



Alkyl Chemistry

Rose Ravelo

GRES Fellow

Purdue University



Outline

- Methyl Nitrite and Methyl Nitrate
 - Methyl Peroxynitrate
- PAN and its Homologues



Methyl Nitrite & Methyl Nitrate

Background

Methyl Nitrite (CH_3ONO):

- Known as alkyl nitrites (RONO)
- $\text{RO} + \text{NO} + \text{M} \rightarrow \text{RONO} + \text{M}$
- Rapid photolysis in the troposphere.

Methyl Nitrate (CH_3ONO_2):

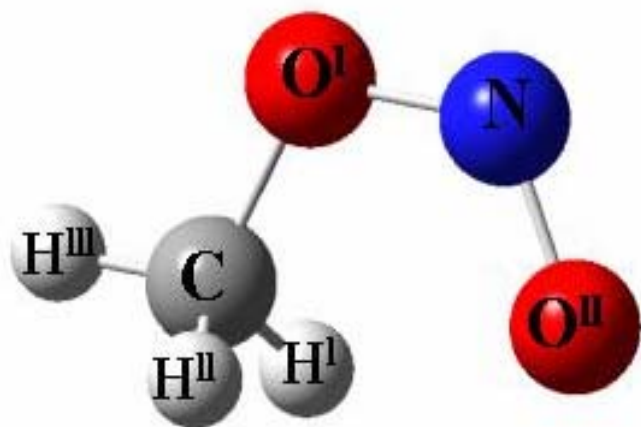
- Known as alkyl nitrates (RONO_2)
- $\text{RO} + \text{NO}_2 + \text{M} \rightarrow \text{RONO}_2 + \text{M}$
- $\text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2$
 $\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$
 $\text{O} + \text{O}_2 \rightarrow \text{O}_3$
- $\text{RO}_2 + \text{NO} \rightarrow \text{RONO}_2$



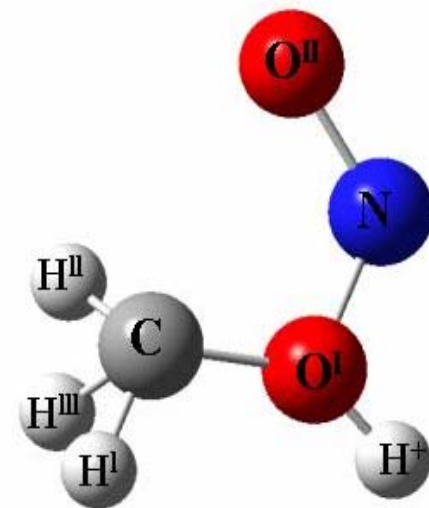
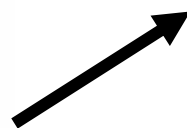
Approach

- *Ab Initio* Calculations using GAUSSIAN 03 software.
- Geometry Optimizations and Frequency Calculations
 - * Levels of Theory: B3LYP, QCISD, QCISD(T)
 - * Basis Set: 6-31G(d)

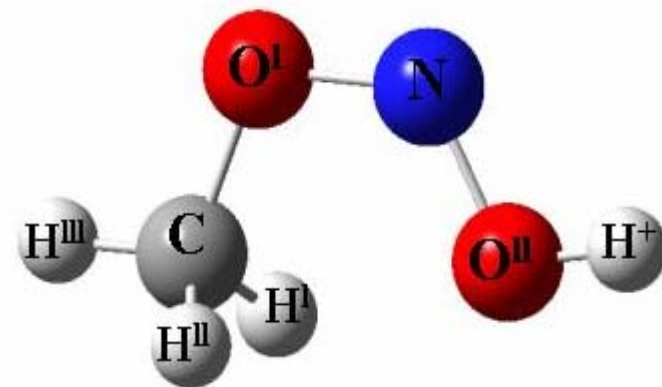
Results: Methyl Nitrite



CH₃ONO (tc)



CH₃OHNO (tct)



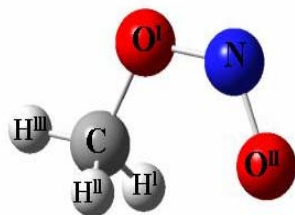
CH₃ONOH (tct)



Proton Affinities for the protonated structures of CH₃ONO (kcal/mol)

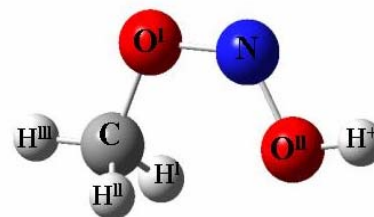
Species	B3LYP	QCISD	QCISD(T)
CH ₃ ONO	0.0	0.0	0.0
CH ₃ OHNO	190.8	193.1	191.8
CH ₃ ONOH	175.8	174.3	173.5

Stability of protonated CH_3ONO



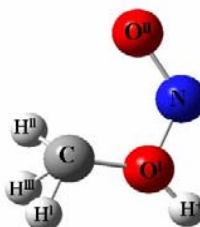
CH_3ONO (tc)

0.0 kcal/mol



CH_3ONOH (tct)

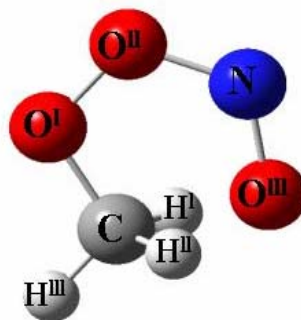
173.5 kcal/mol



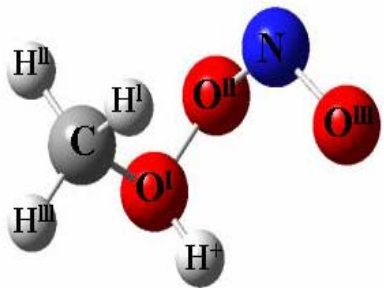
CH_3OHNO (tct)

191.8 kcal/mol

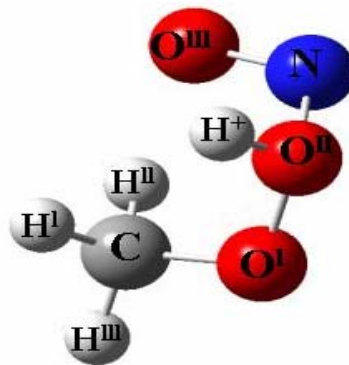
Results: Methyl Peroxynitrite



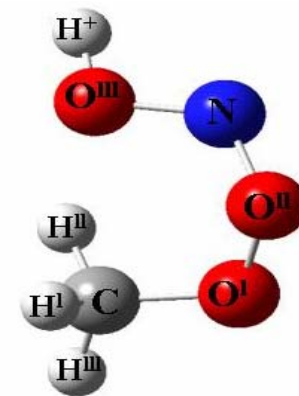
CH₃OONO (tcc)



CH₃OHONO (c)



CH₃OOHNO (c)



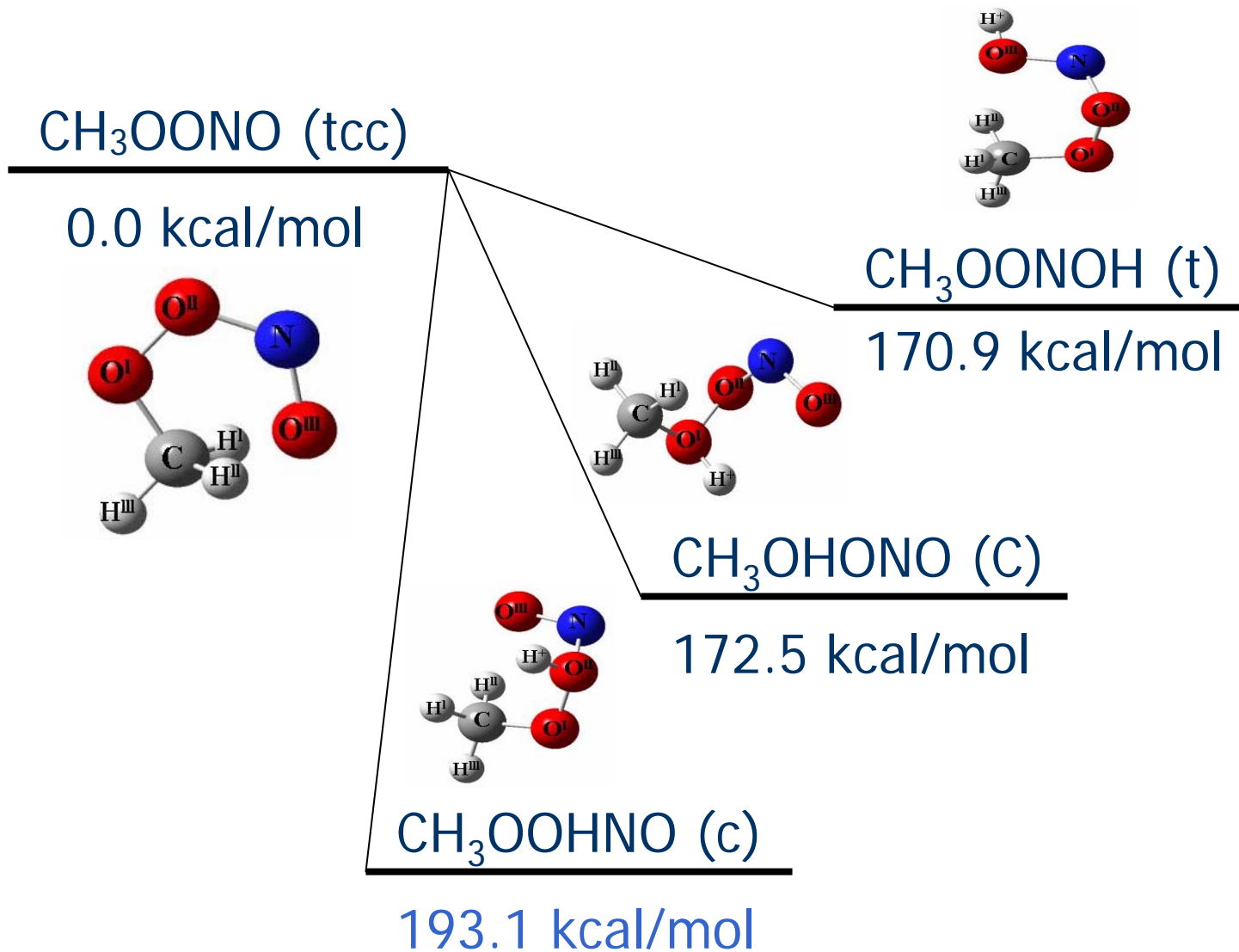
CH₃OONOH (t)



Proton Affinities for the protonated structures of CH₃OONO (kcal/mol)

Species	B3LYP	QCISD	QCISD(T)
CH ₃ OONO	0.0	0.0	0.0
CH ₃ OHONO	172.2	171.7	172.5
CH ₃ OOHNO	192.1	195.8	193.1
CH ₃ OONOH	174.9	171.7	170.9

Stability of protonated CH_3OONO





Conclusions

Our Results:



Literature Results:



J.S. Francisco, J. Chem. Phys. 115, 211 (2001)



T.J. Lee and J.E. Rice, J. Am. Chem. Soc. 114, 8247 (1992)



Methyl Peroxynitrate



Background

- Alkyl Peroxynitrates are formed from the reaction of RO_2 with NO_2 :



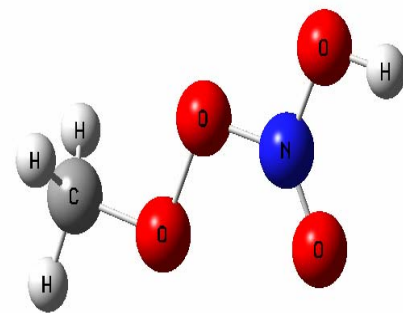
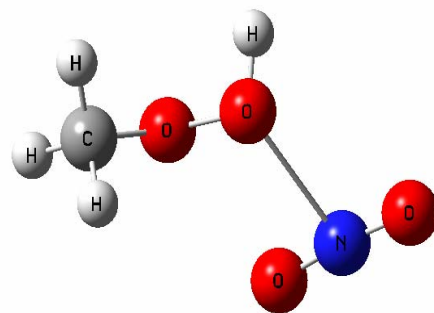
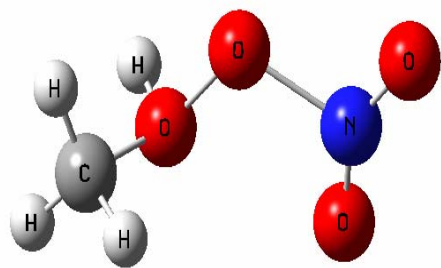
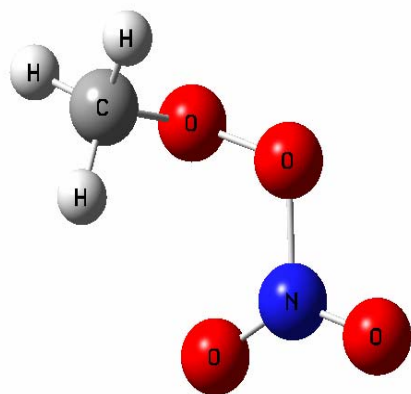
- They can go on to form alkyl nitrates (RONO_2) and alkyl nitrites (RONO).
- Methyl Peroxynitrate (CH_3OONO_2) plays a role in the NO_x budget and in urban smog formation.



Approach

- *Ab Initio* Calculations using GAUSSIAN 03 software.
- Geometry optimizations and Frequency Calculations
 - * Levels of Theory: B3LYP, QCISD, QCISD(T)
 - * Basis Set: 6-31G(d), 6-311++G(2d,2p),
6-311++G(2df,2p), 6-311++G(3df,3pd)
- Composite Methods: G2(MP2), CBS-Q, CBS-APNO

Results: Methyl Peroxynitrate

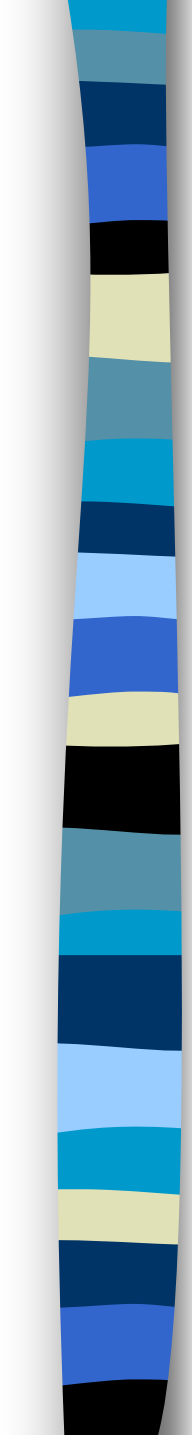


Proton Affinities for the protonated structures of CH_3OONO_2 (kcal/mol)

Species	B3LYP	QCISD	QCISD(T)
CH_3OONO_2	0.0	0.0	0.0
$\text{CH}_3\text{OHONO}_2$	163.7	160.9	162.9
$\text{CH}_3\text{OOHNO}_2$	173.7	173.5	174.0
$\text{CH}_3\text{OONO}_2\text{H}$	163.9	163.7	162.2

Proton Affinities for the protonated structure of CH_3OONO_2 (kcal/mol)

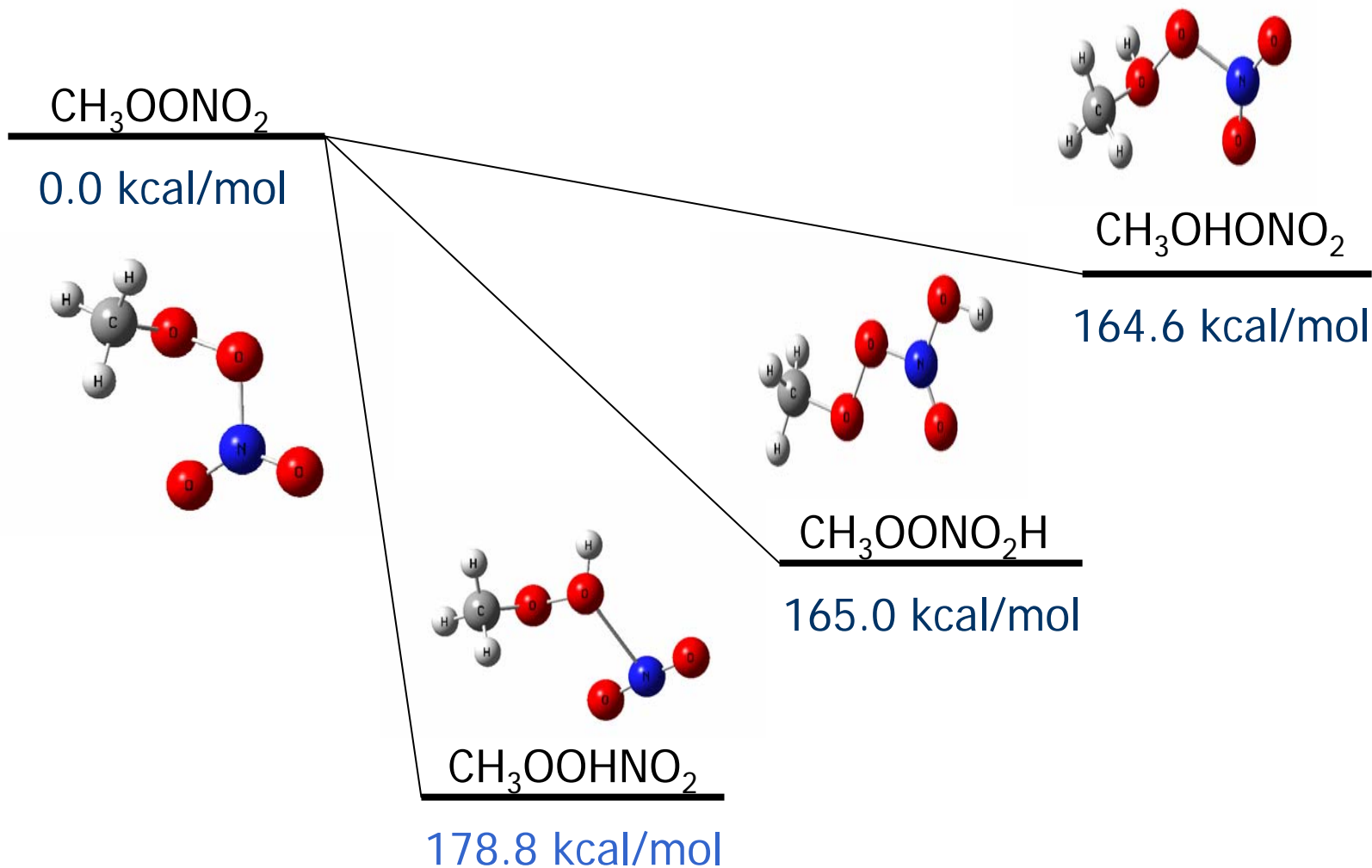
QCISD(T)	CH_3OONO_2	$\text{CH}_3\text{OOHNO}_2$	$\text{CH}_3\text{OHONO}_2$	$\text{CH}_3\text{OONO}_2\text{H}$
6-31G(d)	0.0	174.0	162.9	162.2
6-311++G (2d,2p)	0.0	178.8	165.0	164.8
6-311++G (2df,2p)	0.0	177.9	163.9	164.3
6-311++G (3df,3pd)	0.0	178.8	164.6	165.0



Proton Affinities for the lowest energy structure of CH_3OONO_2 (kcal/mol)

Composite Methods	$\text{CH}_3\text{OOHNO}_2$
G2(MP2)	177.2
CBS-Q	175.6
CBS-APNO	176.8

Stability of protonated CH_3OONO_2



Comparison of Proton Affinities for the $XOONO_2$ species

Method	Basis Set	CH_3OONO_2 (kcal/mol)	$HOONO_2^A$ (kcal/mol)
QCISD(T)	6-31G(d)	174.0	170.0
	6-311++G(2d,2p)	178.8	175.4
	6-311++G(2df,2pd)	177.9	174.2
	6-311++G(3df,3pd)	178.8	175.1

A. R.L. Santiano and J.S. Francisco, *J.Chem. Phys.*, **2004**, *121*(19), 9498-9509.

Comparison of Proton Affinities

Species	PA (kcal/mol)	Species	PA (kcal/mol)
CH ₃ ONO	191.8	HONO ^A	191.5
CH ₃ OONO	193.1	HOONO ^B	182.1
CH ₃ ONO ₂ ^C	176.9 ± 5	HONO ₂ ^C	182.5
CH ₃ OONO ₂	178.8	HOONO ₂ ^B	175.1

A. J.S. Francisco, *J. Chem. Phys.* 115, 211 (2001).

B. R.L. Santiano and J.S. Francisco, *J. Chem. Phys.*, **2004**, 121(19), 9498-9509.

C. T.J. Lee and J.E. Rice, *J. Am. Chem. Soc.*, **1992**, 114, 8247.



Conclusions

- We find a general trend for the proton affinities of the $XONO_2$ and $XOONO_2$ species.
- We find a methyl effect for these species as well.



PAN and its Homologues



Background

- Peroxyacetyl Nitrate or PAN ($\text{CH}_3\text{C}=\text{OO}_2\text{NO}_2$) is the most abundant and simplest member of the peroxyacyl nitrates.
- PAN is produced from the photochemical reactions of hydrocarbons and nitrogen oxides in the atmosphere:



Background

- GC-ECD, luminol chemiluminescence detector and FTIR are among some of the ways in which PAN has been measured.
- PANs that have been observed are typically at concentrations much less than PAN and include: PPN, MPAN, APAN, and PFN.
- PPN: $\text{CH}_3\text{CH}_2\text{C}=\text{OO}_2\text{NO}_2$
MPAN: $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}=\text{OO}_2\text{NO}_2$
APAN: $\text{CH}_2=\text{C}(\text{H})\text{C}=\text{OO}_2\text{NO}_2$
PFN: $\text{HC}=\text{OO}_2\text{NO}_2$



Approach

- *Ab Initio* Calculations using GAUSSIAN 03 software.
- Geometry Optimizations and Frequency Calculations
 - * Composite Methods: G2(MP2) & CBS-Q
 - * Basis Set: 6-311+G(3df,2p)

Results

Unprotonated

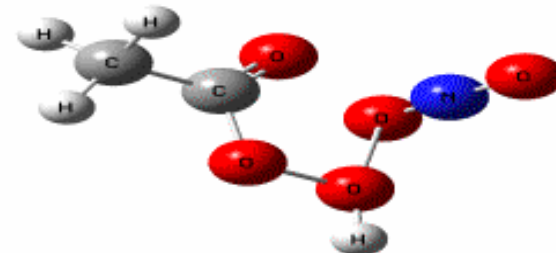
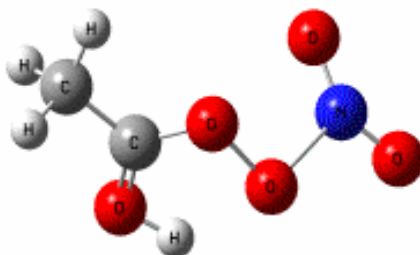
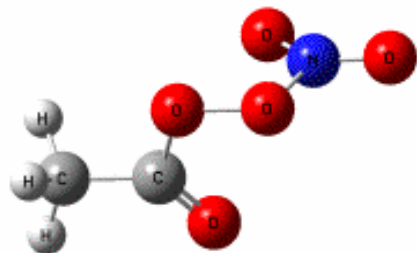
Protonated Structures

Structure

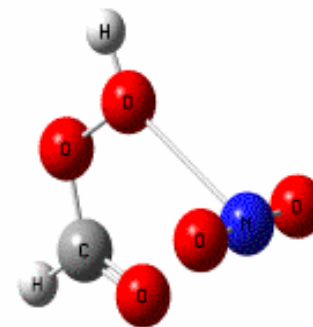
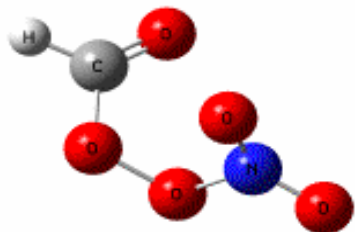
Structure 1

Structure 2

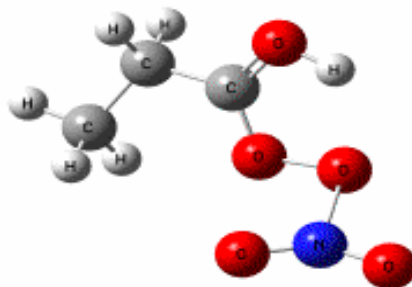
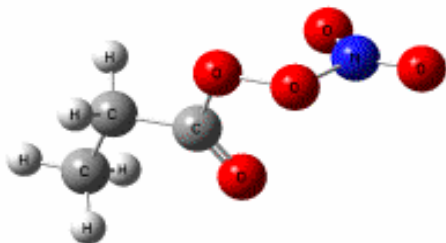
PAN



PFN



PPN



Results

Unprotonated

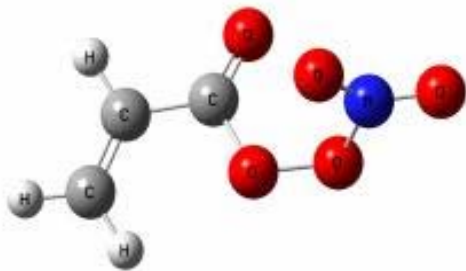
Structure

Protonated Structures

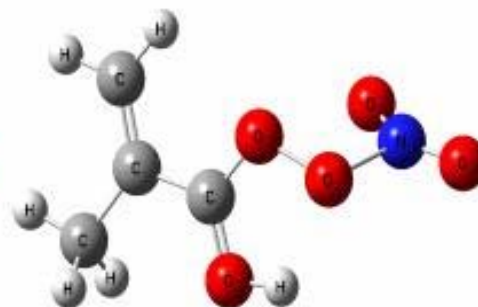
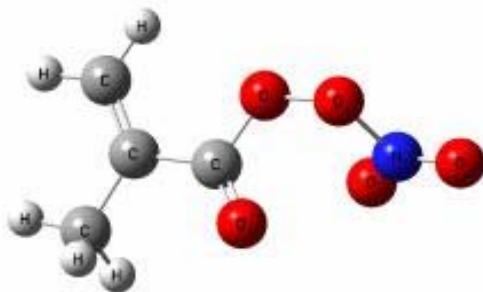
Structure 1

Structure 2

APAN



MPAN



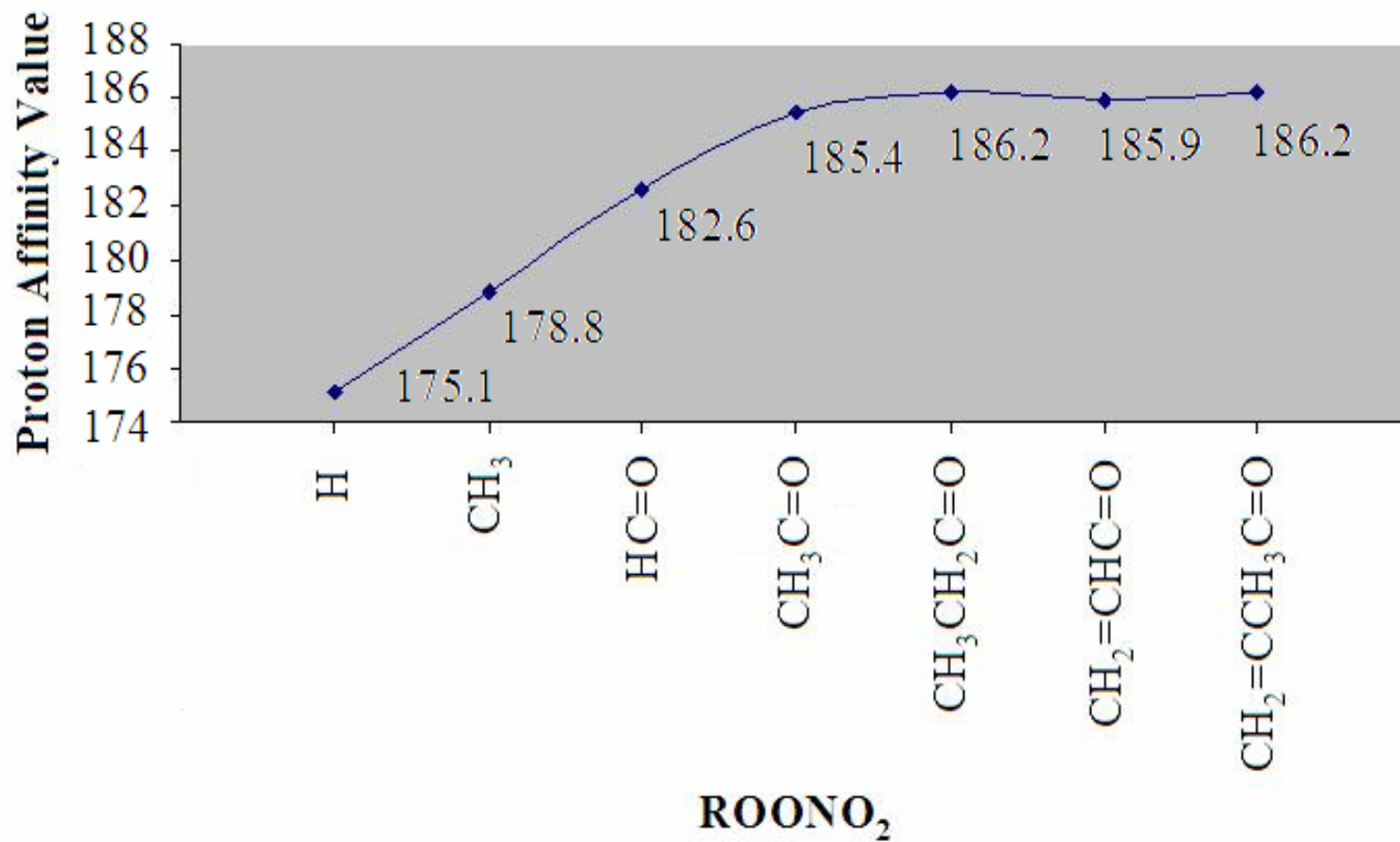
Proton Affinities of PAN, PPN, MPAN, APAN, PFN & their protonated structures (kcal/mol)

Species	G2(MP2)	CBS-Q
PAN	0.0	0.0
Structure 1	180.1	179.4
Structure 2	185.4	184.9
PPN	0.0	0.0
Structure 1	181.7	182.1
Structure 2	185.8	186.2
MPAN	0.0	0.0
Structure 1	185.2	185.4
Structure 2	186.2	186.1
APAN	0.0	0.0
Structure 1	183.4	183.2
Structure 2	185.9	185.4
PFN	0.0	0.0
Structure 1	170.9	170.3
Structure 2	182.6	181.9

Structure 1: Structure protonated on the oxygen of the carbonyl group

Structure 2: Structure protonated on the tertiary oxygen

Proton Affinity versus R Group Functionality





Conclusions

- We find the lowest energy structure throughout the PANs to be protonated at the tertiary oxygen, which results in a complex between $\text{RC}=\text{OOOH}$ and NO_2^+ .
- We find a trend in the proton affinities with respect to the R- group.



Acknowledgements

- Dr. Joseph S. Francisco
 - Dr. Jeff Gaffney
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- Milt Constantin & Alicia Wells
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