | 57.1[e] | 55.4[e] |
| $H_2NN$ (singlet) | 79.8[e] | 78.1[e] |
| $H_2NN$ (triplet) | 94.6[e] | 92.9[e] |
| HNN | 69.2[f] | 68.5[f] |
| HON=N | | 50.3[g] |
| $H_2NNH_2$ | 26.16 | 22.79 |

[a] Based on JANAF unless otherwise mentioned. [b] Foner, S. N.; Hudson, R. L. *J. Chem. Phys.* 1981, *74*, 5017–5021. [c] Bohme, D. K.; Hemsworth, R. S.; Rundle, H. W., ref 21. [d] Foner, S. N.; Hudson, R. L., ref 63. [e] Using energy relative to trans HNNH from ref 8. [f] See ref 22. [g] See ref 23.



(7)

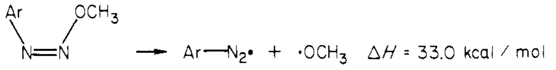
$$Ar\text{—}N_2\cdot \rightarrow Ar\cdot + N_2 \quad (8)$$



(9)

32.4 68.5 9.5

IV



(10)

The N–O bond energy of IV is much lower than the energy needed to cleave the N–H bond in *cis*-diimide ($\Delta H$ = 66.8 kcal[8]) but close to the experimental N–O bond energy for the related nitrous acid (eq 11).

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(6) Schmid, H.; Pfeifer, R. *Monatsh. Chem.* **1953**, *84*, 829–841.

(7) Štĕrba, V. In "The Chemistry of Diazonium and Diazo Groups"; Patai, S., Ed.; Wiley: New York, 1978; Chapter 2.

(8) Casewit, C. J.; Goddard III, W. A. *J. Am. Chem. Soc.* **1980**, *102*, 4057–4062.

(9) Broxton, J. T.; Bunnett, J. F. *Nouv. J. Chim.* **1979**, *3*, 133–138 and references cited therein.

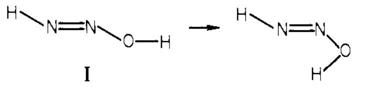
(10) Szele, I.; Zollinger, H. *Helv. Chim. Acta* **1978**, *61*, 1721–1729.

(11) Stull, D. R.; Prophet, H. *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1971**, *NSRDS-NBS 37.*

(12) Based on $D(MeO\text{–}NO) - D(HO\text{–}NO) = -8.6$ kcal/mol. Benson, S. W. "Thermochemical Kinetics", Wiley: New York, 1976.

$$\underset{-18.3}{\mathrm{O{=}N{-}OH}} \rightarrow \underset{21.6}{\mathrm{O{=}N\cdot}} + \underset{9.5}{\mathrm{\cdot OH}} \qquad \Delta H = 49.4\ \mathrm{kcal/mol} \qquad (11)$$

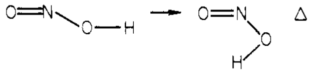
Isomers I and II differ only in the position of the OH bond relative to the NN bond. The trans OH (I) is 0.9 kcal higher than the cis OH (II), (12). A very small energy difference of



I II

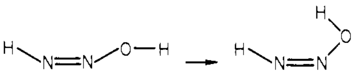
$\Delta H = -0.9$ kcal / mol (12)

0.5 kcal/mol has also been reported (Table IV)[13] for the related *cis*- and *trans*-nitrous acids, but with the trans somewhat lower than the cis (eq 13).



$\Delta H = 0.5$ kcal / mol (13)

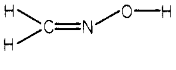
Isomers III and IV also differ only in the placement of the OH bond relative to the NN double bond. However, in this case the energy difference is large, 8.4 kcal, due to the 1,3-hydrogen steric interactions present in III (eq 14). Consistent with this result,



IV III

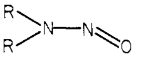
$\Delta H = 8.4$ kcal/ mol (14)

only the trans isomer of the related molecule formaldoxime (structure 15) has been experimentally observed.[14]

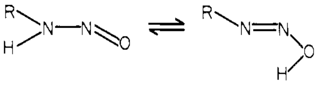


(15)

**B. Nitrosamide (IX).** Disubstituted *N*-nitrosamines are relatively stable entities (structure 16).[15] However, if one R is replaced by H, a fast, tautomeric equilibrium usually takes place, forming the substituted hydroxydiimide (eq 17). Primary alkyl[16] and aryl[17] *N*-nitrosamines have been spectroscopically observed at low temperatures, and primary heterocyclic *N*-nitrosamines have been characterized.[18] The tautomeric equilibrium (17) will be discussed in detail in section IIC.

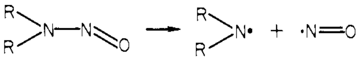


(16)

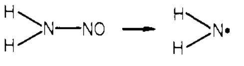


(17)

Secondary *N*-nitrosamines decompose thermally to give substituted amine radicals and nitric oxide (eq 18).[19] The reverse reaction, the scavenging of nitric oxide by substituted amine radicals producing secondary *N*-nitrosamines, has also been observed.[20] Our calculations suggest that the N–N bond for the model compound IX is very weak, 30.6 kcal. This is much weaker than the NN bond energy of hydrazine (66.0 kcal) and somewhat smaller than the value of 44 kcal that would be obtained by averaging the HO–NO bond energy of nitrous acid (49.9 kcal) and the $H_3C$–NO bond energy of nitrosomethane (39.0 kcal).[24]



(18)

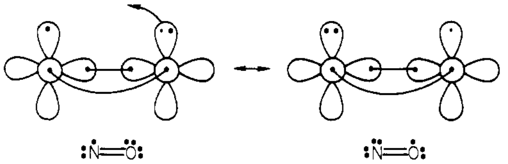


35.4 44.4 21.6

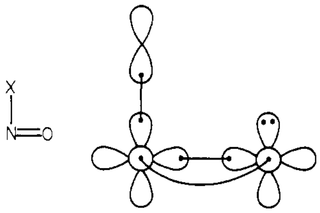
IX

$\Delta H = 30.6$ kcal / mol (19)

The reasons for low X–NO bond energies can be understood by considering the GVB diagrams for bonding to nitric oxide. NO is a radical which is significantly stabilized by a three-electron $\pi$ bond[25,26] involving delocalization of the oxygen p$\pi$ lone pair into the space occupied by the nitrogen p$\pi$ radical orbital. In order to bond to the nitrogen of nitric oxide, one must lose the right resonance structure of (20), thereby disrupting the three-electron $\pi$ bond and leading to a weak X–NO bond (structure 21). In MO terms, NO has a triple bond but one electron in an antibonding $\pi^*$ orbital. In this description, localization of the $\pi^*$ orbital on the N for bonding to X forces the bonding $\pi$ pair to localize on the oxygen, losing much of the bonding in this orbital.

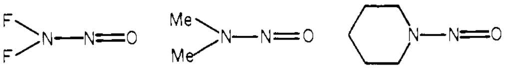


(20)

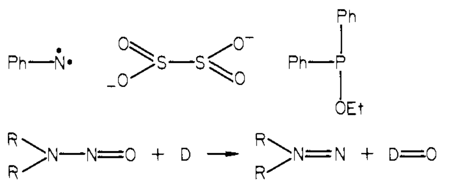


(21)

It is not possible at the present time to apply a correction to the NN bond energy of IX to estimate the NN bond energy for substituted *N*-nitroso compounds because the thermochemistry of similar molecules (e.g., the difference between the $H_2N$–CHO bond of formamide vs. dimethylformamide) is not available. Experimental NN bond energies of nitrosamines have, however, been reported, and it appears that the bond energy is extremely sensitive to the nitrogen substituents. For example, the NN bond energies of *N*-nitrosodifluoroamine, *N*,*N*-dimethylnitrosamine, and *N*-nitrosopiperidine are reported to be 10.1,[27] 55.2,[28] and 42.0[29] kcal/mol, respectively.



A novel method of in situ generation of 1,1-diazene intermediates involves the deoxygenation (eq 22)



(22)

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[13] McGraw, G. E.; Bernitt, D. L.; Hisatsune, I. C. *J. Chem. Phys.* **1966**, *45*, 1392–1399.

[14] Levine, I. N. *J. Chem. Phys.* **1963**, *38*, 2326–2328.

[15] For reviews of *N*-nitrosamines, see: (a) Fridman, A. L.; Mukhametshin, F. M.; Novikov, S. S. *Russ. Chem. Rev.* (*Engl. Transl.*) **1971**, *40*, 34–50. (b) Feuer, H., Ed. "Chemistry of the Nitro and Nitroso Groups", Interscience: New York, 1969. (c) Anselme, J. P., Ed. "*N*-Nitrosamines"; American Chemical Society: Washington, D. C., 1978; *ACS Symp. Ser.*

[16] Müller, E.; Haiss, H.; Rundel, W. *Chem. Ber.* **1960**, *93*, 1541–1552.

[17] Müller, E.; Haiss, M. *Chem. Ber.* **1963**, *96*, 570–583.

[18] Butler, R. N. *Chem. Rev.* **1975**, *75*, 241–257.

[19] (a) Rickatson, W.; Stevens, T. S. *J. Chem. Soc.* **1963**, 3960–3967. (b) Welzel, P. *Chem. Ber.* **1971**, *104*, 808–821.

[20] Flournoy, J. M. *J. Chem. Phys.* **1962**, *36*, 1106–1107.

[21] Bohme, D. K.; Hemsworth, R. S.; Rundle, H. W. *J. Chem. Phys.* **1973**, *59*, 77–81.

[22] Based on experimental $\Delta H_f$(HNNH) from ref 63 and calculated $D_0$(HNN–H) of 71.5 kcal from ref 8.

[23] Assuming $D_0$(HONN–H) is the same as $D_0$(HNN–H).

[24] Batt, L.; Milne, R. T. *Int. J. Chem. Kinet.* **1973**, *5*, 1067–1069.

[25] Baird, N. D. *J. Chem. Educ.* **1977**, *54*, 291–293.

[26] Greene, F. D.; Burrington, J. D.; Karkowsky, A. M. In "Organic Free Radicals", Pryor, W. A., Ed.; American Chemical Society: Washington, D.C., 1978; *ACS Symp. Ser.* pp 122–133.

[27] Johnson, F. A.; Colburn, C. B. *Inorg. Chem.* **1963**, *2*, 24–26.

[28] Korsunskii, B. L.; Pepekin, V. I.; Lebedev, Y. A.; Apin, A. Y. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967**, *3*, 509–511.

[29] Golovanova, O. F.; Pepekin, V. I.; Korsunskii, B. L.; Gafurov, R. G.; Eremenko, L. T.; Dubovitskii, F. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1974**, *7*, 1417–1419.

of *N*-nitroso compounds by reagents such as arylnitrenes,[30a] sodium hydrosulfite,[30b] and ethyl diphenylphosphinite.[30c] It is therefore of interest to determine the energy of the N–O bond for the model nitrosamide. We find the N–O bond energy for IX is 102.3 kcal (eq 23).[32] This is smaller than the experimental N–O bond energy

$$H_2N{-}NO \rightarrow H_2N{=}N + O \quad \Delta H = 102.3\ \text{kcal/mol}^{11} \quad (23)$$

35.4 78.1 59.6
IX

for HNO, eq 24, by 17.8 kcal. In order to compare processes 23

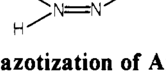

$\Delta H$ = 120.1 kcal/mol[11] (24)

23.8 84.3 59.6

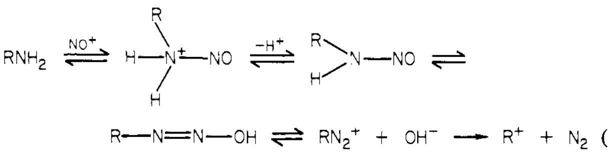
and 24, we should use the triplet state for 1,1-diazene in (23)[31]

$$H_2N{-}NO \rightarrow H_2N{-}\dot{N}\cdot + O \quad \Delta H = 117.1\ \text{kcal/mol} \quad (25)$$

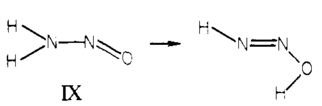
leading to a bond energy quite similar to that in (24). Thus, despite the view[15a] that *N*-nitrosamines posses substantial NN double bond character due to the resonance form, structure 26, as indicated by the 25-kcal barrier to rotation observed for dimethylnitrosamine,[33] the bond energies of IX are consistent with an N–N single bond and NO double bond.


(26)

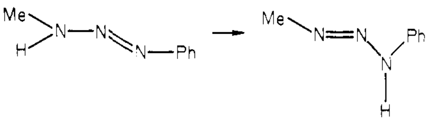
**C. Mechanism of Diazotization of Amines.** The nitrosation of aliphatic and aromatic amines to diazonium salts is proposed to occur via the mechanism 27.[34] A similar process is thought to occur in the reaction of ammonium salts with nitrous acid.[6]

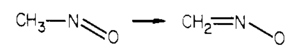

(27)

Central to this mechanism is the tautomerization of the primary nitrosamine to the diazo hydroxide. Although in some cases primary nitrosamines have been observed,[16-18] the energetics of this tautomerization are unknown. Understanding the thermochemistry of this reaction is important because the carcinogenicity of secondary *N*-nitrosamines has been suggested[35] to be related to the formation of diazonium salt alkylating agents by metabolic activation of secondary nitrosamines. Secondary nitrosamines may be degraded to a primary nitrosamine that tautomerizes to the diazo hydroxide. Subsequent decomposition of the diazo hydroxide affords the active carbonium ion alkylating agent.[35] We find the energy of the 1,3-hydrogen shift for the model compounds is −2.6 kcal (eq 28). We estimate that the activation energy for this tautomerization in solution will be on the order of 10–15 kcal on the basis of tautomerization activation energies for (29) of 12 kcal[36] and for the heterogeneous isomerization of nitrosomethane (eq 30) of 10–14 kcal.[37] The activation energy for the gas phase isomerization of IX to II should be quite a bit higher (30–40 kcal, based on nitrosomethane values).


$\Delta H$ = −2.6 kcal/mol (28)

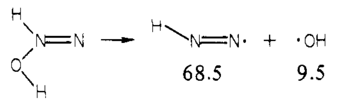
IX II


(29)

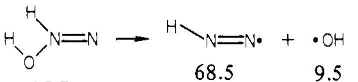

(30)

The isomerization of IX to II has been studied recently at the Hartree–Fock level (STO-4G) by Thomson et al.[5b] They find the reaction is 12.7-kcal downhill with a 91-kcal barrier. Allowing a molecule of water to interact with IX lowered the barrier by ~10%. We suspect (but have carried out no calculations to confirm this suspicion) that contrary to the results of Thomson et al., the isomerization of IX to II should be facile in solution and should also occur in the gas phase. To establish the barrier of IX to II, it is necessary to use a larger basis set and to include electron correlation in carrying out calculations for the potential surface.

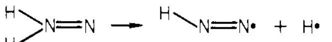
**D. Hydroxy-1,1-diazenes (V and VI).** The hydroxy-1,1-diazenes are clearly very high energy isomers of $N_2H_2O$. Substituted hydroxy-1,1-diazenes have not yet been characterized or isolated. The energy to cleave the N–O bond is calculated to be very low, 12–21 kcal (eq 31 and 32). This is substantially lower than the N–H bond energy[8] for the parent 1,1-diazene (eq 33) but comparable to that predicted[8] for an N–CH$_3$ bond cleavage (eq 34).


$\Delta H$ = 21.3 kcal/mol (31)

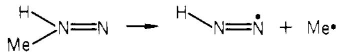
68.5 9.5
56.7
V


$\Delta H$ = 12.3 kcal/mol (32)

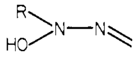
68.5 9.5
65.7
VI

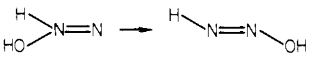

$\Delta H$ = 42.5 kcal/mol (33)

68.5 52.1
78.1


$\Delta H$ ≈ 24 kcal/mol (34)

Correcting the NO bond energy of V by the energy difference between an N–OCH$_3$ and N–OH bond (8.6 kcal),[12] we predict that the N–O bond energy for methoxy-1,1-diazene will be 12.7 kcal. Considering that a dialkyl-1,1-diazene ($E_A$ for decomposition of ~20 kcal) has recently been isolated and characterized,[38] we expect that hydroxy-1,1-diazenes might be obtained from the reduction of *N*-nitrosohydroxylamines (structure 35). The energy difference between the hydroxy-1,1- and hydroxy-1,2-diazenes is 23.9 kcal (eq 36) close to the difference calculated for the hydrogen-substituted diazenes (eq 37).[8]


(35)


$\Delta H$ = −23.9 kcal/mol (36)

V II

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[30] (a) Nishiyama, K.; Anselme, J.-P. *J. Org. Chem.* **1977**, *42*, 2636–2637. (b) Overberger, C. G.; Narullo, N. P. *J. Am. Chem. Soc.* **1961**, *83*, 1378–1381. (c) Cadogan, J. I. G.; Thomson, J. B. *J. Chem. Soc., Chem. Commun.* **1969**, 770.

[31] Davis, J. H.; Goddard III, W. A. *J. Am. Chem. Soc.* **1977**, *99*, 7111–7121.

[32] Note that the spin-allowed dissociation would yield O atom in the excited singlet state (46 kcal higher). Although this might be the relevant limit to use for some processes, we will use the ground triplet state of O atom in discussing bond energies.

[33] Glidewell, S. M. *Spectrochim Acta, Part A* **1977**, *33A*, 361–368.

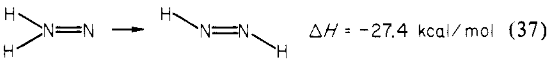
[34] (a) Crampton, M. R.; Thompson, J. T.; Williams, D. L. H. *J. Chem. Soc., Perkin Trans. 2* **1979**, 18–22. (b) Hegarty, A. F. In "The Chemistry of Diazonium and Diazo Groups"; Patai, S., Ed.; Wiley: New York, 1978; Chapter 12.

[35] (a) Grilli, S.; Prodi, G. *Gann* **1975**, *66*, 473–480. (b) Heidelberger, C. *Annu. Rev. Biochem.* **1975**, *44*, 79–121.

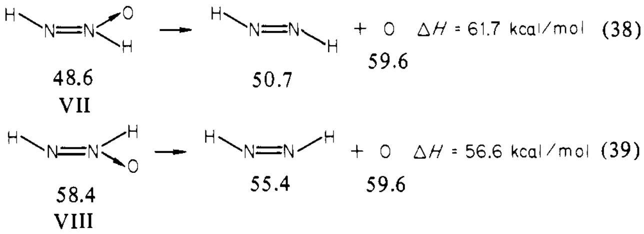
[36] Lunazzi, L.; Panciera, G.; Guerra, M. *J. Chem. Soc., Perkin Trans. 2* **1980**, 52–55.

[37] Batt, L.; Gowenlock, B. G. *Trans. Faraday Soc.* **1960**, *56*, 682–690.

[38] (a) Hinsberg III, W. D.; Dervan, P. B. *J. Am. Chem. Soc.* **1978**, *100*, 1608–1610. (b) Hinsberg III, W. D.; Dervan, P. B. *Ibid.* **1979**, *101*, 6142–6144.



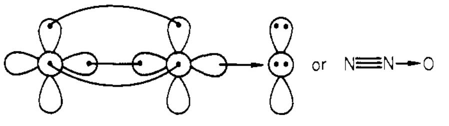
**E. Diimide *N*-Oxide (VII and VIII).** Although VII and VIII are unknown, substituted azoxy compounds[39] can be synthesized[40] by oxidation of azo compounds with per acids. In fact, it has been suggested that labile azo compounds be stored as their more stable azoxy derivatives.[41] The abstraction of the azoxy oxygen by reducing agents to give azo compounds has also been reported.[42] Thus it is of interest to determine the N–O bond energy of azoxy compounds. We find that[32]



These Lewis acid–base N—O bond energies are significantly lower than the covalent N=O bond energies for HNO (120 kcal) and $H_2NNO$ (102 kcal). It is interesting to compare the above bond energies with the NO bond energy[32] of $N_2O$ (eq 40) which also

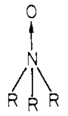
$$\underset{19.6}{N{\equiv}N{-}O} \rightarrow \underset{0}{N{\equiv}N} + \underset{59.6}{O} \quad \Delta H = 40.0\ \text{kcal/mol} \quad (40)$$

possesses a Lewis acid–base bond (structure 41). It is apparent



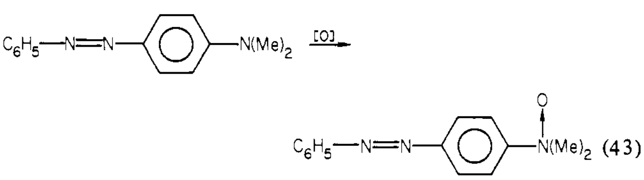
(41)

that the strength of the N–O bond is highly dependent on the character of the donor orbital. $N_2O$ has a donor orbital of high s character, leading to a weaker N–O bond than azoxy compounds which have a donor orbital with more p character. This analysis suggests that amine *N*-oxides should have relatively strong N–O bonds (>60 kcal) (structure 42).

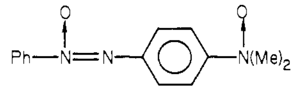


(42)

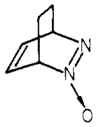
In agreement with this prediction, the monooxidation of 4-(dimethylamino)azobenzene by perbenzoic acid has been reported to give almost exclusively the amine *N*-oxide (eq 43).[40b] Further



oxidation leads to the α-azoxy amine *N*-oxide



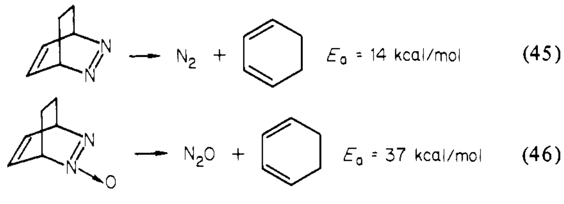
Using the thermochemical data of Oth and co-workers,[43] we find the N–O bond energy for structure 44 is 73 kcal, somewhat higher



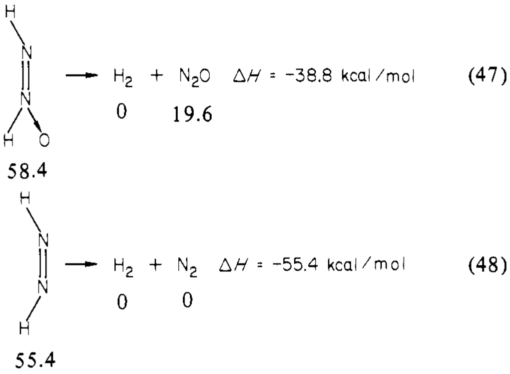
(44)

than the 56.6 kcal calculated for the parent compound. The stronger N→O bond in the bicyclic azoxy compound may reflect enhanced p character in the N lone pair. An X-ray[56b] structure of the related 2,3-diazabicyclo[2.2.2]oct-2-ene *N*-oxide has an NNO bond angle of 122°, whereas the NNO angle of the parent compound is 126°, supporting greater p character of the N lone pair in the bicyclic system.

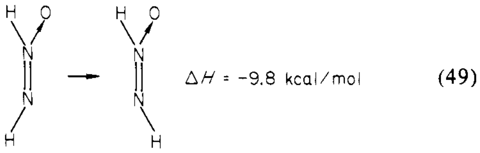
There has been much discussion[26,43,44] on the reason for the great energy difference between the concerted fragmentation of (45) and (46). The $E_a$ for azoxy decomposition is 23 kcal higher than



for the azo decomposition.[45] Using the thermochemistry in this paper, we find that the difference in reaction enthalpies for fragmentation of model systems VIII and *cis*-diimide is 16.6 kcal, on the same order as the difference in activation energies for the substituted systems (eq 47 and 48). Thus, as suggested by Oth and co-workers,[43] the large difference in $E_a$ for the concerted reactions is probably directly related to the large difference in reaction enthalpy.



The energy difference between *trans*- and *cis*-diimide *N*-oxide is a rather large 9.8 kcal (eq 49) compared with the corresponding calculated energy difference between *cis*- and *trans*-diimide of 4.7 kcal.[8] This is discussed in section IIH.



**F. The Reaction of Nitrosobenzene with Hydrazoic Acid.** The reaction of nitrosobenzene with hydrazoic acid to give phenyl azide is thought to involve the loss of nitrogen from the coupling product of hydrazoic acid with the nitroso group[46] to give the unstable hydroxy-1,1-diazene derivative that further rearranges to give the azoxy compound or the diazo hydroxy derivative (eq 50). Further reaction ultimately gives the phenyl azide.[46]

Using the thermochemistry developed in this paper, we can evaluate the reaction for the model compound HNO (eq 51). The

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[39] For review, see: Patai, S., Ed. "The Chemistry of the Hydrazo, Axo and Azoxy Groups"; Wiley: New York, 1975.

[40] (a) Badger, G. M.; Buttery, R. G.; Lewis, G. E. *J. Chem. Soc.* **1953**, 2143–2147. (b) Pentimalli, L. *Tetrahedron* **1959**, *5*, 27–37.

[41] Snyder, J. P.; Lee, L.; Bandurco, C. Y. Y.; Boyd, R. J. *J. Am. Chem. Soc.* **1972**, *94*, 3260–3261.

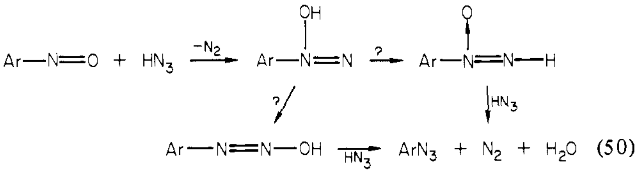
[42] For example, see: Vozza, J. *J. Org. Chem.* **1969**, *34*, 3219–3220.

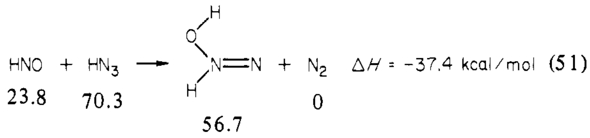
[43] Oth, J. F. M.; Olsen, H.; Snyder, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 8505–8507.

[44] Olsen, H.; Snyder, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 1524–1536.

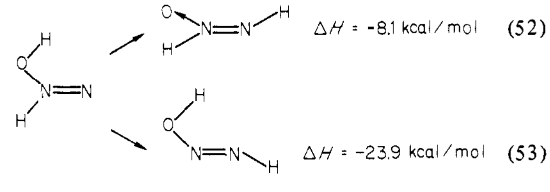
[45] Olsen, H.; Snyder, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 7839–7841.

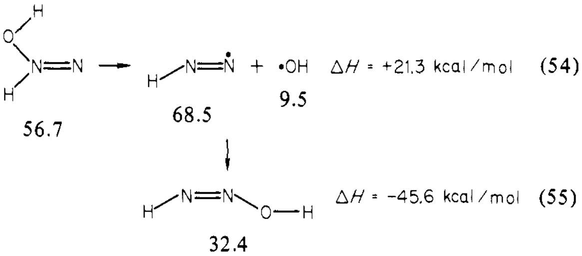
[46] Reference 15b, p 271.





first reaction is highly exothermic. Next we must investigate which rearrangement of the 1,1-diazene is most likely: a 1,3-hydrogen shift to give the *N*-oxide or a 1,2-hydroxy shift (or 1,2-hydrogen shift) to give the hydroxydiimide (eq 52 and 53). Both intermediates are thermodynamically acessible. However, the 1,2 shift (reaction 53) likely has a very large activation energy.[47] Alternatively, this rearrangement might occur by a dissociation–recombination pathway, eq 54 and 55. Because of the high exothermicity of the first reaction 51, the dissociation–recombination mechanism is likely.





Thus a concerted rearrangement of the first formed hydroxy-1,1-diazene to give an azoxy intermediate (eq 52) or a stepwise dissociation–recombination of the hydroxy-1,2-diazene (eq 54 and 55) are both possible. An ionic dissociation of the hydroxy-1,1-diazene cannot, of course, be ruled out. Clearly, more studies are needed to clarify the mechanism of this interesting reaction.

**G. The Thermal DeNO$_x$ Process.** A promising suggestion for eliminating NO in stationary combustion systems is the thermal DeNO$_x$ process[2-4] in which nitrogen-containing species such as $NH_3$, amines, hydrazine, or urea are used to reduce NO to $N_2$. Kinetic models indicate that the key to the reduction process[4] is the production of $NH_2$ via eq 56 followed by a sequence of steps

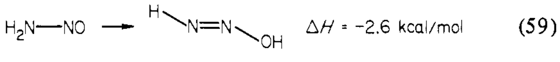
$$NH_3 + OH \rightarrow NH_2 + H_2O \quad \Delta H = -11.9 \text{ kcal/mol} \tag{56}$$

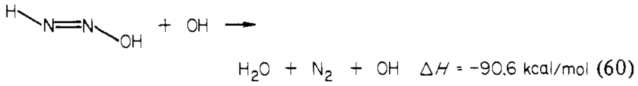
$$NH_2 + NO \rightarrow \ \rightarrow N_2 + H_2O \tag{57}$$

leading to $N_2$, eq 57. The mechanism for (57) is not known; however, some clues are available.[4] The overall reaction rate exhibits a negative temperature dependence,[48] suggesting that endothermic steps may not be important.[4] A salient feature that the mechanism for (57) must explain is the presence of a temperature window near $T = 1250$ K for reduction of NO to $N_2$. Below 1000 K very little NO is reduced and above 1500 K, the reaction leads to a net *production* of NO.[2-4]

Some steps involved in (57) might be eq 58–60. The net

$$NH_2 + NO \rightarrow H_2N{-}NO \quad \Delta H = -30.6 \text{ kcal/mol} \tag{58}$$



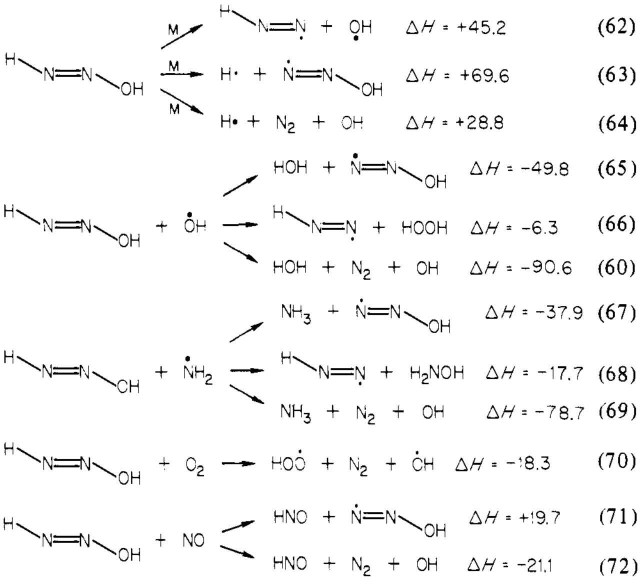


reaction for the sequence (56) → (58) → (59) → (60) is eq 61

$$NH_3 + NO + OH \rightarrow N_2 + 2H_2O \tag{61}$$

requiring both one $NH_3$ and one OH for each NO reduced. This reaction sequence may dominate at lower temperatures but could not reduce much NO. A branching step must be involved in the mechanism prevailing at operating temperatures for thermal DeNO$_x$. Possible steps include those in Scheme I ($\Delta H$ in kcal/mol).

Scheme I



Miller et al.[4] have suggested that the branching step involves (58) → (59) → (62), followed by eq 73 and 74, leading to a net

$$NNH + NO \rightarrow N_2 + HNO \quad \Delta H = -66.3 \text{ kcal/mol} \tag{73}$$

$$HNO \xrightarrow[M]{} H + NO \quad \Delta H = +49.9 \text{ kcal/mol} \tag{74}$$

$$NH_3 + NO \xrightarrow[M]{} H_2O + N_2 + H \tag{75}$$

reaction of eq 75 followed by H reacting with $H_2O$ or $O_2$ to yield two to four additional OH. However, they felt that this was consistent with the negative temperature dependence of the reaction only if eq 76 is exothermic. Unfortunately our results make this overall reaction endothermic by 12.0 kcal.

$$H_2N + NO \rightarrow H_2N{-}NO \rightarrow HN{=}NOH \rightarrow HNN + OH \tag{76}$$

An alternative sequence is (58) → (59) → (72), each step of which is exothermic, leading to an overall reaction of eq 77. This

$$NH_3 + NO + NO \rightarrow H_2O + N_2 + HNO \tag{77}$$

$$HNO + \underset{23.8}{O_2} \rightleftharpoons \underset{21.6}{NO} + \underset{5}{HO_2} \quad \Delta H = +2.8 \text{ kcal/mol} \tag{78}$$

$$\underset{5}{HO_2} + \underset{21.6}{NO} \rightarrow \underset{9.5}{HO} + \underset{7.9}{NO_2} \quad \Delta H = -9.2 \text{ kcal/mol} \tag{79}$$

could be followed by the highly endothermic process (74) as in the Miller mechanism or by eq 78 and 79. The sequence (58) → (59) → (72) → (78) → (79) leads to an overall reaction of eq 80 which would possibly lead to the branching responsible for

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[47] Extensive, large basis set ab initio calculations indicate that the 1,2-hydrogen shift for the parent 1,1-diazene has an activation energy of ~60 kcal. Parsons, C. A.; Dykstra, C. E. *J. Chem. Phys.* **1979**, *71*, 3025–3033. Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem.* **1978**, *14*, 545–560.

[48] Hack, W.; Schacke, H.; Schröter, M.; Wagner, H. G., see: ref 3, p 505.

[49] Gehring, M.; Hoyermann, K.; Schacke, H. J.; Wolfram, J. "14th Symposium (International) on Combustion"; Combustion Institute: Pittsburgh, Pa., 1972; p 99.

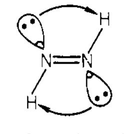
the NO reduction in the temperature window for thermal DeNO$_x$.

$$NH_3 + NO + NO + O_2 \rightarrow H_2O + N_2 + HO + NO_2 \quad (80)$$

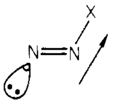
At higher temperature, reaction of OH (or NH$_2$) with HNO, NH$_2$, or HO$_2$ can lead to termination of NO reduction and (as suggested by Miller et al.[4]) a net production of NO (via NH).

**H. Preferred Geometry of Diimides.** Electronegative substituents on diimide appear to lower the energy of the cis isomer. For example, diimide processes a trans structure,[50] with a calculated trans–cis energy difference of 4.7 kcal,[8] whereas difluorodiimide has been shown experimentally[51] to favor the cis structure by 3 kcal. In addition, we have calculated that *cis*-hydroxydiimide is ~1 kcal lower than the trans isomer. The trend of stabilization of the cis isomer by electronegative substituents has also been noted by Howell and Kirschenbaum in their HF (STO-3G) calculations of substituted diimides.[52]

In order to understand these effects, we must first examine diimide. The higher energy of the cis isomer cannot be explained by invoking steric congestion.[53] Instead, we suggest that delocalization of the lone pair onto the adjacent N–X bond (structure 81) is favored by the trans geometry. (This delocalization is apparent in the GVB wave functions.) Such lone pair delocalization is not possible in the cis isomer. In terms of this model, the effect of electronegative substituents is twofold. First, the lone-pair delocalization in the trans isomer should decrease because the s character of the lone pair increases. Secondly, the cis isomer is favored because of polarization of the adjacent trans lone pair by the electronegative substituent (structure 82). We believe that this latter effect is responsible for the trans isomer of diimide *N*-oxide being stabilized an additional 5.1 kcal relative to diimide.



(81)



(82)

In summary, we suggest that adjacent cis lone pairs stabilize the trans geometry by a bonding interaction, and that adjacent trans lone pairs stabilize the cis geometry by charge polarization. For diimides with electronegative substituents, we suggest that stabilization by charge polarization dominates. These suggestions, although consistent with current theoretical calculations (and experiments) cannot be considered as proved by these calculations. (We cannot unambiguously decompose ab initio energy contributions in such terms.) We hope, however, that they will serve to stimulate additional theoretical and experimental studies to provide a firmer basis for predicting cis–trans relative stabilities.

## III. Calculational Details

**A. Geometry.** The geometries of the isomers of N$_2$H$_2$O were optimized at the RHF level using the Gaussian 80[54] program with a 4-31G basis set. Structural data are presented in Figure 1. The NN, NO distances and NNO angle of the nitrosamide are in reasonable agreement with the experimental structure of *N*-nitrosodimethylamine[55] (e.g., NN = 1.329 Å, NO = 1.233 Å, NNO = 114.0°). The NN, NO distances and the NNO angle of *trans*-diimide *N*-oxide are in good agreement with the X-ray structure of ethyl *p*-azoxybenzoate[56a] (e.g., NN = 1.22 Å, NO = 1.28 Å, NNO = 134.7°). The NN, NO distances and the NNO angle of *cis*-diimide *N*-oxide are comparable to the X-ray structure of 2,3-diazabicyclo[2.2.2]oct-2-ene *N*-oxide (e.g., NN = 1.27 Å, NO = 1.27 Å, NNO = 122.2°).[56b] The OH, NO distances and HON angles of I and II are close to the gas-phase structures of the related *trans*- and *cis*-nitrous acids,[57] respectively (e.g., trans, OH = 0.958 Å, NO = 1.432 Å, NOH = 102.1°; cis, OH = 0.982 Å, NO = 1.392 Å, NOH = 104.0°).

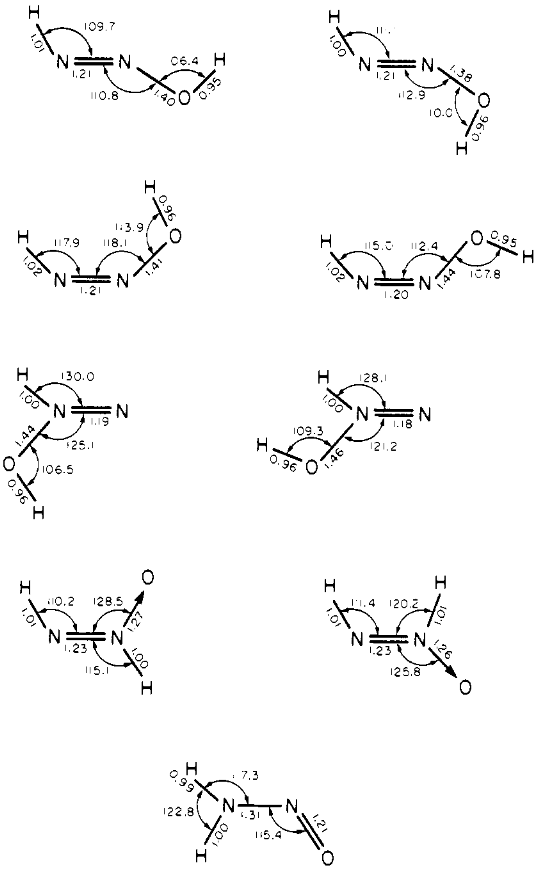


Figure 1. Optimized geometries for N$_2$H$_2$O isomers. Angles in degrees and distances in ångstroms.

**B. Basis Set.** For all thermochemical calculations, the Dunning valence double-ζ Gaussian basis set was used.[58] This basis was augmented by a set of d polarization functions on each nitrogen ($\alpha$ = 0.8) and on the oxygen ($\alpha$ = 0.85).

**C. GVB-CI Calculations.** In order to determine the energy differences among the isomers of N$_2$H$_2$O, we carried out GVB calculations[59] correlating all valence electron pairs (two natural orbitals for each of the nine valence pairs). Within the set of GVB orbitals we allowed all quadruple excitations with the restriction that the two orbitals of each pair have two electrons total [GVB-RCI(4)]; in addition, we allowed all single excitations from the nine configurations resulting from RCI singles plus the dominant configuration. Isodesmic heats of formation[8,60] of the isomers were obtained by comparing their total energies with the total energies of water and molecular nitrogen calculated at the same level. Total energies are presented in Table III.

**D. Heat of Formation at 298 K.** To obtain enthalpies at 0 K, we must add the zero-point energy to the calculated energies. The zero-point energies for the N$_2$H$_2$O isomers were obtained by

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(60) Hehre, W. J. *Acc. Chem. Res.* **1976**, *9*, 399–406.

estimating the nine fundamental vibrational frequencies using model compounds.[61] The zero-point corrections in kcal/mol are as follows: I (20.2), II (20.2), III (20.0), IV (20.2), V (19.5), VI (19.5), VII (21.4), VIII (21.1), and IX (18.9). These vibrational frequencies and the rotational constants were used to estimate the $C_p(T)$ in order to convert $\Delta H(0\ \mathrm{K})$ to $\Delta H(298\ \mathrm{K})$. The enthalpy corrections[62] in kcal/mol were as follows: I (2.7), II (2.6), III (2.6), IV (2.6), V (2.7), VI (2.7), VII (2.5), VIII (2.5), and IX (3.0).

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**Registry No.** I, 81407-93-4; III, 81390-26-3; V, 67615-78-5; VII, 63831-72-1; VIII, 63831-71-0.

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(61) For example, for I we estimate the following fundamental frequencies of vibration: NH stretch = 3120, NNH bend = 1434, NO stretch = 791, NN stretch = 1529, OH stretch = 3588, NNO bend = 593, NOH bend = 1265, and torsional = 1286 and 540 cm$^{-1}$.

(62) Calculated by using the program THERMO written by A. K. Rappé.

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# Hydrocarbon Oxidation by High-Valent Group 6 Oxides

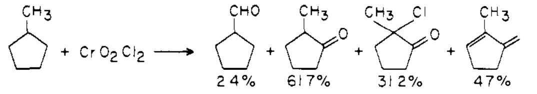
**Anthony K. Rappé† and William A. Goddard, III***

*Contribution No. 6511 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125.* *Received August 20, 1981*

**Abstract:** The results of a mechanistic study using ab initio theoretical methods are used to outline plausible mechanistic sequences for alkane, alcohol, and alkene oxidation by chromyl and molybdyl chlorides. We suggest that the second oxo group is intimately involved in the reaction sequence. This spectator oxo group is suggested to play a central role in stabilizing critical intermediates in these reactions and may be important in other oxidation reactions of metal oxides ($MnO_4^{2-}$, $OsO_4$, $RuO_4$, and supported transition metal oxides).

## I. Introduction

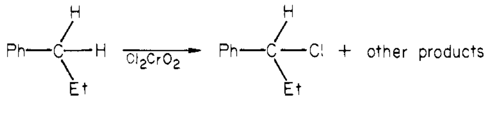
Chromic acid and related chromyl and molybdyl compounds form a class of versatile oxidizing agents[1] capable of delivering oxygen atoms to most types of oxidizable organic groups. This versatility can be a drawback since specificity in reaction site is at times a desirable quality. An example of this is the product distribution for the oxidation of methylcyclopentane by chromyl chloride[2]



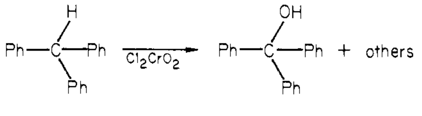
(1)

Clearly this product mixture is neither synthetically useful nor mechanistically straightforward. Scheme I illustrates likely primary, secondary, and even higher-order reaction products of chromyl compounds reacting with a general alkane.

The likely primary processes a and b form alcohols (and alkyl chlorides if the oxidant is chromyl chloride). For example, propylbenzene reacts with chromyl chloride to form substantial 1-chloro-1-phenylpropane (eq 2),[1b,3]



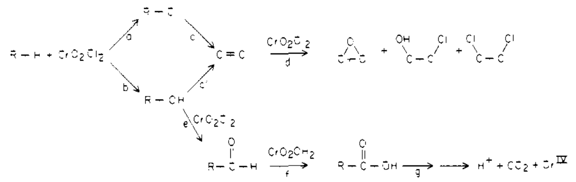
(2)



(3)

whereas triphenylmethane forms predominantly triphenyl carbinol[4] upon hydrolysis (eq 3). It is likely that alcohols and alkyl chlorides will be dehydrated under the reaction conditions[1c] as implied in path c of Scheme I. The olefins generated in situ can be subsequently oxidized as shown in path d of Scheme I. Alternatively, the alcohols may be oxidized to aldehydes and ketones as shown in path e of Scheme I. Finally, aldehydes can be oxidized by chromic acid to carboxylic acids as shown in path f of Scheme I and eventually to $CO_2$ and $H_2O$ as shown in path g of Scheme I.

Scheme I



Out studies will concentrate on the energetics of chromyl chloride and molybdyl chloride oxidation of alkanes, alcohols, and alkenes. Section II provides a discussion of a significant mechanistic feature found to be common to each of the oxidation steps. Section III presents the results for alkane oxidation, Section IV, alcohol oxidation, and finally, Section V, the alkene oxidation. Some details of the theoretical calculations are presented in Section VI.

## II. The Metal-Oxo Bond

The primary reaction step common to all of the reactions of chromyl chloride discussed in the sections that follow is the addition of either a $\sigma$ or $\pi$ bond across a Cr-O $\pi$ bond. We find that these processes depend critically upon whether there is an

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