Alkyl Chemistry

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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)
- $RO + NO + M \rightarrow RONO + M$
- Rapid photolysis in the troposphere.

Methyl Nitrate (CH_3ONO_2):

- Known as alkyl nitrates ($RONO_2$)
- $RO + NO_2 + M \rightarrow RONO_2 + M$
- $RO_2 + NO \rightarrow RO + NO_2$
  $NO_2 + hv \rightarrow NO + O$
  $O + O_2 \rightarrow O_3$
- $RO_2 + NO \rightarrow RONO_2$

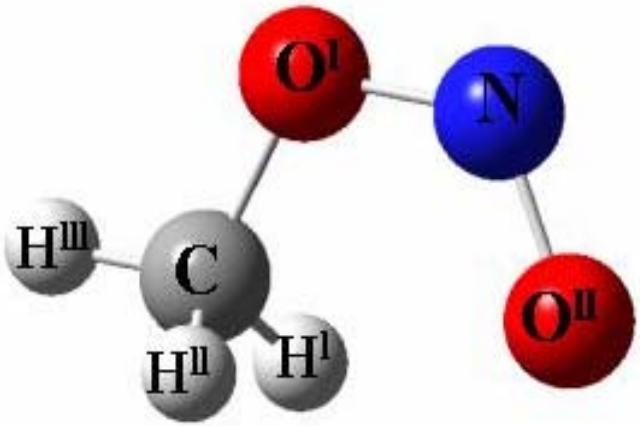
Approach

- *Ab Initio* Calculations using GAUSSIAN 03 software.
- Geometry Optimizations and Frequency Calculations

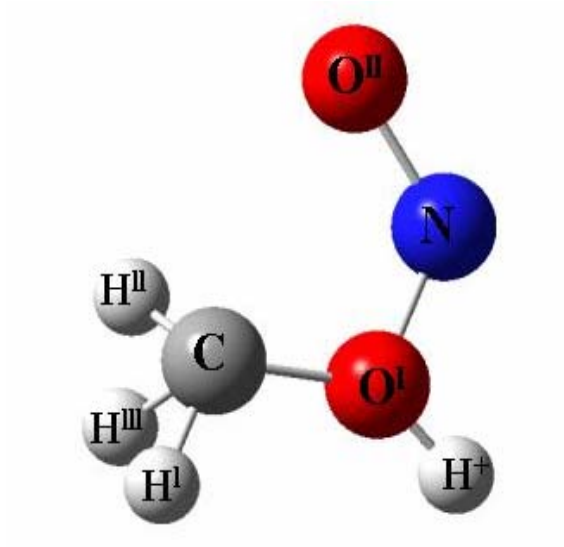
  * Levels of Theory: B3LYP, QCISD, QCISD(T)

  * Basis Set: 6-31G(d)

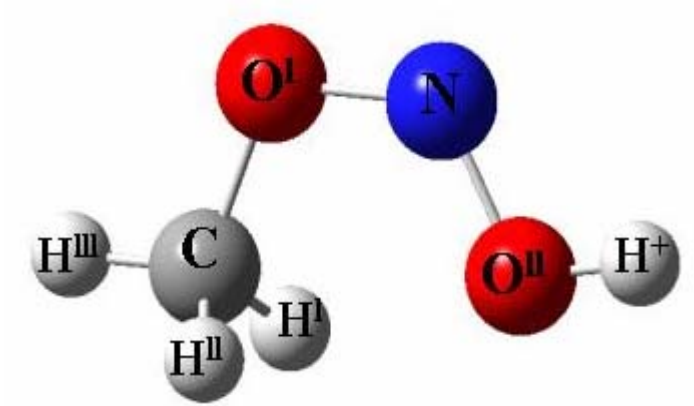
Results: Methyl Nitrite



CH_3ONO (tc)



CH_3OHNO (tct)

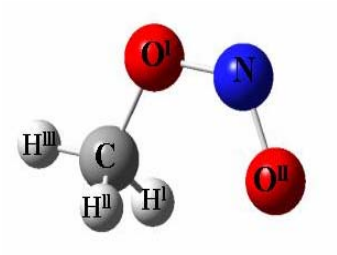


CH_3ONOH (tct)

Proton Affinities for the protonated structures of CH_3ONO (kcal/mol)

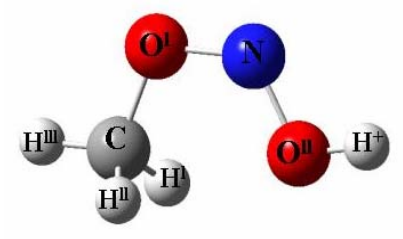
Species	B3LYP	QCISD	QCISD(T)
CH_3ONO	0.0	0.0	0.0
CH_3OHNO	190.8	193.1	191.8
CH_3ONOH	175.8	174.3	173.5

Stability of protonated CH_3ONO



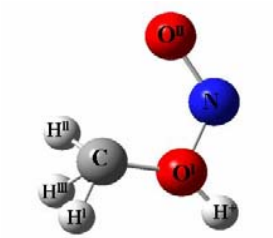
CH_3ONO (tc)

0.0 kcal/mol



CH_3ONOH (tct)

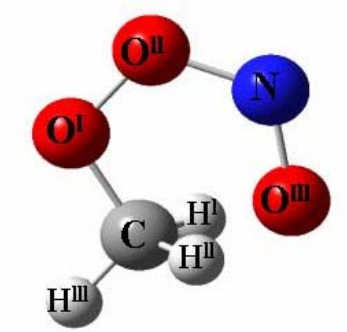
173.5 kcal/mol



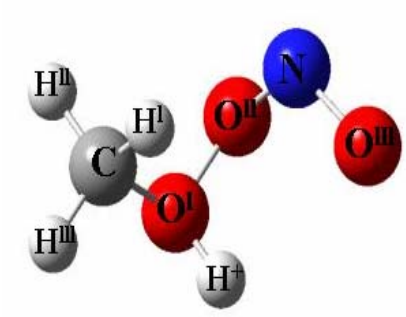
CH_3OHNO (tct)

191.8 kcal/mol

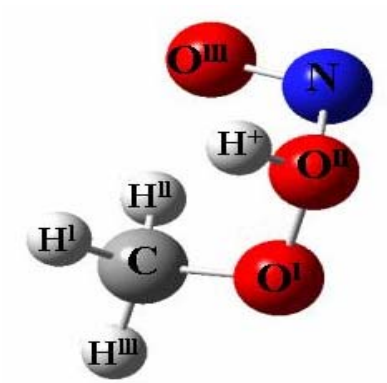
Results: Methyl Peroxynitrite



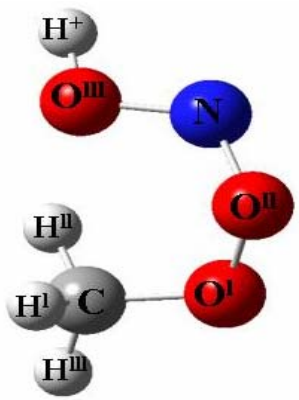
CH_3OONO (tcc)



CH_3OHONO (c)



CH_3OOHNO (c)



CH_3OONOH (t)

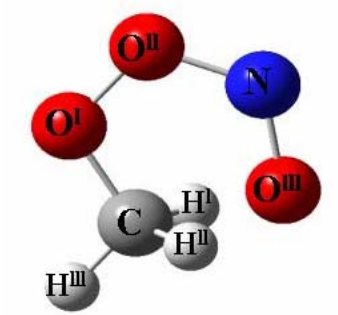
Proton Affinities for the protonated structures of CH_3OONO (kcal/mol)

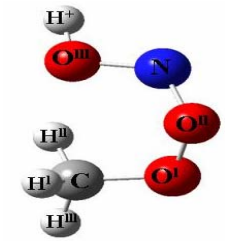
Species	B3LYP	QCISD	QCISD(T)
CH_3OONO	0.0	0.0	0.0
CH_3OHONO	172.2	171.7	172.5
CH_3OOHNO	192.1	195.8	193.1
CH_3OONOH	174.9	171.7	170.9

Stability of protonated CH_3OONO

CH_3OONO (tcc)

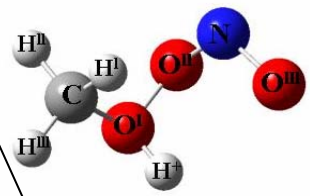
0.0 kcal/mol





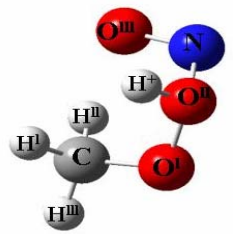
CH_3OONOH (t)

170.9 kcal/mol



CH_3OHONO (C)

172.5 kcal/mol



CH_3OOHNO (c)

193.1 kcal/mol

Conclusions

Our Results:

$CH_3ONO + H^+ \rightarrow CH_3OH \bullet NO^+$ 191.8 kcal/mol

$CH_3OONO + H^+ \rightarrow CH_3OOH \bullet NO^+$ 193.1 kcal/mol

Literature Results:

$HONO + H^+ \rightarrow H_2O \bullet NO^+$ 191.5 kcal/mol

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

$CH_3ONO_2 + H^+ \rightarrow CH_3OH \bullet NO_2^+$ 176.9 kcal/mol

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:

$$RO_2 + NO_2 + M \rightarrow ROONO_2 + M$$

- 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

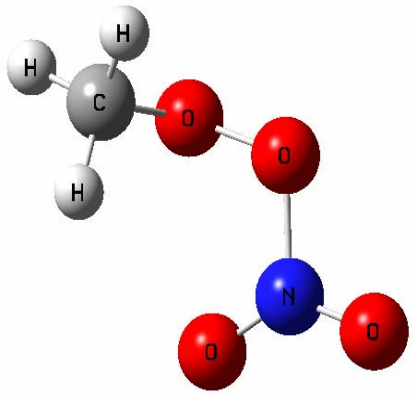
- *Ab Initio* Calculations using GAUSSIAN 03 software.
- Geometry optimizations and Frequency Calculations

  * Levels of Theory: B3LYP, QCISD, QCISD(T)

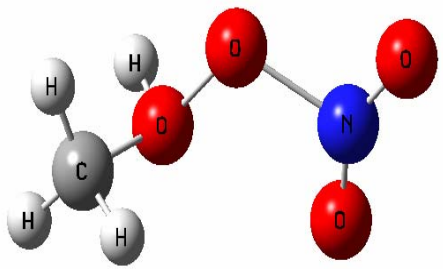
  * Basis Set: 6-31G(d), 6-311++G(2d,2p), 6-311++G(2df,2p), 6-311++G(3df,3pd)

- Composite Methods: G2(MP2), CBS-Q, CBS-APNO

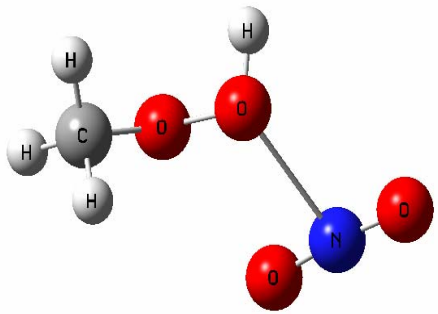
Results: Methyl Peroxynitrate



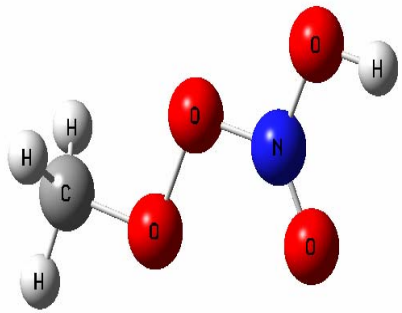
CH_3OONO_2



CH_3OHONO_2



CH_3OOHNO_2



CH_3OONO_2H

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
CH_3OHONO_2	163.7	160.9	162.9
CH_3OOHNO_2	173.7	173.5	174.0
CH_3OONO_2H	163.9	163.7	162.2

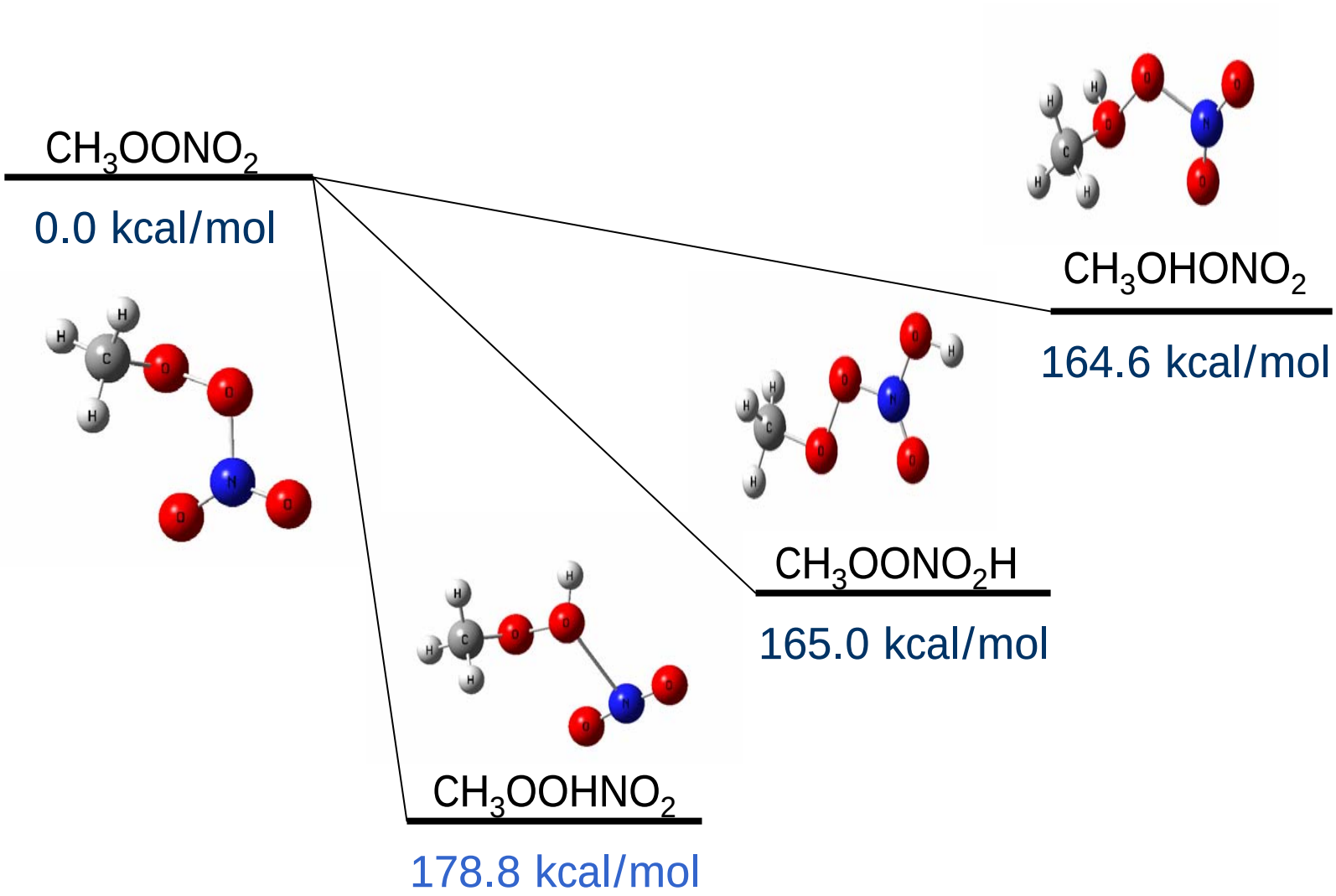
Proton Affinities for the protonated structure of CH_3OONO_2 (kcal/mol)

QCISD(T)	CH_3OONO_2	CH_3OOHNO_2	CH_3OHONO_2	CH_3OONO_2H
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	CH_3OOHNO_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_3ONO	191.8	HONO[A]	191.5
CH_3OONO	193.1	HOONO[B]	182.1
CH_3ONO_2[C]	176.9 ± 5	$HONO_2$[C]	182.5
CH_3OONO_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 ($CH_3C{=}OO_2NO_2$) 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:

$$CH_3CO_3 + NO_2 + M \leftrightarrow CH_3CO_3NO_2 + M$$

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: $CH_3CH_2C(=O)OONO_2$
  MPAN: $CH_2=C(CH_3)C(=O)OONO_2$
  APAN: $CH_2=C(H)C(=O)OONO_2$
  PFN: $HC(=O)OONO_2$

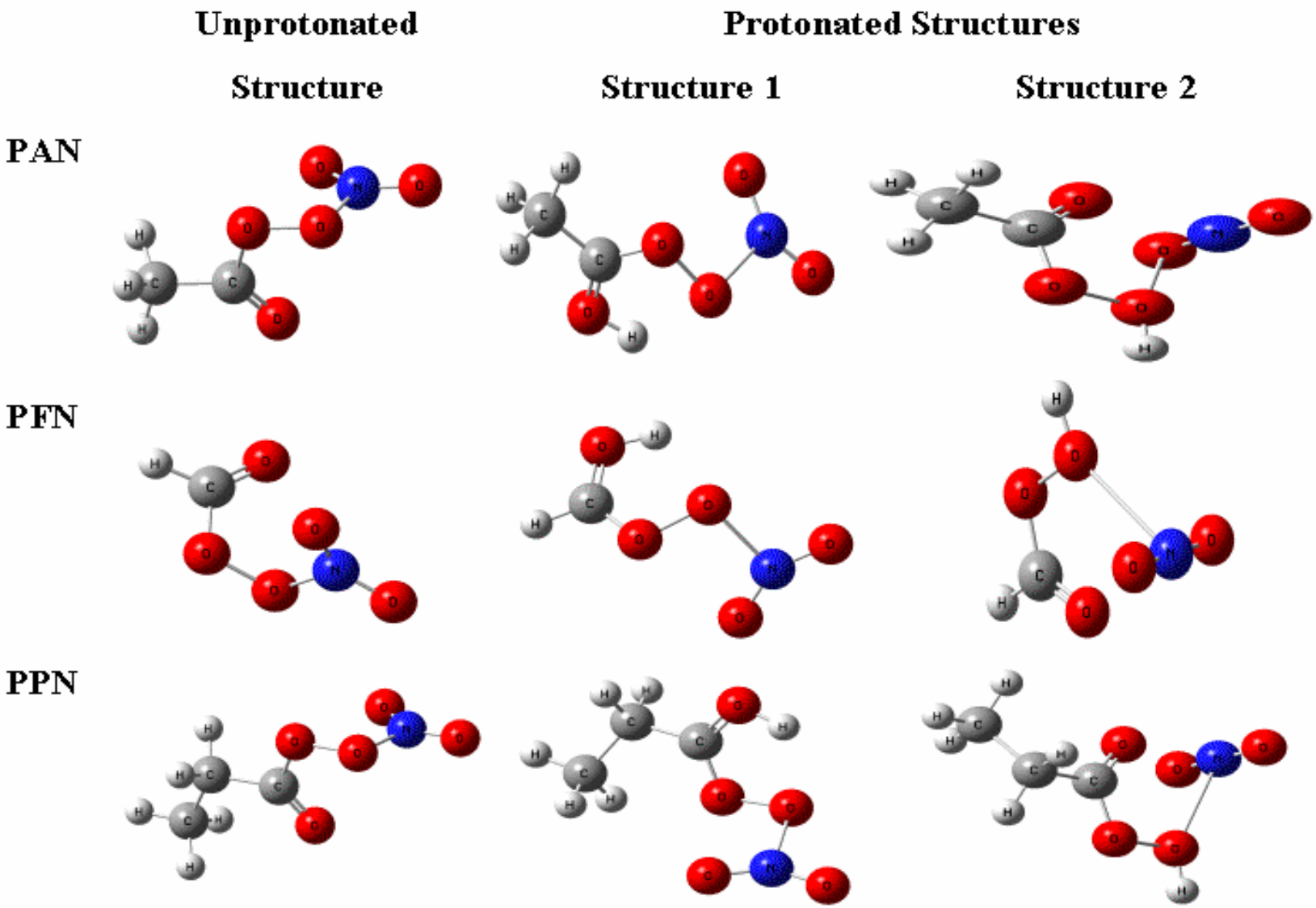
Approach

- *Ab Initio* Calculations using GAUSSIAN 03 software.
- Geometry Optimizations and Frequency Calculations

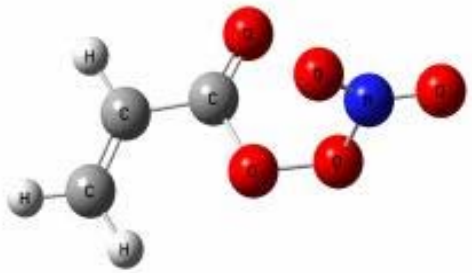
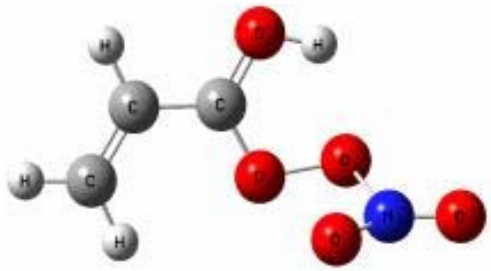
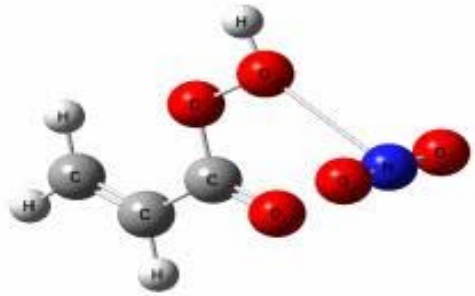
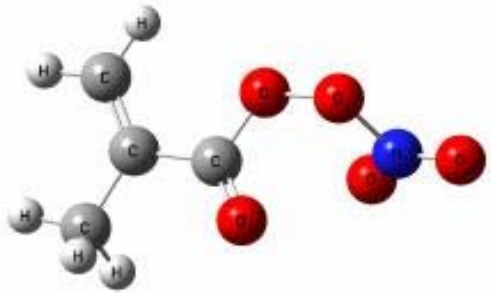
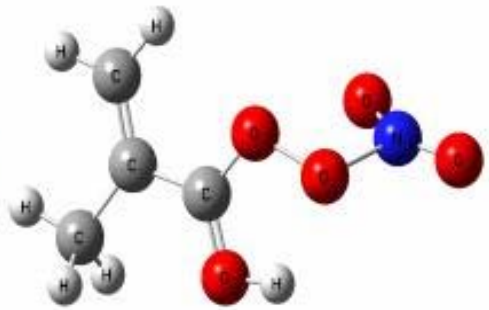
  * Composite Methods: G2(MP2) & CBS-Q

  * Basis Set: 6-311+G(3df,2p)

Results


Unprotonated Structure
Protonated Structures
Structure 1
Structure 2
PAN
PFN
PPN

Results

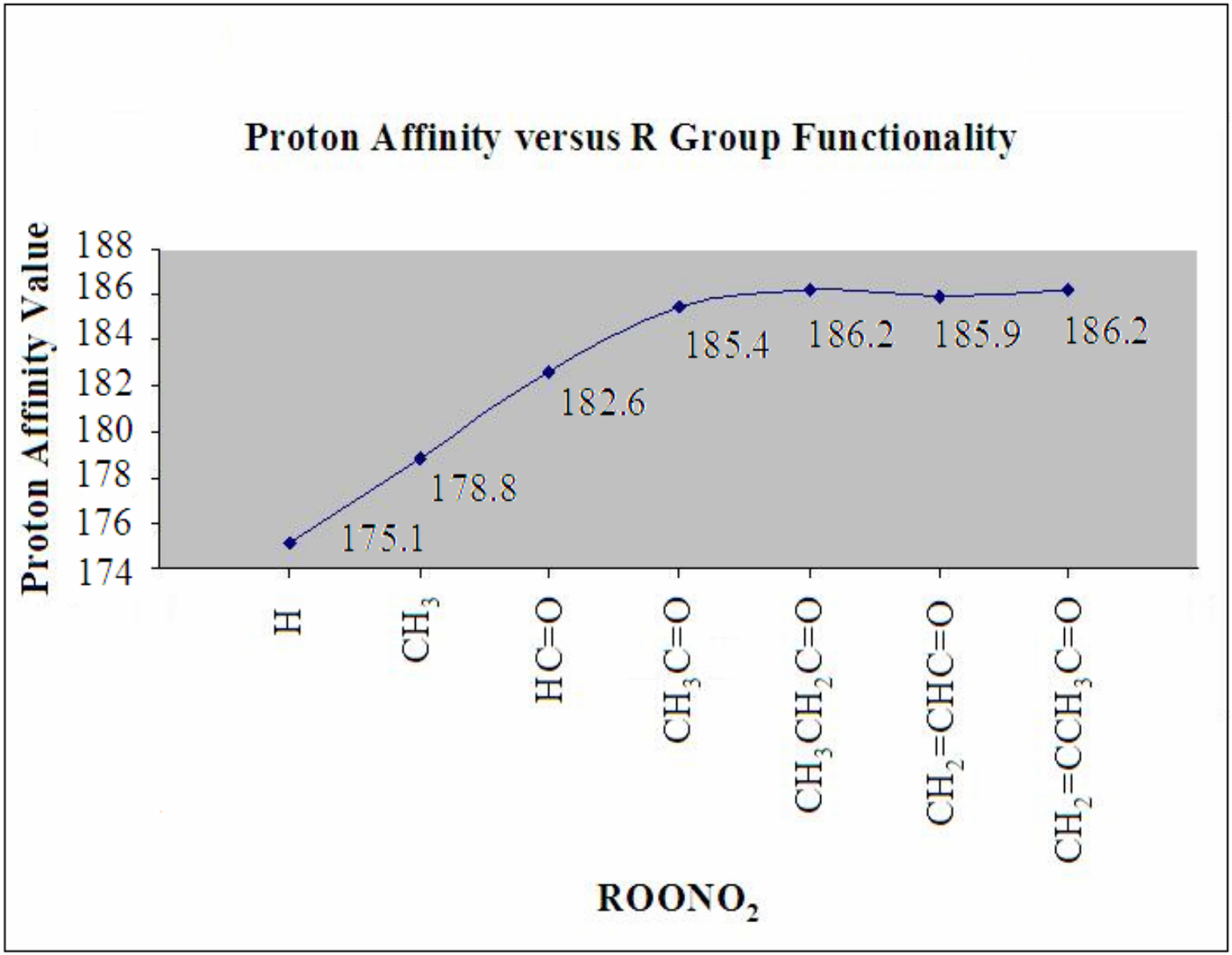
	Unprotonated Structure	Protonated Structures: Structure 1	Protonated Structures: Structure 2
APAN			
MPAN			

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
Proton Affinity Value
188
186
184
182
180
178
176
174
175.1
178.8
182.6
185.4
186.2
185.9
186.2
H
CH3
HC=O
CH3C=O
CH3CH2C=O
CH2=CHC=O
CH2=CCH3C=O
ROONO2

Conclusions

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

Acknowledgements

- Dr. Joseph S. Francisco
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- Dr. Nancy Marley
- Milt Constantin & Alicia Wells
- GCEP/GREF