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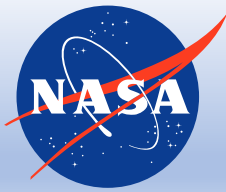
Elucidation of Electrolyte Decomposition Pathways in Li-O₂ Batteries using Ab Initio Computations

J. Wayne Mullinax,^{1,2,3} Charles W. Bauschlicher,^{2,4} John W. Lawson^{2,3}

1. KBR, Inc.
2. NASA Ames Research Center
3. Intelligent Systems Division
4. Thermal Protection Materials Branch



Introduction



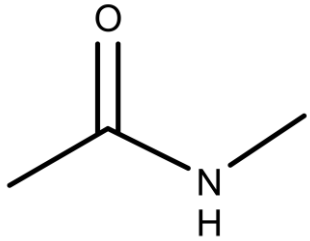
- The promise of Li-O₂ batteries
 - High theoretical specific energy
 - Transform electric transportation
- Parasitic chemistry in Li-O₂ batteries
 - Electrolyte decomposition
 - Harsh environment near cathode
 - Reactive oxygen species
- Computational quantum chemistry
 - Elucidation of decomposition pathways



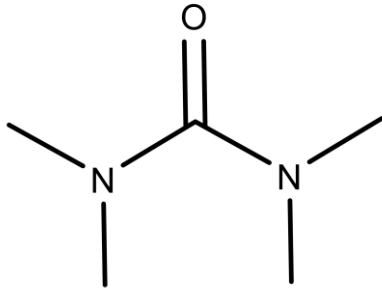
- Investigate 4 decomposition reactions
 - Proton abstraction
 - Hydrogen atom abstraction
 - Baeyer—Villiger oxidation
 - Singlet oxygen
- Ten aprotic organic solvents
- DFT, CASPT2, and MRCI



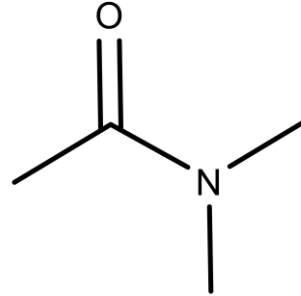
Solvents



NMA



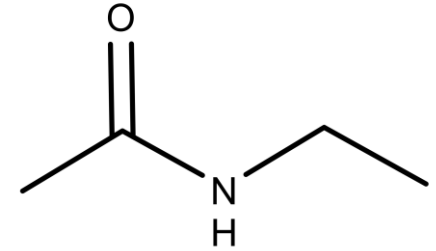
TMU



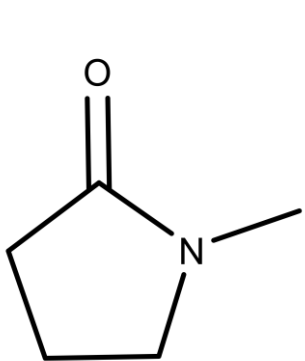
DMA



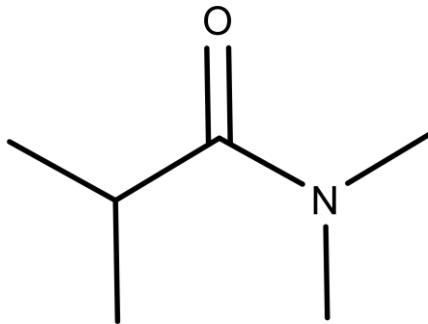
DME



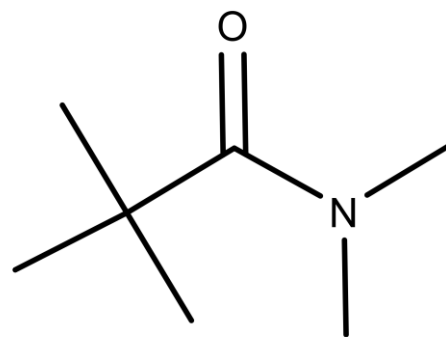
EMA



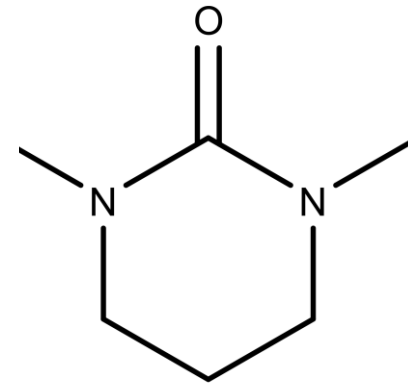
NMP



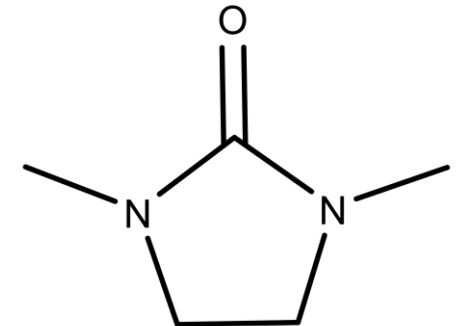
DMDMA



TMDMA



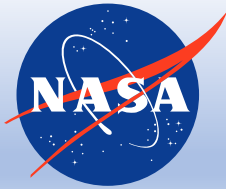
DMPU



DMI



Experimental Work



Experimental Techniques

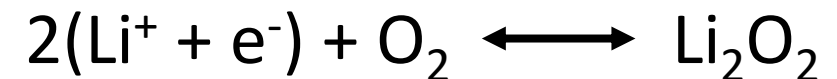
- Differential electrochemical mass spectrometry (DEMS)
- Iodometric titrations
- ^1H -NMR
- Isotopic labeling

Results and Conclusions

- OER/ORR single measure of cell performance
- Decomposition products suggest a Baeyer—Villiger oxidation mechanism

$$\frac{\text{OER}}{\text{ORR}} = \frac{\text{Oxygen Evolved}}{\text{Oxygen Consumed}}$$

Electrochemical Reaction



Knudsen, K. B.; Arrechea, P.; McCloskey, B. D.; Viggiano, R. P. *Manuscript in preparation.*



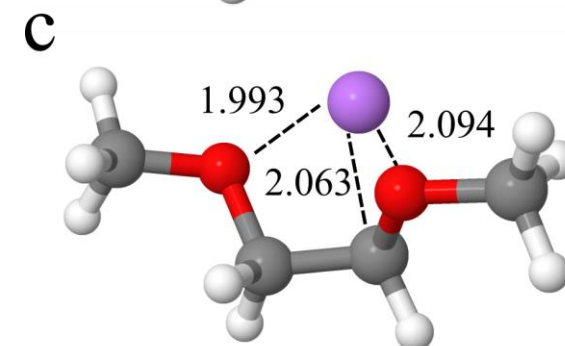
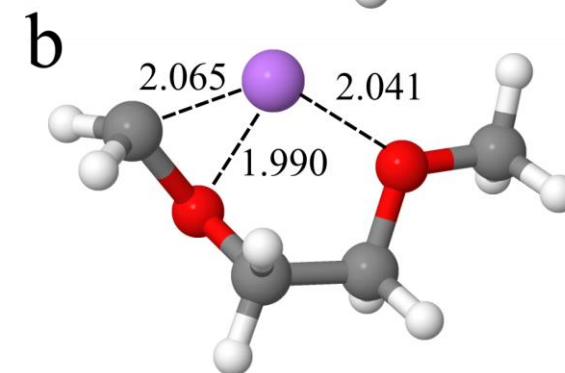
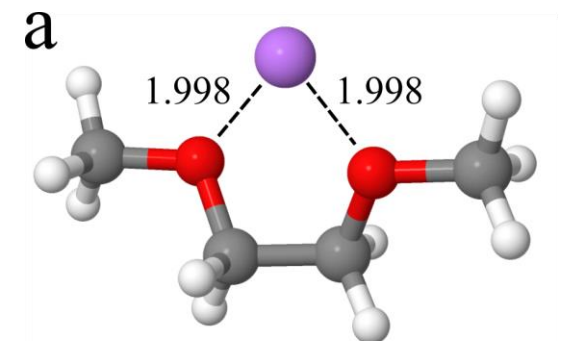
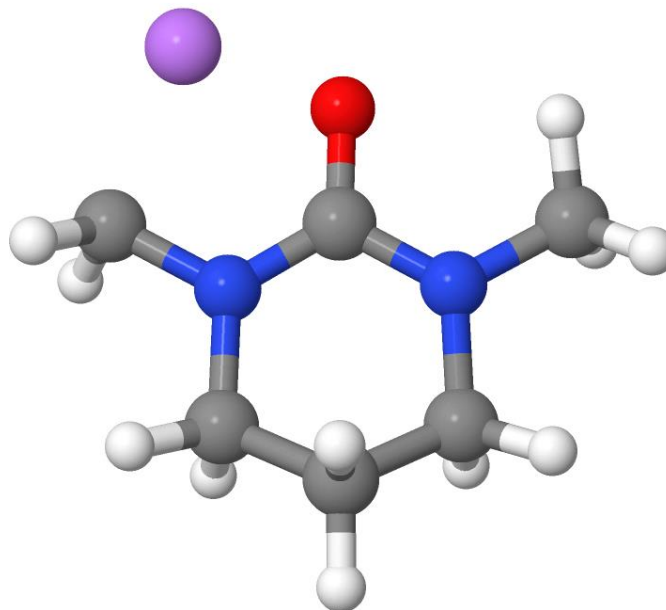
Computational Model

Computational Details:

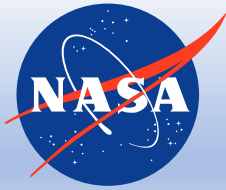
- Gaussian 16
- B3LYP/6-31+G**
- PCM Solvent
- ZPE

Reaction Mechanisms

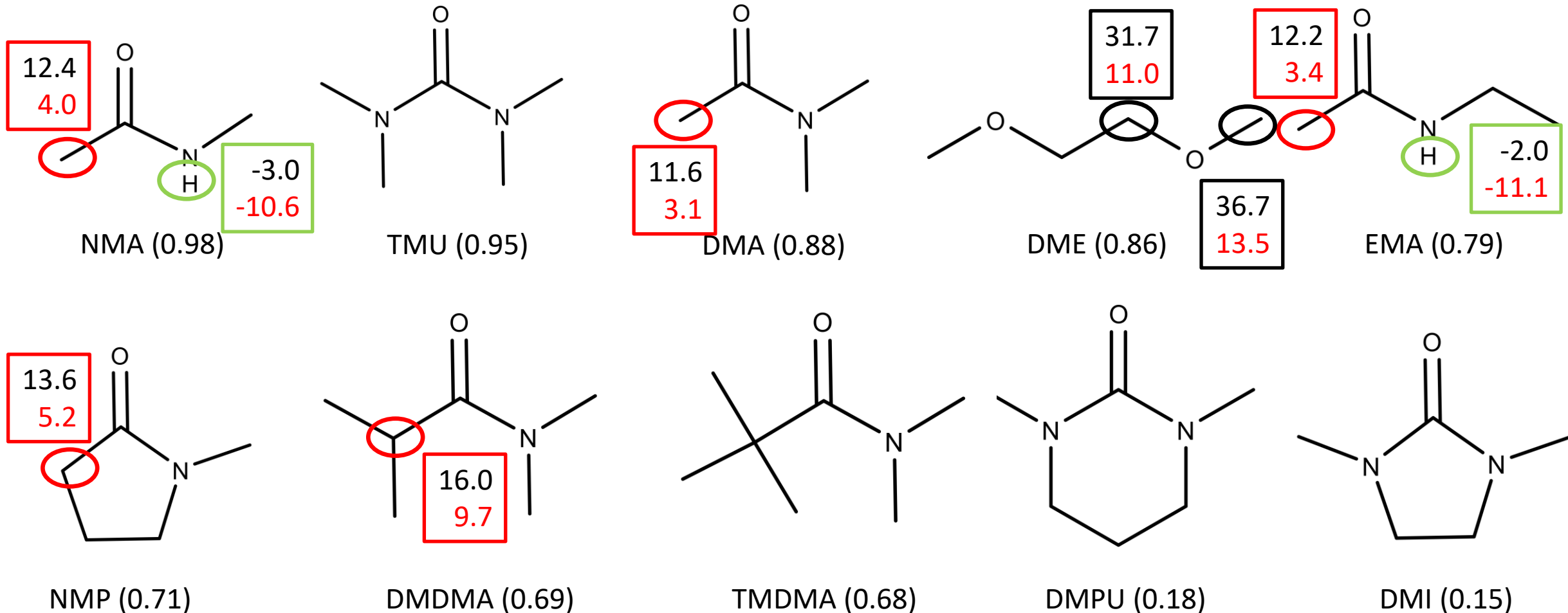
- Proton Abstraction
- Hydrogen Abstraction
- Baeyer—Villiger Oxidation



Proton Abstraction



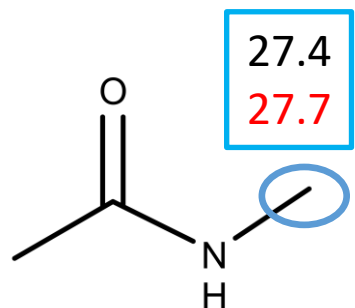
Energies in kcal/mol.



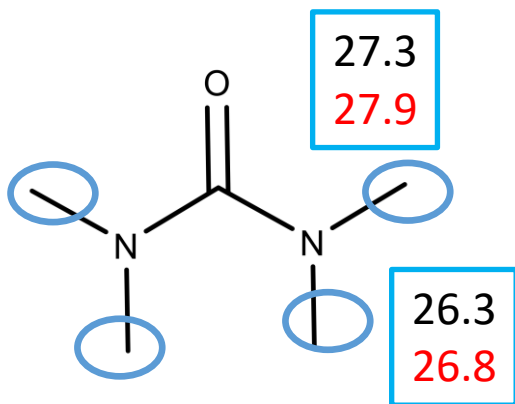
Hydrogen Atom Abstraction



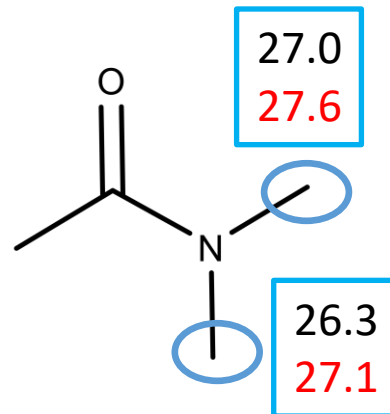
Energies in kcal/mol.



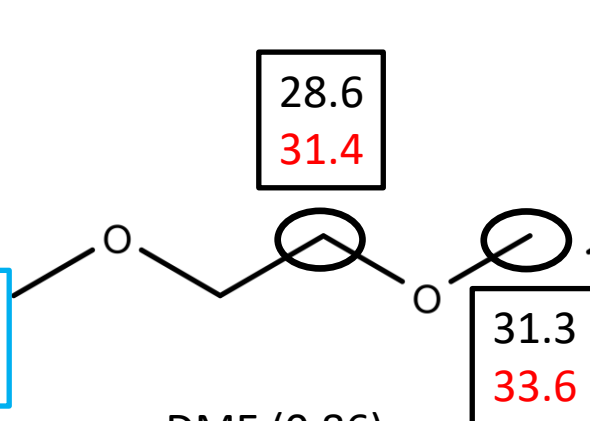
NMA (0.98)



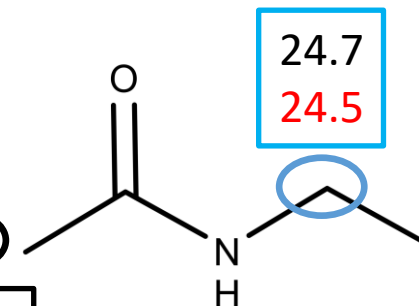
TMU (0.95)



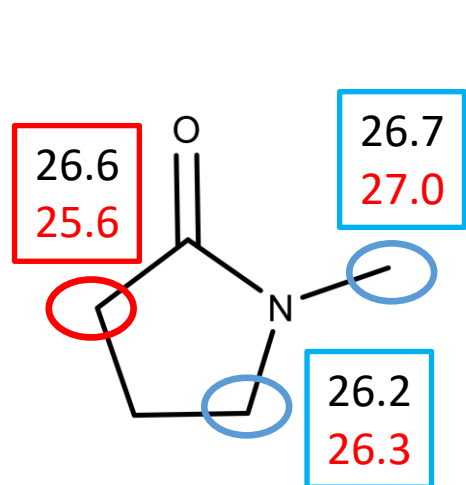
DMA (0.88)



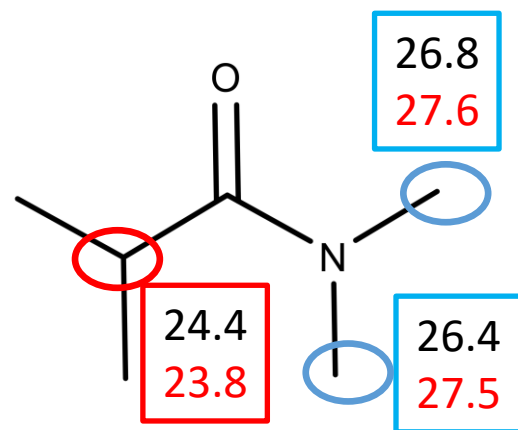
DME (0.86)



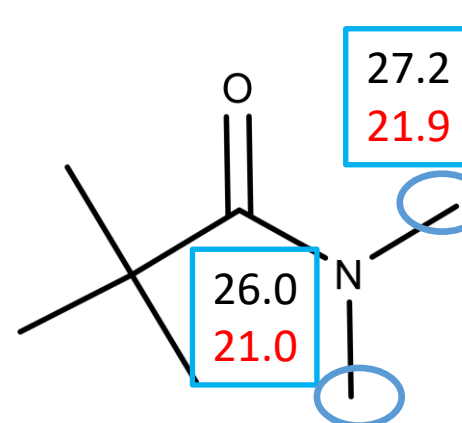
EMA (0.79)



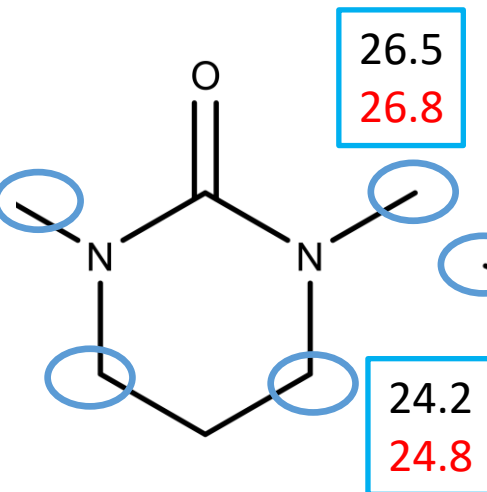
NMP (0.71)



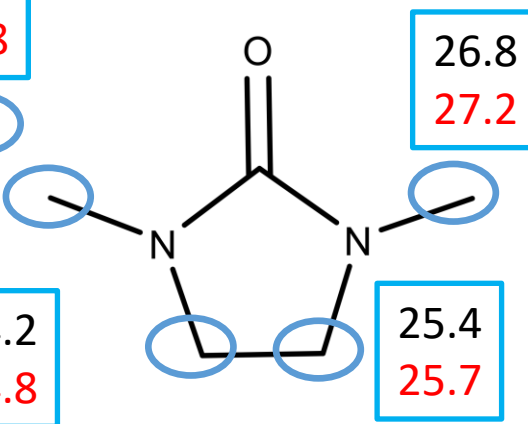
DMDMA (0.69)



TMDMA (0.68)



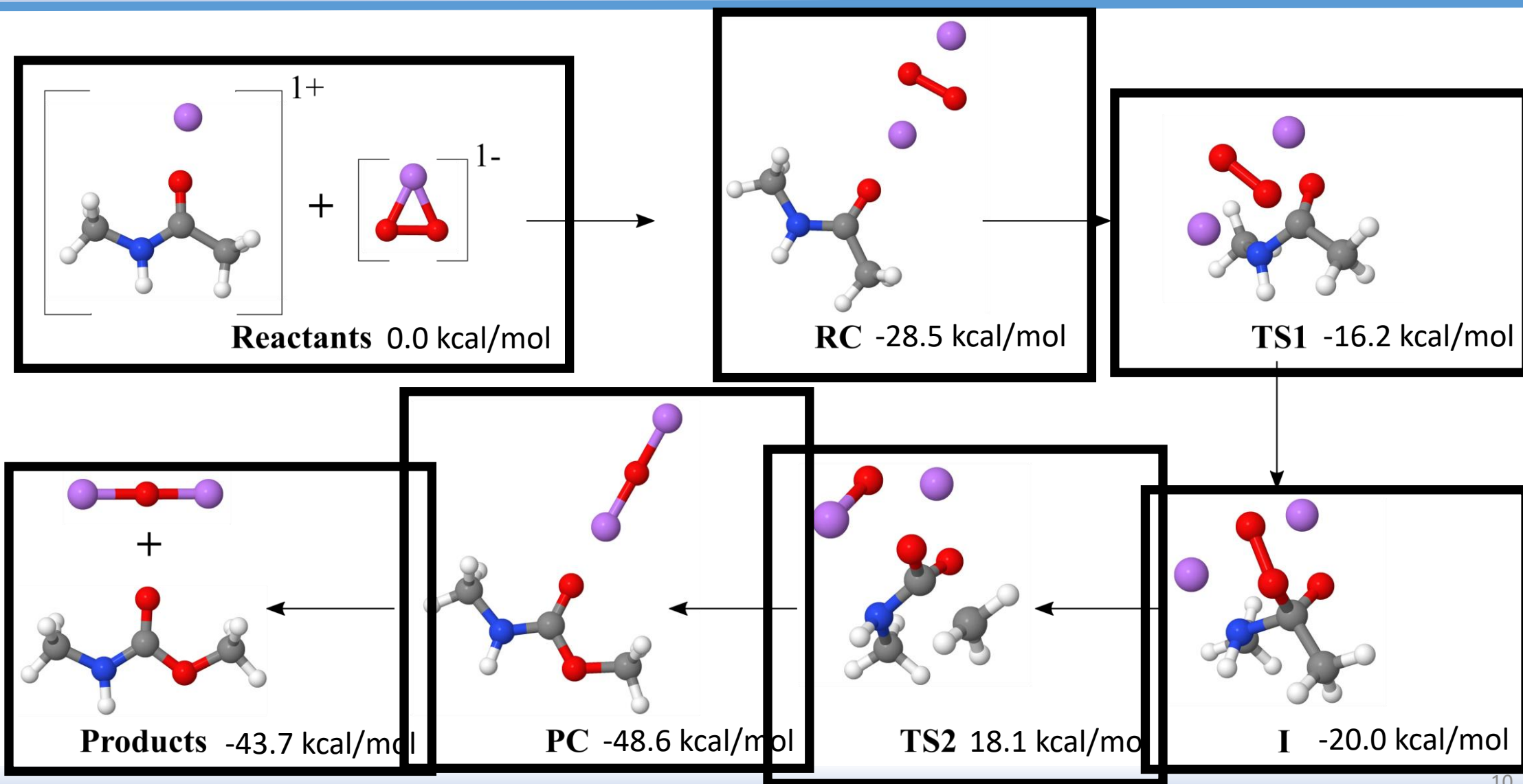
DMPU (0.18)



DMI (0.15)



Baeyer—Villiger Path A



Baeyer—Villiger Path A

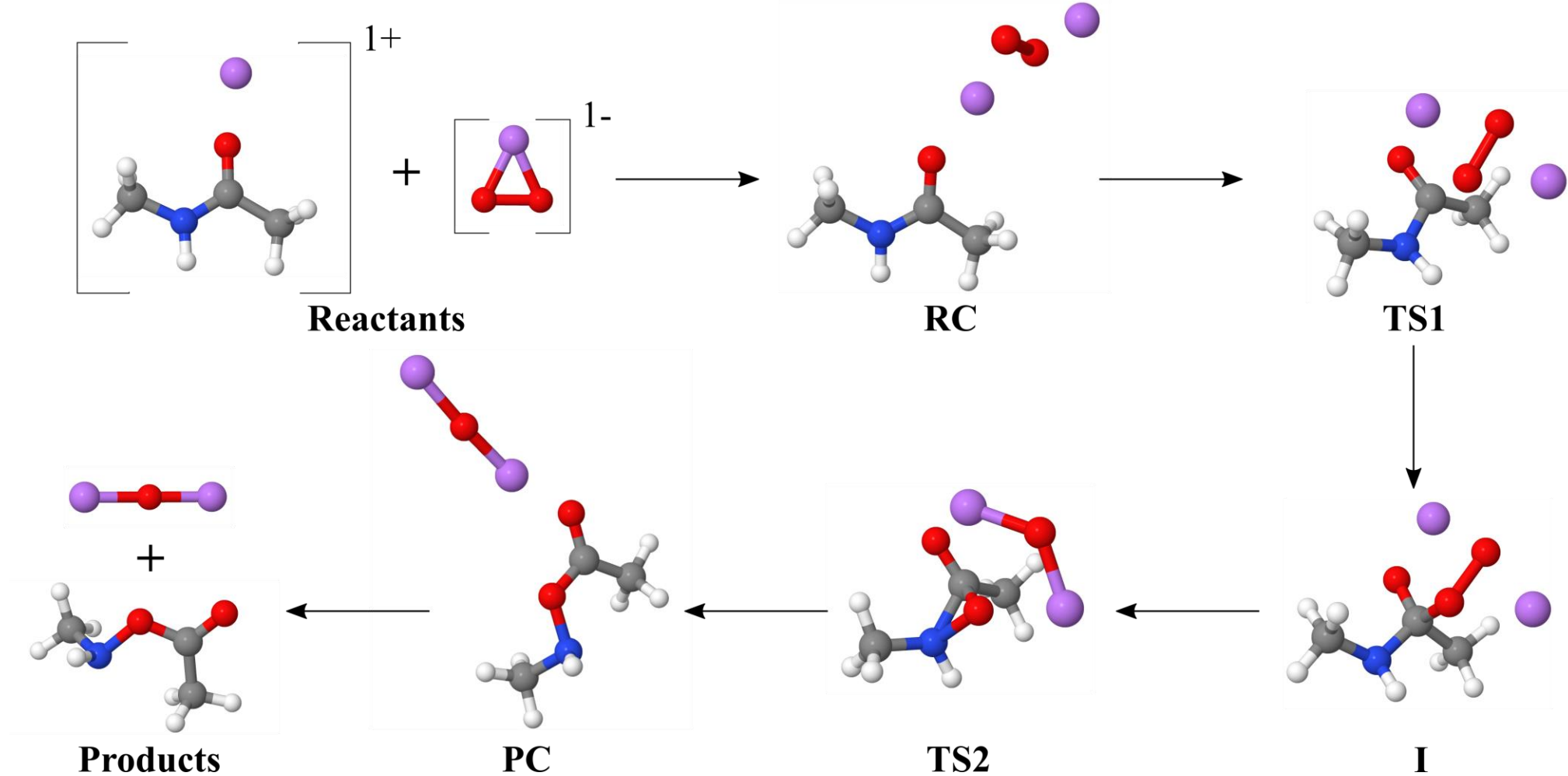


Solvent	OER/ORR	LiO ₂ ⁻		HO ₂ ⁻	
		TS2	Products	TS2	Products
NMA	0.98	18.1	-43.7	17.1	-66.9
DMA	0.88	17.7	-44.4	16.4	-67.5
EMA	0.79	19.2	-44.0	19.2	-67.2
NMP	0.71	20.3	-43.0	19.9	-66.1
DMDMA	0.69	13.2	-49.2	14.5	-72.3
TMDMA	0.68	1.7	-63.6	5.3	-86.7

- kcal/mol
- Energies relative to Reactants (Solvent + XO₂⁻ for X = Li, H)



Baeyer—Villiger Path B



Baeyer—Villiger Path B

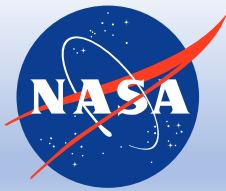


Solvent	OER/ORR	LiO ₂ ⁻		HO ₂ ⁻	
		TS2	Products	TS2	Products
NMA	0.98	24.8	-4.3	12.0	-27.4
TMU	0.95	23.9	-16.0	14.4	-39.1
DMA	0.88	20.0	-9.9	9.6	-33.0
EMA	0.79	24.2	-4.9	11.5	-27.9
NMP	0.71	20.0	-4.8	9.0	-27.8
DMDMA	0.69	15.7	-10.2	10.4	-33.3
TMDMA	0.68	7.7	-17.6	5.1	-46.4
DMPU	0.18	18.1	-4.8	17.4	-27.9
DMI	0.15	29.4	-7.1	17.1	-30.3

- kcal/mol
- Energies relative to Reactants (Solvent + XO₂⁻ for X = Li, H)



Singlet Oxygen



Singlet oxygen formation during the charging process of an aprotic lithium-oxygen battery

Wandt, J.; Jakes, P.; Granwehr, J.; Gasteiger, H. A.; Eichel, R.-A. *Angew. Chem. Int. Ed.* **2016**, 55, 6892-6895.

Singlet oxygen generation as a major cause for parasitic reactions during cycling of aprotic lithium-oxygen batteries

Mahne, N.; Schafzahl, B.; Leypold, C.; Leypold, M.; Grumm, S.; Leitgeb, A.; Strohmeier, G. A.; Wilkening, M.; Fontaine, O.; Kramer, D.; Slugovc, C.; Borisov, S. M.; Freunberger, S. A. *Nat. Energy* **2017**, 2, 17036.

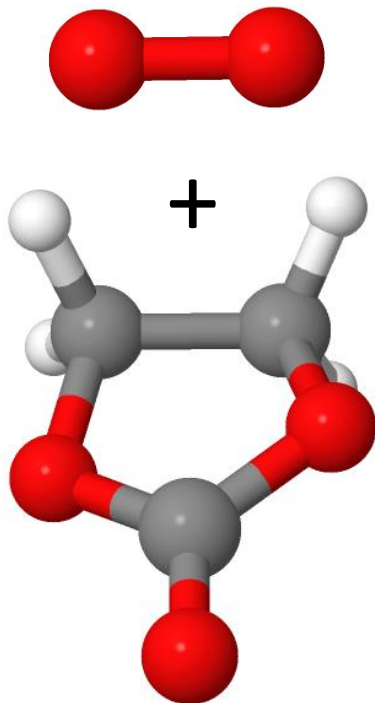


Ethylene Carbonate

Reactants

0.0 kcal/mol

0.0 kcal/mol



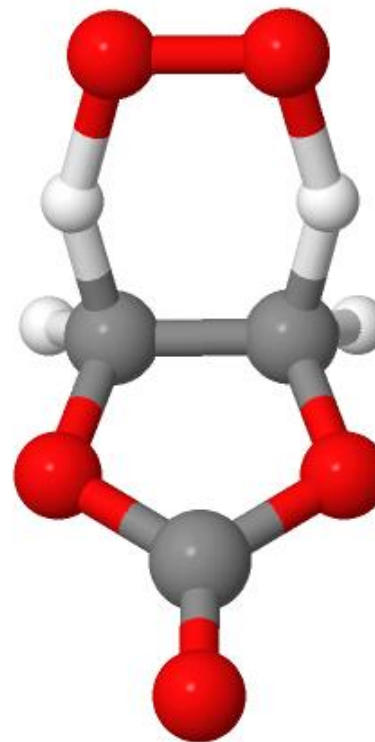
B3LYP/6-311++G**

CASPT2(12,10)/ANO-L-VDZP

TS

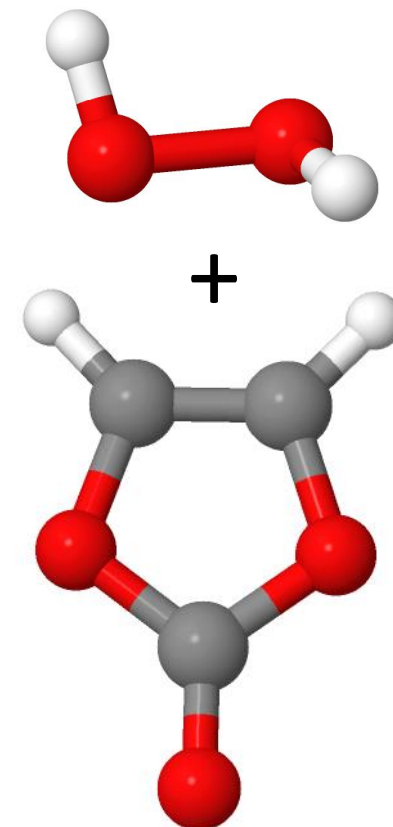
21.2 kcal/mol

29.3 kcal/mol

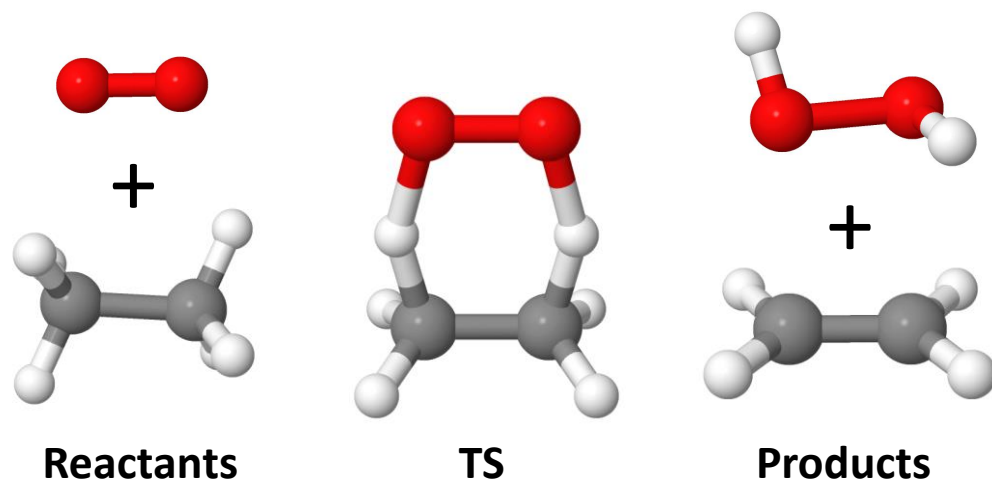


Products

-40.8 kcal/mol



Ethane and Singlet Oxygen



*For DFT calculations, the reactants used the triplet ground state of oxygen shifted by 22.5 kcal/mol, which is the experimental singlet-triplet gap for molecular oxygen.

UCCSD(T)/cc-pVDZ: 28.6 kcal/mol

Sharipov, A. S.; Starik, A. M. *J. Phys. Chem. A* **2012**, *116*, 8444-8454.

Transition State Energies

Basis	CASSCF	CASPT2	MRCI	MRCI+Q
cc-pVDZ	57.7	37.9	40.9	35.1
cc-pVTZ	58.4	35.6	40.1	33.2
cc-pVQZ	58.7	35.3	40.0	32.8
aug-cc-pVDZ	57.0	33.9	37.4	30.4
aug-cc-pVTZ	58.1	34.4	38.9	31.7
aug-cc-pVQZ	58.8	34.7		

- kcal/mol
- B3LYP/6-31+G^{**}: 29.2 kcal/mol
- Molpro 2015



Ethane and Singlet Oxygen



	Gas		Toluene		Water	
Method	TS	Product	TS	Product	TS	Product
B3LYP/6-31+G**	29.2	-15.5	27.1	-18.2	24.9	-21.4
UB3LYP/6-31+G**	28.9	-15.5	26.8	-18.2	24.6	-21.4
B3LYP/6-311++G(2df,2pd)	29.1	-17.8	27.3	-20.2	25.3	-23.1
M11/6-311++G(2df,2pd)	27.1	-22.9	25.4	-25.6	23.7	-28.7

*For DFT calculations, the reactants used the triplet ground state of oxygen shifted by 22.5 kcal/mol, which is the experimental singlet-triplet gap for molecular oxygen.

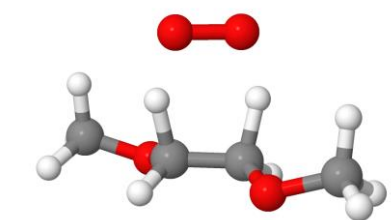


Singlet Oxygen

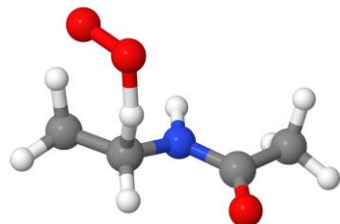
Transition State Energies

Solvent	OER/ORR	CASPT2/cc-pVDZ	M11/6-311++G(2df,2pd)
NMA	0.98	NA	NA
TMU	0.95	NA	NA
DMA	0.88	NA	NA
DME	0.86	37.1	25.5
EMA	0.79	35.3	26.4
NMP	0.71	33.2	23.9
DMDMA	0.69	34.7	24.0
TMDMA	0.68	NA	NA
DMPU	0.18	32.0	23.7
DMI	0.15	31.8	19.4

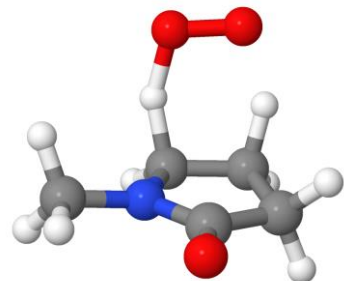
Geometries optimized at the M11/6-311++G(2df,2pd) level of theory.



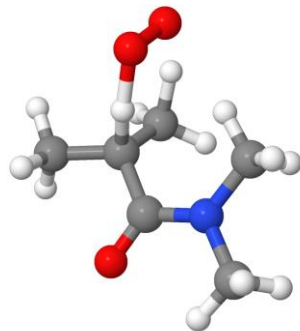
DME



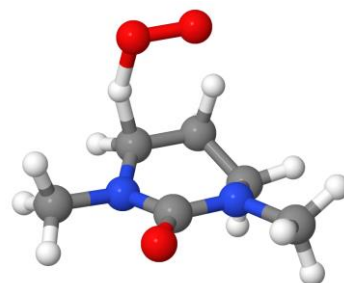
EMA



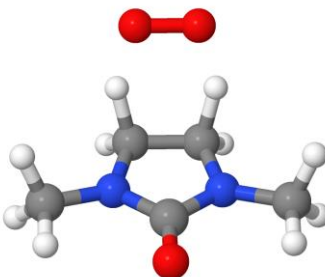
NMP



DMDMA



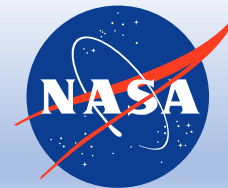
DMPU



DMI



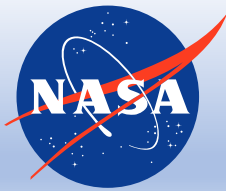
Summary



- Examined 4 decomposition pathways for 10 solvents
 - Proton abstraction
 - Hydrogen atom abstraction
 - Baeyer—Villiger oxidation
 - Singlet oxygen
- No single decomposition pathway explains the experimental performance of each solvent
- Other mechanisms involving singlet oxygen are likely and will be studied in future



Acknowledgements



University of California, Berkeley

- Bryan D. McCloskey
- Kristian B. Knudsen
- Pedro Arrechea

NASA Glenn Research Center

- Rocco P. Viggiano

Funding

NASA ARMD Convergent
Aeronautics Solutions (CAS)
Project

