Activation of hydrogen peroxide by the nitrate anion in micellar media

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Electronic Supporting Information

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1. Experimental Part

1.1. Materials and instrumentation

All synthesis and catalysis runs were, if not stated other, carried out under air. 1-methylimidazole, 1,2-dimethylimidazole, 1-bromooctane, 1-chlorooctane, nitric acid 65%, sodium nitrate, sodium tetrafluoroborate, mesitylene and deuterated chloroform were purchased from Sigma-Aldrich. Sodium hydroxide pellets, 50 wt.% H_2O_2 and *cis*-cyclooctene were purchased from VWR, Amberlite 402 (OH) and 1-bromododecane from abcr. Cis-cyclooctene was distilled under reduced pressure prior to use and all further chemicals were used as received.

All synthesis and catalysis runs were, if not stated otherwise, carried out under air. Structural characterisations and solubility measurements were conducted by NMR spectroscopy using a Bruker AVANCE-III 400-US at 400 MHz (^{1}H) in $CDCl_3$ at room temperature. Chemical shifts [ppm] are reported relative to tetramethylsilane for ^{1}H and ^{13}C detection.

Elemental Analysis (CHNS) were conducted by the Mikroanalytisches Labor of the Technical University of Munich on an Euroanalysis instrument by HEKAtech via flash combustion and subsequent chromatographic separation.

1.2. Catalysis Procedures

Catalysis runs were performed in 20 mL screw-neck vials equipped with a 20 mm PTFE stirring bar in a temperature-adjustable tight-fitting metal vial holder. 1.35 mL (10 mmol, 1.0 eq) *cis*-cyclooctene and 1.40 mL H_2O_2 50 wt.% (25 mmol, 2.5 eq.) as well as 69 µL mesitylene as internal standard were added to the ionic liquid catalyst (0.5-2.0 mmol, 5-20 mol-%) and consequently stirred at 500 min^{-1} at 80 °C. After certain time intervals, 10 µL aliquots are taken from the supernatant organic phase, diluted in 500 µL $CDCl_3$ and investigated by ^{1}H NMR spectroscopy.

For the recycling procedure, the substrate/product overlayer was decanted and the aqueous phase residual organic compounds inside the micelles extracted with toluene (3 × 20 mL). Next, the residual hydrogen peroxide was decomposed with a platinum wire at 80 °C prior to evaporation of all volatile compounds under reduced pressure. The remaining IL was then subjected to catalysis as described above.

1.3. Dynamic light scattering (DLS)

DLS was performed on a Malvern Zetasizer Nano in quartz cuvettes using 173° angle backscattering mode. 0.50 mmol (c = 357 mmol/L) [RMIM][NO_3] was dissolved in 25 mmol 50 wt.% aq.H_2O_2 (1.4 mL, 50 eq.) and measured at 20 °C and upon heating at 80 °C. In subsequent experiments, 10 mmol COE (1.35 mL, 20 eq.) were added to the mixture, creating a biphasic system where the aqueous phase is used for DLS

investigation. Micelle size (distribution) were interpreted from the correlograms using a general-purpose method.

The dynamic viscosity of 50 wt.% H_2O_2 at 20 °C (1.17 mPas) and 80 °C (0.485 mPas) were determined using a Ubbelohde capillary viscosimeter, temperature-adjusted in a water bath.

1.4. Tensiometry and Conductometry

Tensiometry measurements were conducted with a K11 tensiometer (Krüss GmbH, Germany) according to the Willhelmy plate method with an accuracy of 0.01 N/m². For accurate determination of the surface tension, the standard platinum plates were substituted by square glass plates (18 × 18 mm) used for microscopy, to avoid decomposition of hydrogen peroxide. Prior to any measurement, the glass plates were washed with isopropyl alcohol and flame treated to clean the plate from any organic impurities; The general method was validated by test measurements with aqueous sodiumdodecyl sulfate (SDS) solutions. Glass utensils were cleaned carefully with water, acetone and dichloromethane. Prior to each experiment, a test with pure water in the used glass vessel was conducted to ensure that no foreign ions affect the measurements. Experiments at elevated temperatures were performed using an aluminum jacket heated with two heating cartridges to ensure a homogeneous temperature distribution. The CMC is obtained when the surface tension remains constant upon addition of further surfactant. The data ware drawn in figure S2 with the surface tension over the logarithmic concentration of the surfactant.

Conductivity was measured with a Metrohm 712 conductometer with a modified tin probe (99.99% purity, supplied by EvoChem) to avoid the catalytic decomposition of H_2O_2. The tin foil was cut to two square plates (area of 0.64 cm^2) and the cell constant of the electrode was determined by calibration with aqueous KCl solution (concentration ranging from 0.01 mol/L to 1 mol/L) to 0.85 mS/cm. The temperature of the sample was monitored using a PT100 thermo couple surrounded by a glass tube. The IL concentration, at which he first stepwise change of the slope of the conductivity versus the IL concentration occurred, was set as the CMC.

1.5. Mangoanometric determination of the H_2O_2 decomposition

Neat hydrogen peroxide in absence of organic media was stirred for 24 h at 80 °C and an overall thermal decomposition of 6% of pure aqueous H_2O_2 was determined by manganometric titration. 0.4 mL of the H_2O_2 solution was taken and diluted in 50 mL H_2O, acidified with 1 mL conc. H_2SO_4. Then a 0.05 M $KMnO_4$ solution was added dropwise till a pinkish colour remained. The addition of $NaNO_3$ did not increase the permanganate consumption, so a nitrate induced H_2O_2-decomposition could be excluded for catalytic epoxidations, allowing for its catalytic use in presence of hydrogen peroxide.

1.6. Synthesis of imidazolium halides

Imidazolium halide ionic liquids RR'MIM X (R = Octyl, Dodecyl; R' = H, Me; X = Cl, Br) were synthesized in 20 g scales by addition of 1.05 eq. of alkylhalide to 1.00 eq. of (di)methylimidazole and degasses by fine vacuum and argon purging for three times. Then, the solution was heated for 24 h (RBr: 60°C, RCl; 80 °C) under gentle stirring. Purification was performed by removing volatile impurities and excess educts under high vacuum using a turbomolecular pump, yielding the ionic liquids in quantitative yields.

[OMIM][BF_4] was synthesized by equimolar addition of 10 mmol [OMIM]Cl and $NaBF_4$ in 200 mL water. The solution was stirred for 24 h at room temperature and extracted with dichloromethane (3 × 100 mL). The organic phases were combined and washed with water (2 × 50 mL) prior to evaporation of the solvent under reduced pressure. The ionic liquid [OMIM] BF_4 was obtained in 97% yield, dried under high vacuum (10^{-6} bar and stored under argon.

1.7. Catalyst synthesis

The ionic liquids [RR'MIM][NO_3] (R = octyl, dodecyl, R' = H, Me) are prepared using by an anion exchange procedure ($Br^- \rightarrow OH^-$). 30 mmol, 1.0 eq. of the corresponding [RR'MIM] Br ionic liquids are dissolved in 800 mL (Millipore grade, resistance 18.2 MΩ·cm) water and rinsed over 120 g freshly regenerated Amberlite IRA 402 (OH) anion exchange resin within four hours. The basic eluate was neutralized to pH = 7.0 by addition of 2 wt.% aqueous HNO_3 monitored with a calibrated pH meter. After removal of the water and drying under fine vacuum at 80 °C with a turbomolecular pump, the colourless ionic liquids are obtained in yields >95%. The absence of residual bromide contaminations was ensured by titration by Mohr down to a detection limit of 13 ppm using a literature procedure.[1]

1.8. Physical and spectral data of the imidazolium nitrates

1.8.1. 1-Octyl-3-methylimidazolium nitrate [OMIM][NO_3]

Melting range: −40 - −35 °C

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ [ppm]: 9.51 (s, 1H), 7.42 (t, *J* = 1.8 Hz, 1H), 7.34 (t, *J* = 1.8 Hz, 1H), 4.08 (t, ^3J = 7.4 Hz, 2H), 3.86 (s, 3H), 1.73 (dd, ^3J = 7.4, ^3J = 7.1 Hz, 2H), 1.23 – 1.03 (m, 10H), 0.70 (t, ^3J = 7.1 Hz, 3H).

^{13}C{^{1}H}-NMR (400 MHz, $CDCl_3$, 298 K) δ [ppm]: 137.10, 123.59, 122.08, 49.80, 35.94, 31.38, 29.93, 28.72, 28.61, 25.93, 22.28, 13.78.

Elemental analysis calcd. (%) for $C_{12}H_{23}N_3O_3$: C 56.01, H 9.01, N 16.33, O 18.65; found: C 55.62, H 9.13, N 16.02.

1.8.2. 1-Octyl-2,3-dimethylimidazolium nitrate [OMMIM][NO_3]

Melting point: 56 °C

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ [ppm]: 7.45 (d, *J* = 2.2 Hz, 1H), 7.31 (d, *J* = 2.2 Hz, 1H), 4.07 (t, ^3J = 7.6 Hz, 2H), 3.85 (s, 3H), 2.64 (s, 3H), 1.76 (dd, ^3J = 7.6 Hz, ^3J = 7.7 Hz, 2H), 1.33 – 1.18 (m, 10H), 0.83 (t, ^3J = 6.8 Hz 3H).

^{13}C{^{1}H}-NMR (400 MHz, $CDCl_3$, 298 K) δ [ppm]: 143.84, 122.98, 121.07, 48.84, 35.37, 31.72, 29.83, 29.07, 29.03, 26.41, 22.61, 14.10, 9.66.

Elemental analysis calcd. (%) for $C_{13}H_{25}N_3O_3$: C 57.54, H 9.29, N 15.49, O 17.69; found: C 57.33, H 9.45, N 15.65.

1.8.3. 1-Dodecyl-3-methylimidazolium nitrate [DoMIM][NO_3]

Melting point: 43 °C

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ [ppm]: 9.74 (s, 1H), 7.50 (t, *J* = 1.9 Hz, 1H), 7.38 (t, *J* = 1.9 Hz, 1H), 4.15 (t, ^3J = 7.4 Hz, 2H), 3.94 (s, 3H), 1.80 (dd, ^3J = 7.4 Hz, ^3J = 6.8 Hz, 2H), 1.26 – 1.14 (m, 18H), 0.80 (t, ^3J = 6.6 Hz, 3H).

^{13}C{^{1}H}-NMR (400 MHz, $CDCl_3$, 298 K) δ [ppm]: 137.65, 123.78, 122.16, 50.05, 36.21, 31.84, 30.21, 29.54, 29.46, 29.34, 29.27, 28.94, 26.21, 22.62, 14.07.

Elemental analysis calcd. (%) for $C_{16}H_{31}N_3O_3$: C 61.31, H 9.97, N 13.41, O 15.31; found: C 61.11, H 10.17, N 13.23.

1.8.4. 1-Dodecyl-2,3-dimethylimidazolium nitrate [DoMMIM][NO_3]

Melting point: 65 °C

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ [ppm]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.34 (s, 1H), 4.10 (t, ^3J = 7.6 Hz, 2H), 3.90 (s, 3H), 2.69 (s, 3H), 1.78 (dd, ^3J = 7.6 Hz, ^3J = 7.2 Hz, 2H), 1.33 – 1.20 (m, 18H), 0.85 (t, ^3J = 6.7 Hz, 4H).

^{13}C{^{1}H}-NMR (400 MHz, $CDCl_3$, 298 K) δ [ppm]: 143.90, 123.10, 121.07, 48.92, 35.59, 31.99, 29.91, 29.68, 29.61, 29.49, 29.42, 29.15, 26.49, 22.77, 14.21, 9.97.

Elemental analysis calcd. (%) for $C_{17}H_{33}N_3O_3$: C 62.35, H 10.16, N 12.83, O 14.66; found: C 61.82, H 10.11, N 12.33.

2. Micelle Characterisation

2.1. Conductivity

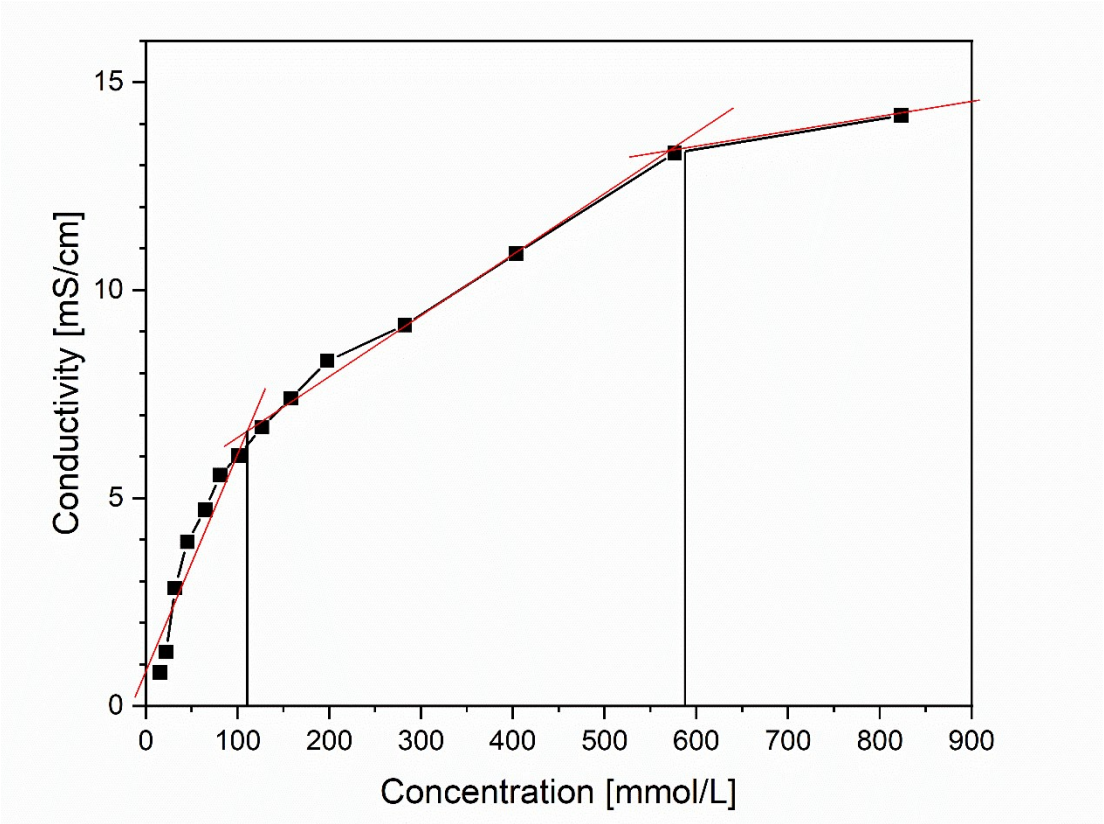


Fig. S1. Conductivity of a solution of [OMIM][NO_3] in 50 wt.% H_2O_2 at room temperature.

2.2. Tensiometry

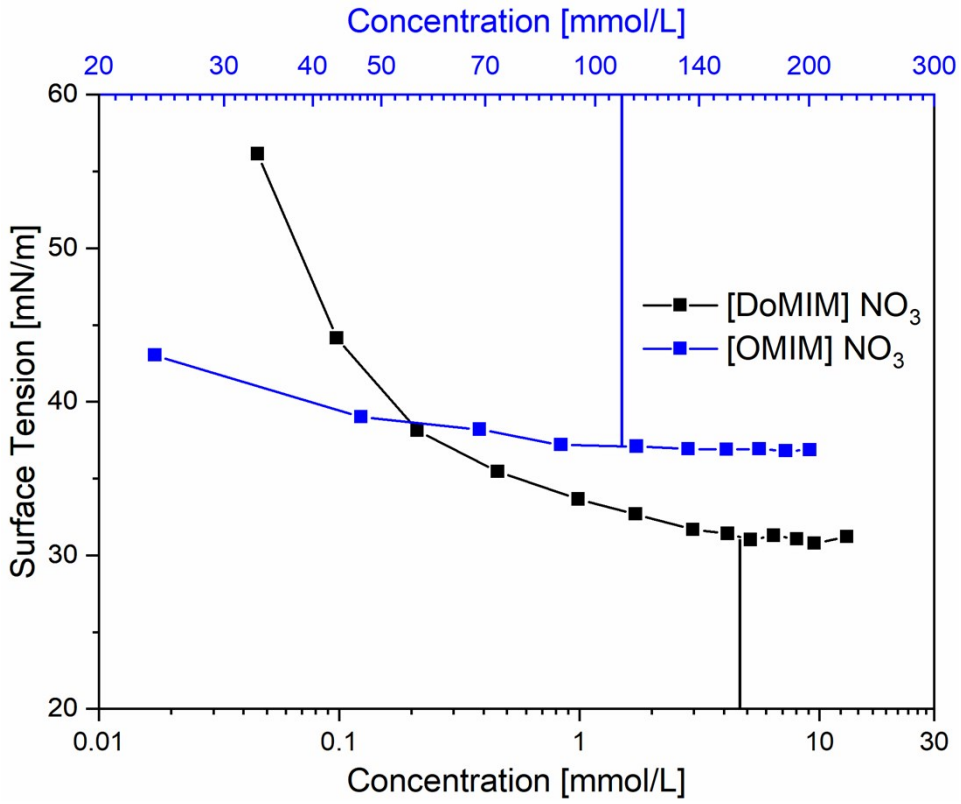


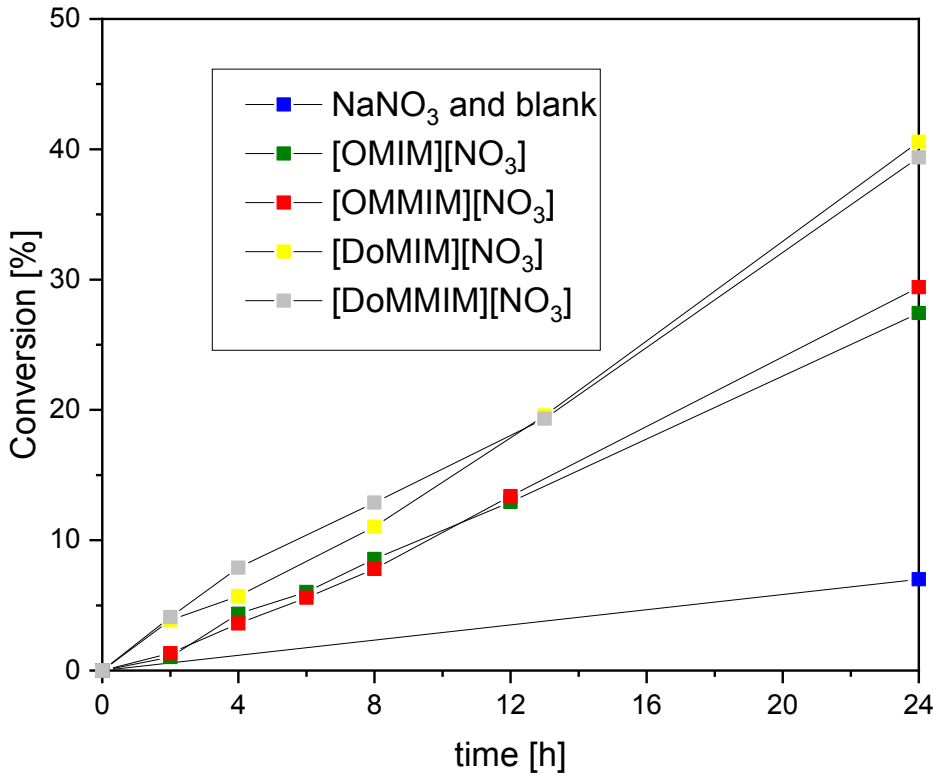
Fig S2. Tensiometric measurement of [OMIM][NO_3] and [DoMIM][NO_3] at 80 °C in 50 wt.% H_2O_2.

2.3. Dynamic light scattering

Table S1. Investigation of micelle size and COE uptake by [OMIM][NO_3] and [DoMIM][NO_3] at 20 and 80 °C.

Catalyst	T [°C]	DLS w/o COE [nm]	DLS with COE [nm]	Uptake of COE per catalyst
[OMIM][NO_3]	20	1.33 ± 0.52	1.61 ± 0.34	traces
[OMIM] [NO_3]	80	1.15 ± 0.20	697 ± 121	2.2
[DoMIM][NO_3]	20	0.83 ± 0.26	0.98 ± 0.19	<0.2
[DoMIM][NO_3]	80	0.84 ± 0.28	383 ± 43	2.6

3. Catalytic Experiments



3.1. Cation Variation

Fig. S3. Kinetic plots of the epoxidation of COE using various imidazolium nitrates in 50 wt.% H_2O_2. Conditions: IL:COE:H_2O_2 = 5:100:250, 80 °C, 24 h.

3.2. Catalyst loading variation

Table S2. Epoxidation of COE using various imidazolium nitrates with 50 wt.% H_2O_2. Reaction Conditions: 24 h at 80 °C.

Entry	Cat	Loading [%]	Conc. [mmol/L]	Conv [%]	Conv.[a] [%]
1	[OMIM][NO_3]	1	71	8	2
2	[OMIM][NO_3]	2	143	13	7
3	[OMIM][NO_3]	5	357	27	20
4	[OMIM][NO_3]	10	714	35	29
5	[OMIM][NO_3]	20	1428	49	43
6	[DoMIM][NO_3]	1	71	19	13
7	[DoMIM][NO_3]	2	143	26	20
8	[DoMIM][NO_3]	5	357	40	34
9	[DoMIM][NO_3]	10	714	50	44

[a] Conversion of COE subtracted by the blind conversion (6%).

3.3. Substrate variation

So far, COE was used as a model substrate for the catalytic epoxidation reactions. It is suitable due to its reactivity caused by ring strain and the stability of the corresponding epoxide but does not have industrial application. Therefore, various substrates were tested under the same reaction conditions and their activity and selectivity elucidated. Cyclohexene and 1-methycyclohexene also feature ring strain and their corresponding epoxides are prone to a fast epoxidation but also ring-opening follow-up reactions under the applied reaction conditions. Therefore, only noteworthy amounts of diols are produced. Since the primary alkene 1-octene shows drastically reduced reactivity, reactions with 2-octenes were performed to elucidate the reactivity of secondary olefins without ring strain. As anticipated, the conversion is lower than for the cyclic substrate but also the selectivity is decreased due to a higher sensitivity towards follow-up hydrolysis.

Table S 3. Substrate scope for epoxidation with [OMIM][NO_3] using 50 wt-% H_2O_2. Conversion and yield of corresponding olefin and epoxide, respectively. Reaction conditions: 24h at 80 °C, [OMIM][NO_3]:olefin:H_2O_2 = 5:100:250.

Entry	Substrate	Conversion [%]	Yield [%]
1	*cis*-cyclooctene	27	20
2	Cyclohexene	42	1
3	1-methylcyclohexene	100	0
4	1-octene	3	trace
5	*trans*-2-Octene	12	1
6	*cis*-2-octene	24	6
7	β-*trans*-methylstyrene	95	6

3.4. Anion variation

For this investigation, common commercially available ionic liquids, [OMIM]Cl and [OMIM][BF_4] were used as a micelle forming agent in combination with equimolar sodium nitrate as nitrate source. At room temperature, the CMCs of the chloride (60 mmol/L) and tetrafluoroborate ionic liquids (48 mmol/L) are in a comparable range of [OMIM][NO_3] (31 mmol/L) in 50 wt.% aqueous hydrogen peroxide and a similar behaviour is expected at elevated temperatures.[2]

[OMIM]Cl is among the most common SAILs commercially available, so the combination of [OMIM]Cl with $NaNO_3$ is of high interest for a biphasic catalytic application. The conversion of the experiment is slightly reduced compared to the pure [OMIM][NO_3] IL (21 vs. 27%) (Table S 4, Entries 1 and 4). The cross-matching experiment [OMIM][NO_3] in addition of NaCl leads to the same result, proving the reliability of the experiment.

However, with NaCl being involved, a severe hydrogen peroxide decomposition is observed, leading to the question if this is the source of the active oxygen. Therefore, the catalytic conditions were mimicked by use of both sodium salts in absence of substrate. While pure H_2O_2 and with dissolved $NaNO_3$ being stirred at 80 °C for 24 h leads to an oxidant decomposition of 6% each, for NaCl 31% of H_2O_2 is decomposed. Lower concentrations of hydrogen peroxide ultimately lead to lower catalytic conversions and explain the decreased activity in the [OMIM]Cl / $NaNO_3$ mixture.

Due to the high loss of valuable hydrogen peroxide, the use of chloride-based micelle forming agents is non-desirable for an efficient catalysis reaction as it would diminish the efficiency and advantages of this metal-free approach.

Therefore, the combination of $NaNO_3$ and [OMIM][BF_4] was investigated next and shows an increased conversion (C = 77%) but a drastically reduced selectivity towards COO. The cross-experiment, using [OMIM][NO_3] with equimolar amounts of $NaBF_4$

gives comparable conversion and yield, demonstrating the interchangeability of the anions and the reliability of the experiment. In literature, hydrolysis of the $[BF_4]^-$ anion in imidazolium based ionic liquids resulting in the formation of fluorooxoboric acids is reported.[3] In our case, ^{11}B-NMR spectroscopy after 24 h of reaction shows a 13% decomposition of $[BF_4]^-$ to oxofluoroborates upon release of toxic HF. The low corresponding selectivity arises from epoxide ring opening to trans-1,2-cyclooctene diol by inorganic borate acids. These drawbacks render the use of common ionic liquids unsuitable for micellar oxidation reactions is aqueous media. Therefore, the imidazolium nitrates have to be isolated for best results in terms of selectivity and H_2O_2-efficiency.

Table S4. Epoxidation of COE using various imidazolium nitrates with 50 wt-% H_2O_2. Conversion and Yield correspond to COE and COO, respectively. Reaction Conditions: 24h at 80 °C, Catalyst:COE:H_2O_2 5:100:250.

Entry	Catalyst	Conversion [%]	Selectivity [%]
1	[OMIM][NO_3]	27	74
2	[OMIM]Cl	21	71
3	[OMIM][NO_3] + NaCl	18	73
4	[OMIM] Cl + $NaNO_3$	20	70
5	[OMIM][BF_4]	65	26
6	[OMIM][BF_4] + $NaNO_3$	77	30
7	[OMIM][NO_3] + $NaBF_4$	71	35

3.5. Catalyst recycling

[DoMIM][NO_3] was subjected to the recycling investigation, as it yields the highest conversion and selectivity after the given time frame of 24 h. After each run, the product phase was separated and the catalyst was isolated as described above. The results show that the ionic liquid can subsequently be used for five times without any observable loss of activity (Figure S 4).

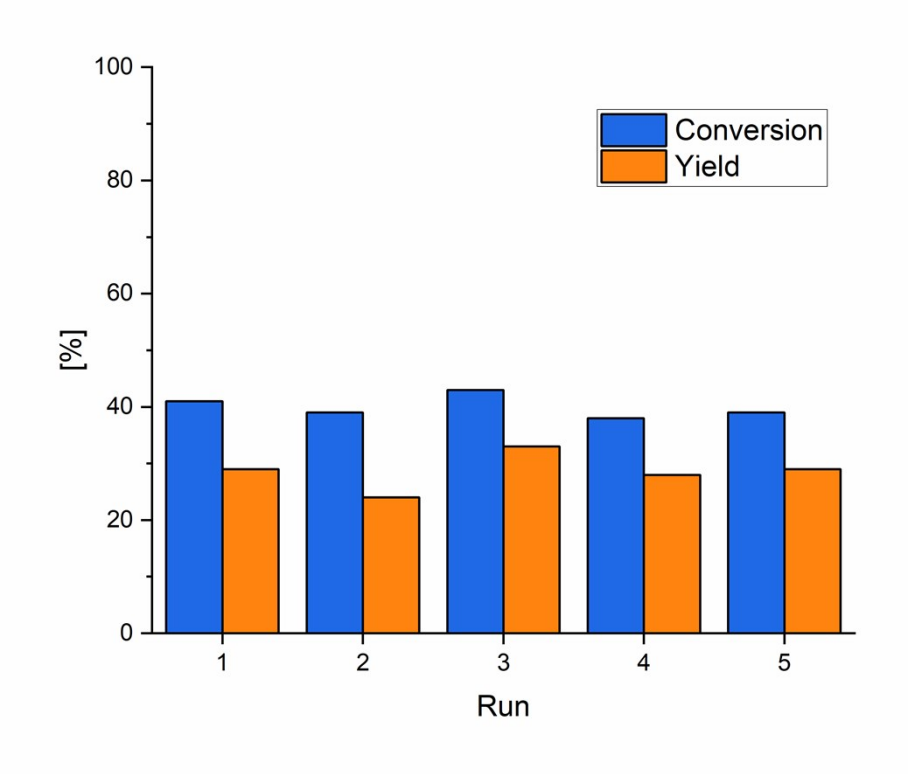


Fig. S4. Recycling study of the catalyst [DoMIM][NO_3]. Reaction conditions: [DoMIM][NO_3]:COE:H2O2 = 5:100:250, 80 °C, 24 h.

4. Vibrational spectroscopy investigations

4.1. Experimental details

Vibrational spectroscopic measurements were performed with the pure ionic liquids or with solutions thereof (c= 357 mmol/L) in water or 50 wt.% aq. H_2O_2.

4.2. FT-IR measurements

Infrared measurements were carried out by means of a dynamically aligned Varian FTS-7000 infrared spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. Some of the solids and liquids were recorded with a dynamically aligned Varian FTS-2000 spectrometer, using a GladiATR accessory with a diamond ATR element and a liquid N_2-cooled MCT detector. MIR spectra were recorded as 256 scans with a resolution of 4 cm^{-1} and have been ATR corrected.

Far-infrared spectra were recorded with a dynamically aligned Digilab FTS-60A spectrometer, equipped with a high pressure mercury lamp source, a 6 µm Mylar beam splitter and a polyethylene windowed DTGS detector. FIR spectra were recorded as 512 scans with resolution of 4 cm^{-1}.

4.3. FT-Raman measurements

Raman measurements were performed with a BioRad (Digilab) dedicated FT-Raman spectrometer equipped with a liquid-nitrogen-cooled germanium detector and a Spectra Physics Nd : YAG excitation laser with radiation line at 1064 nm. All spectra were collected using 500 mW laser power at the sample position, 4 cm^{-1} resolution and co-addition of 256-512 individual spectra. The spectra of the powdered sample [OMMIM] [NO_3] were corrected with white light correction.

Infrared and Raman spectral data was processed using GRAMS/AI (7.02) spectral evaluation program (Galactic Industries Corporation).[4]

4.4. Calculations of force constants

Normal coordinate calculations were performed by means of the Wilson's GF matrix method. Force constants were obtained by optimizing the vibrational frequencies using symmetrized valence force field. For the calculations the PC-based program package developed by J. Mink and L. Mink was used.[5]

4.5. Discussion of the IR spectra

First, an infrared spectrum of the pure [OMIM][NO_3] was measured and the peaks assigned (Fig. S5). The band positions of the $[OMIM]^+$ C2-H vibration (3050 and 3032 cm^{-1}) was determined by deuteration of the position with heavy water after evaporation using a dry nitrogen gas flow as the C2-H stretching overlaps with the HC4=C5H modes of the imidazolium ring. The nitrate asymmetric stretching bands (1343 and 1337 cm^{-1}) are assigned using the second derivative of the pure [OMIM][NO_3] spectrum (Fig. S6).

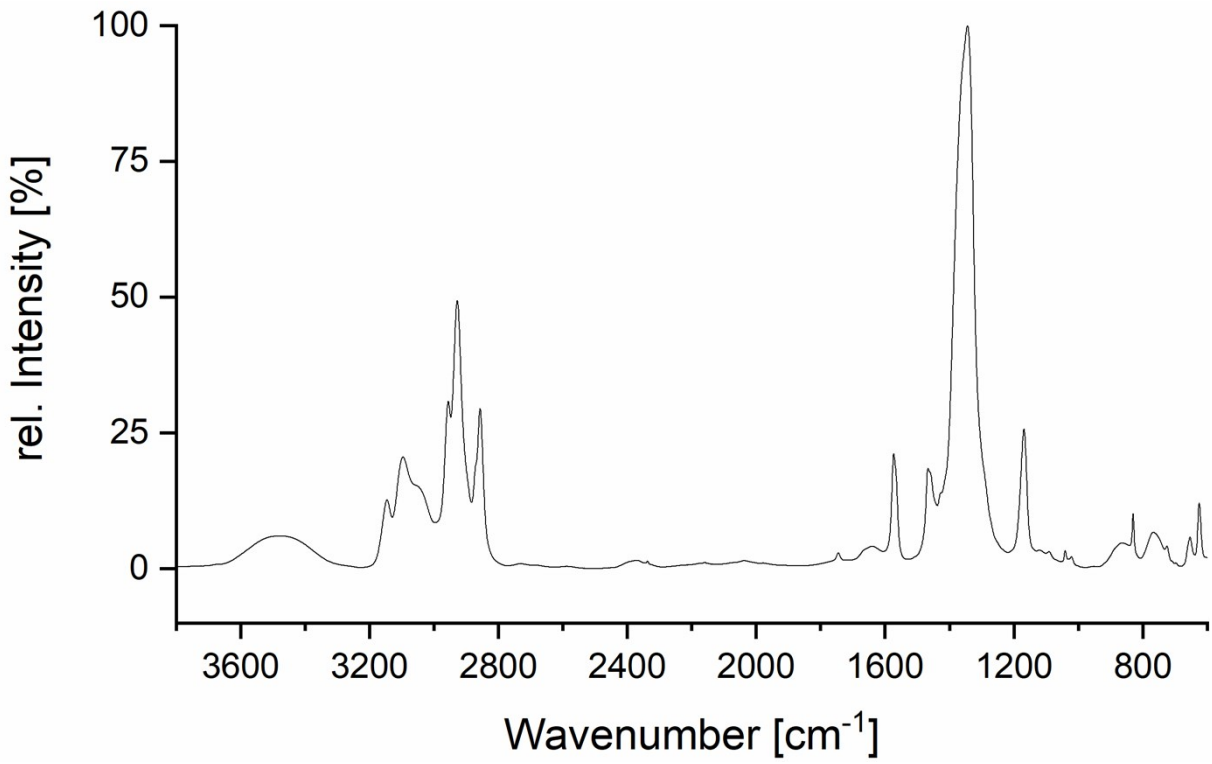


Fig. S5. IR spectrum of pure [OMIM][NO_3].

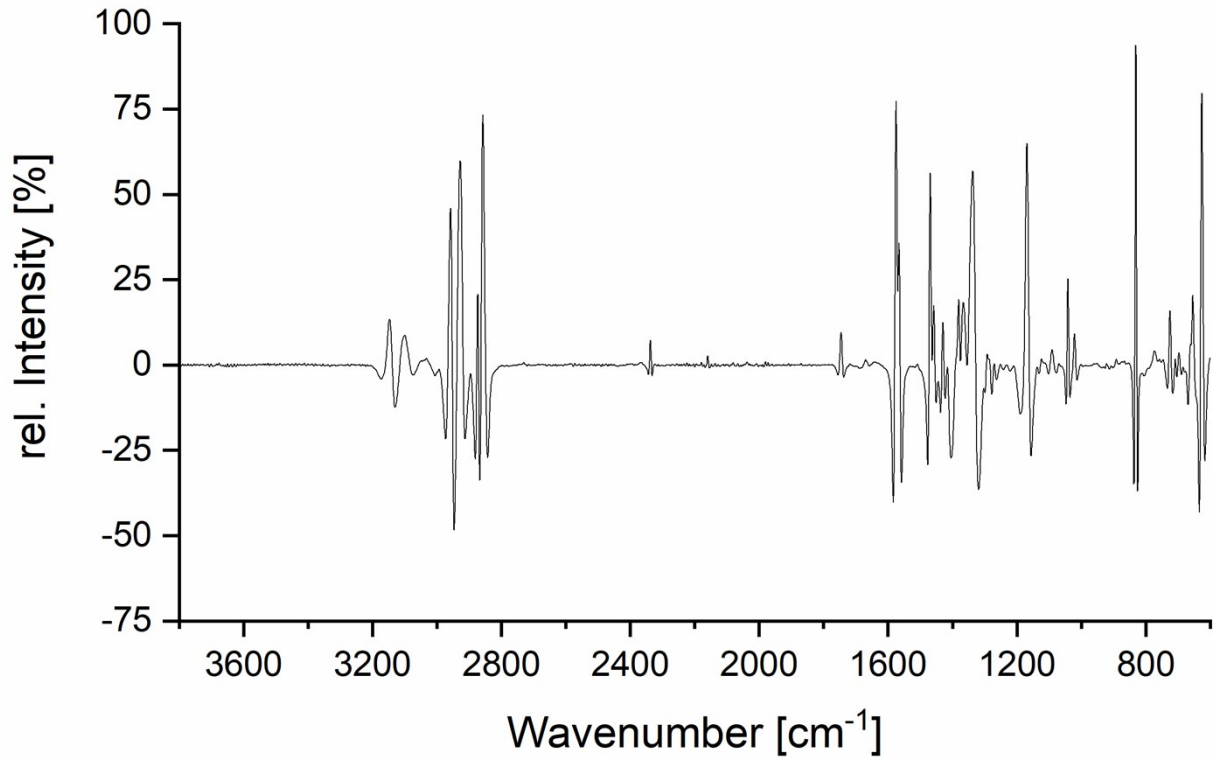


Fig. S6. Second derivative spectrum of Fig. S5.

With all peaks originating from the pure [OMIM][NO_3] ionic liquids, the catalytic mixtures were investigated. First, the interaction of H_2O_2 with $[NO_3]^-$ without any direct cationic contribution was investigated so an IR spectra of a KNO_3 solution in 50 wt.% aqueous H_2O_2 was recorded (Fig. S7). Subtraction of the pure H_2O_2 spectrum (Fig. S8) gives a sufficient shape of the asymmetric nitrate and the OH vibration band (Fig. S9).

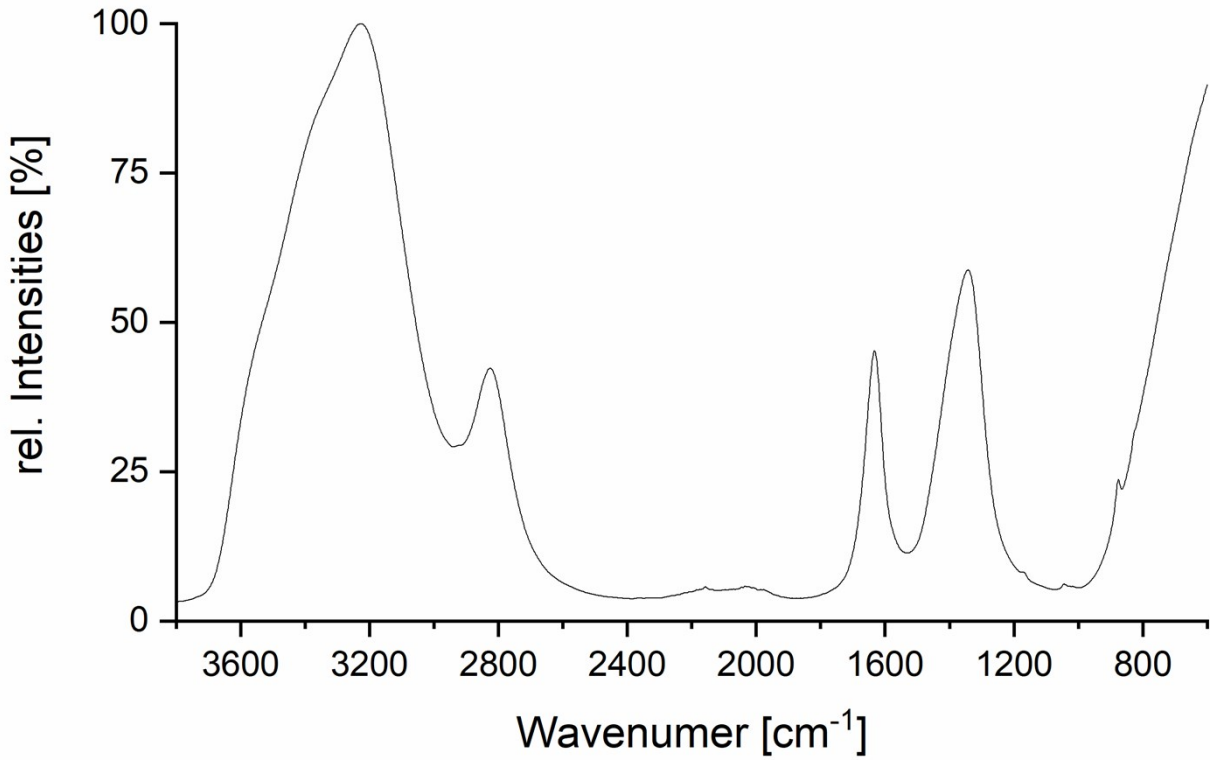


Fig. S7. IR spectrum of 357 mmol/L KNO_3 in 50 wt.% H_2O_2.

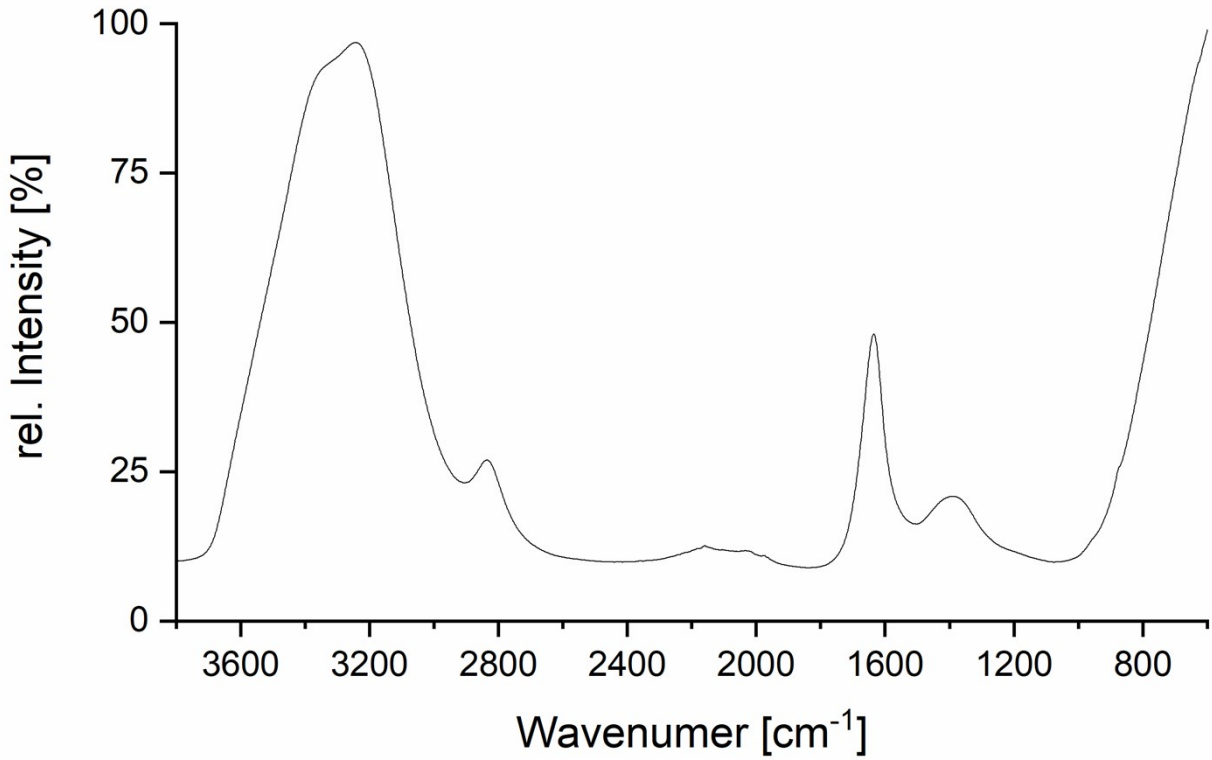


Fig. S8. IR spectrum of 50 wt.% H_2O_2.

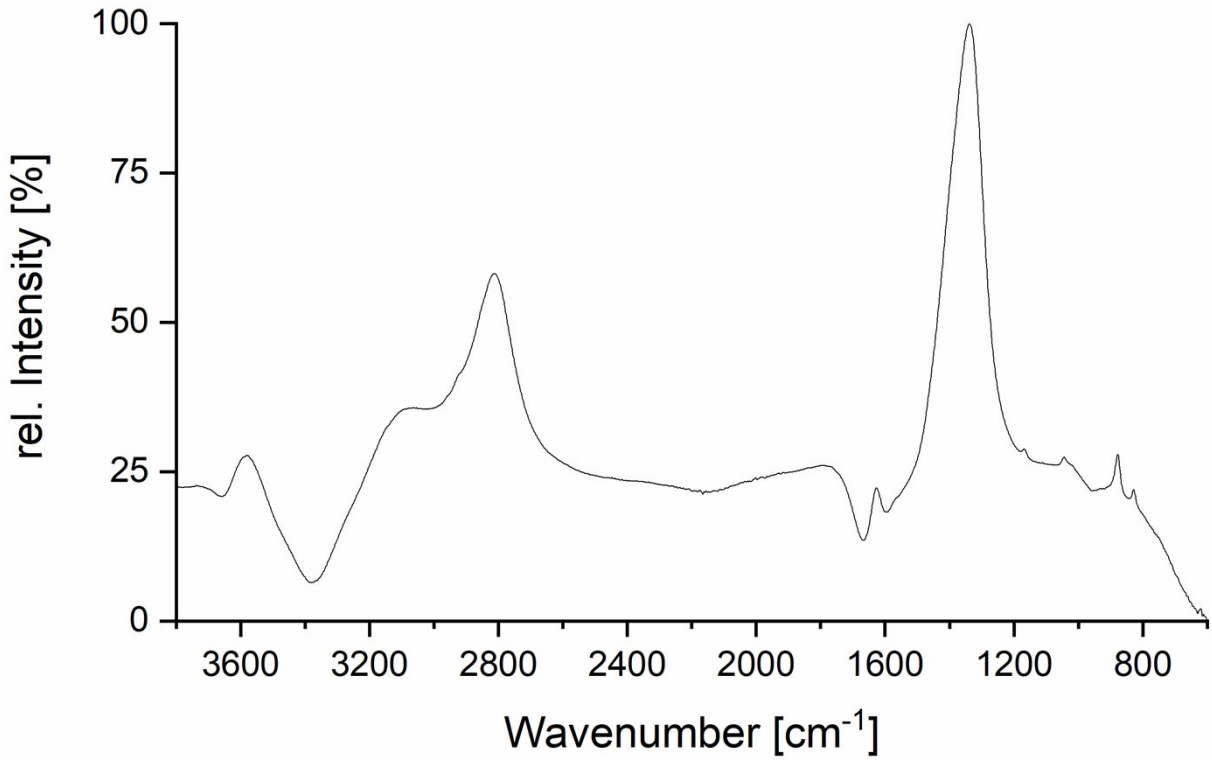


Fig. S9. IR difference spectrum of a solution of KNO_3 in aq. H_2O_2 (Fig. S7) and pure aq. H_2O_2 (Fig. S8).

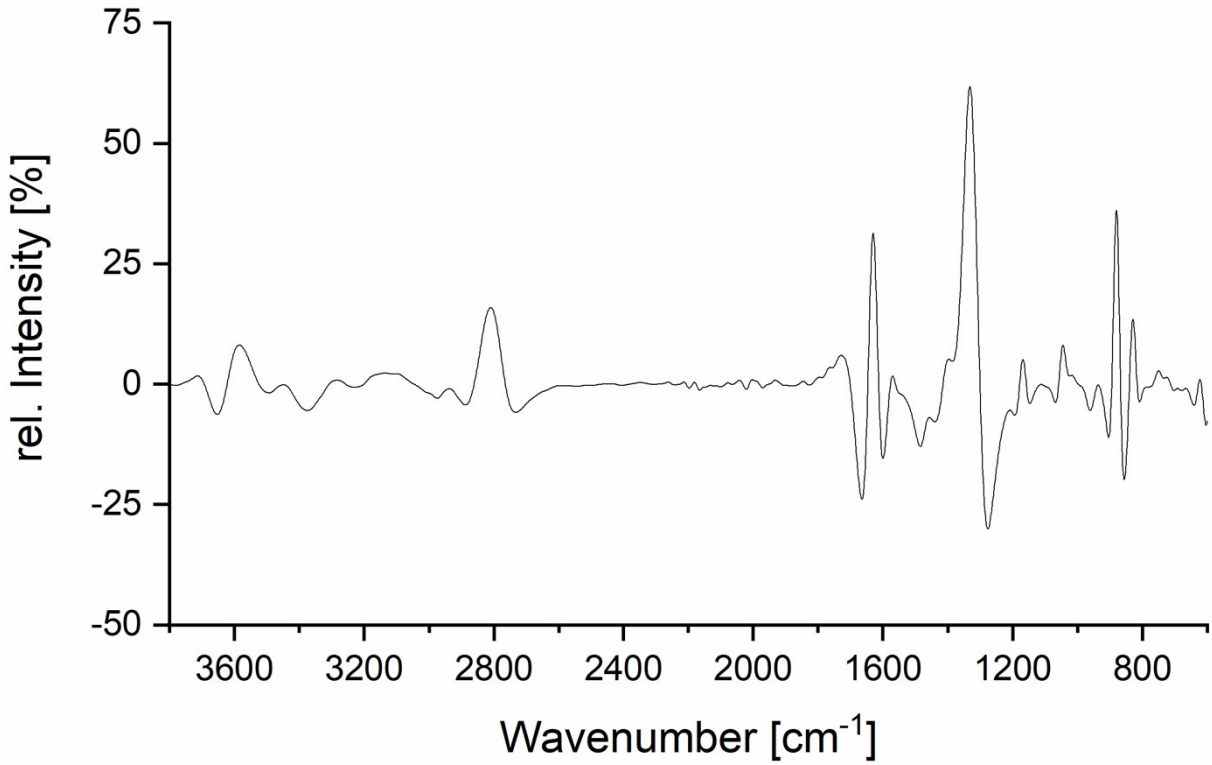


Fig. S10. Second derivative of the IR difference spectrum, shown in Fig. S9.

Using the second derivative spectra (Fig. S10) a nitrate splitting of 48 cm^{-1} was detected in 50 wt.% H_2O_2 with peaks at 1390 and 1342 cm^{-1}. In addition, the second derivative spectrum exhibit two well developed bands at 3444 and 3283 cm^{-1}. A reasonable assignment of this doublet can be the two vibrations of water coordinated to the nitrate. To verify this suggestion the earlier procedure was repeated e.g. from the IR spectrum of KNO_3 in aqueous solution the IR spectrum of pure water has been subtracted and the second derivative of residual spectrum was calculated (Fig. S11**,** upper spectrum) where for comparison the similar spectral features of KNO_3 in aq. H_2O_2 is shown (Fig. S11**,** lower spectrum). In the aqueous solution the symmetric OH stretching of H_2O_2, hydrogen bonded to the nitrate at 3110 cm^{-1} is missing and the characteristic doublet at 3432 and 3264 cm^{-1} is again detected. According to this experimental observation it can be stated clearly that these bands belong to H_2O hydrogen bonded to the nitrate anion.

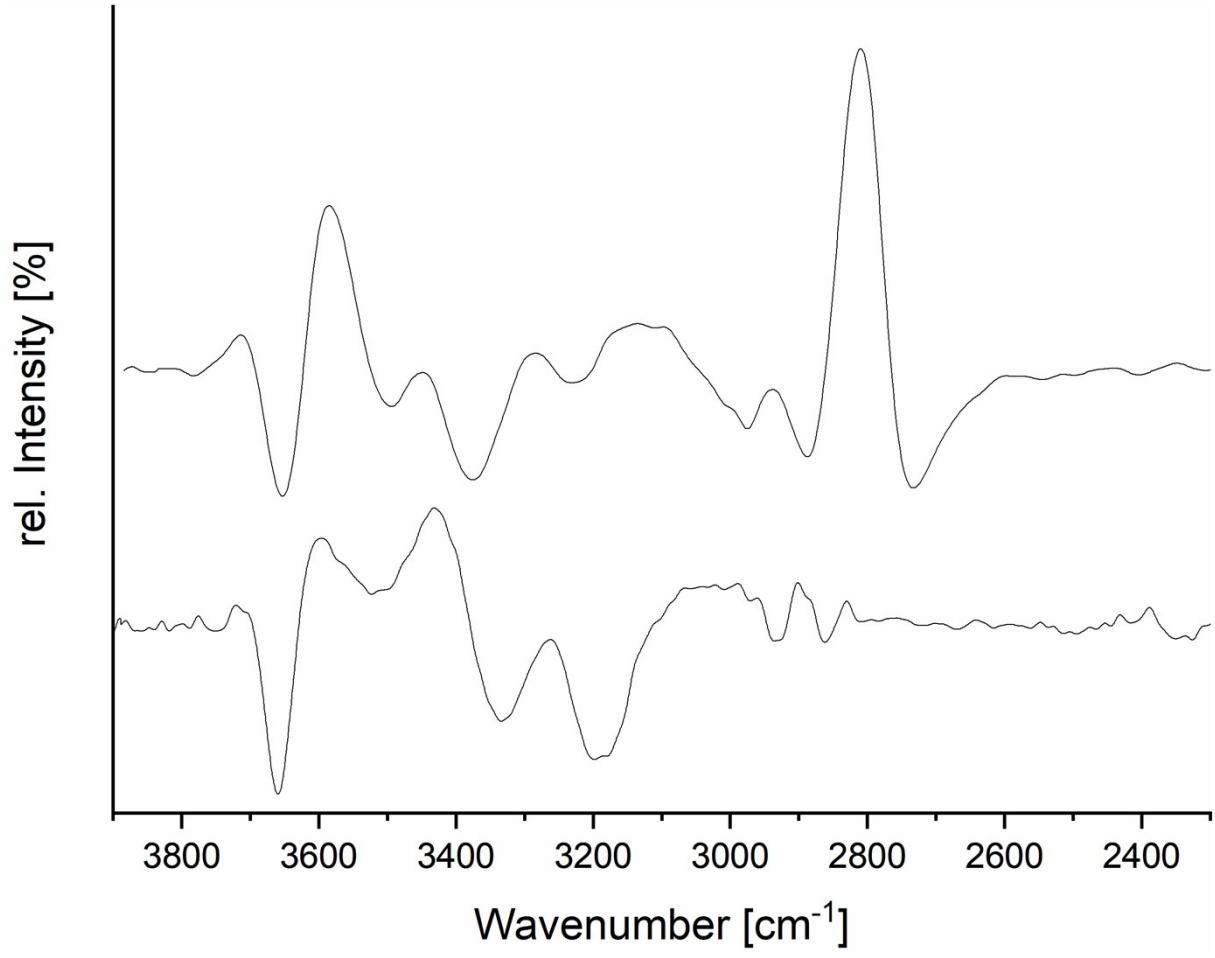


Fig. S11. Second derivative difference spectra of hydrogen peroxide solution of KNO_3 (357 mmol/L) minus pure hydrogen peroxide (upper spectrum) and water solution of KNO_3 minus pure water (lower spectrum) in the region of OH stretchings.

The assignment of this peaks allows for the investigation of this shift in an [OMIM][NO_3] solution in aqueous hydrogen peroxide. The difference spectrum of the solution of

[OMIM][NO_3] in 50 wt.% H_2O_2 (Fig. S12) and pure hydrogen peroxide (Fig. S8) were calculated (Fig. S13). Consequently, its second derivative spectrum (Fig. S14) is used to determine the [OMIM][NO_3]···H_2O_2 adduct peak, which is located at 3118 cm^{-1}, proving an the weakening of the H-O bond of aq. H_2O_2 compared to the KNO_3 solution (3129 cm^{-1}). Similarly, $[OMMIM]^+$ shows an asymmetric OH- Stretching at 3115 cm^{-1} suggesting a slightly stronger activation of H_2O_2 (See Fig. S16).

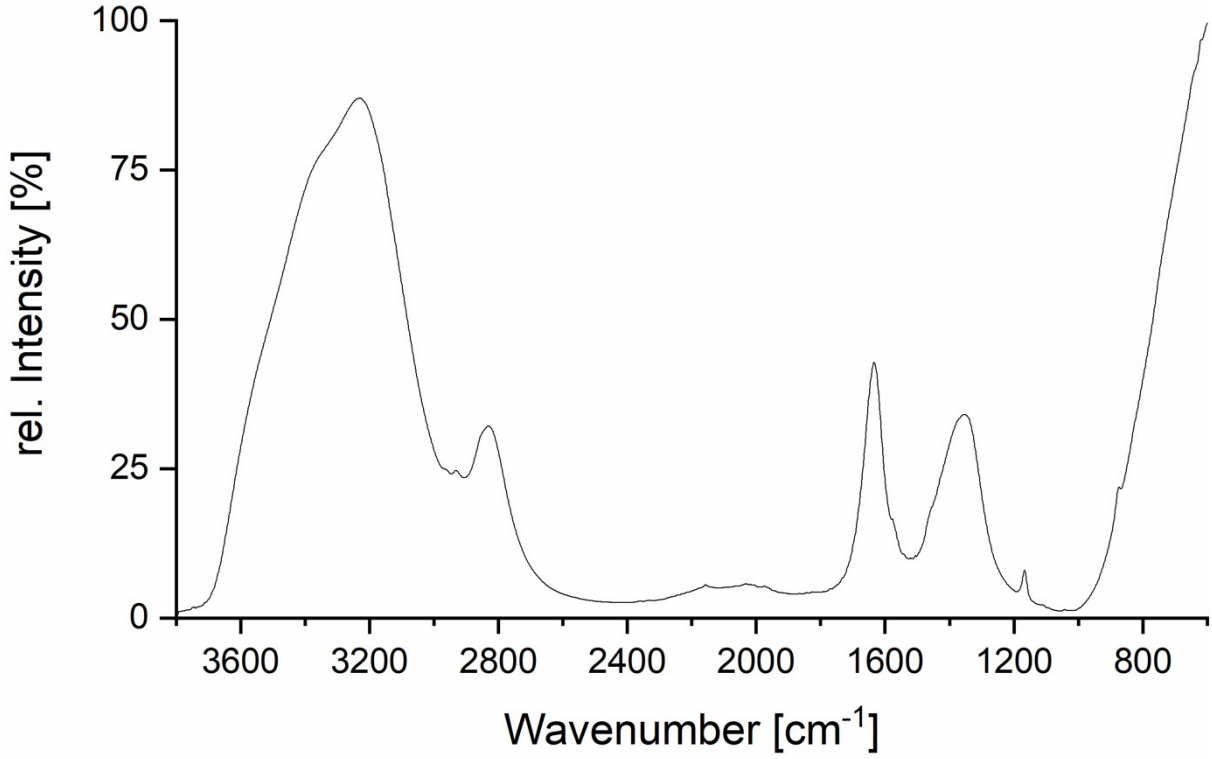


Fig. S12. IR spectrum of 357 mmol/L [OMIM][NO_3] in 50 wt.% H_2O_2.

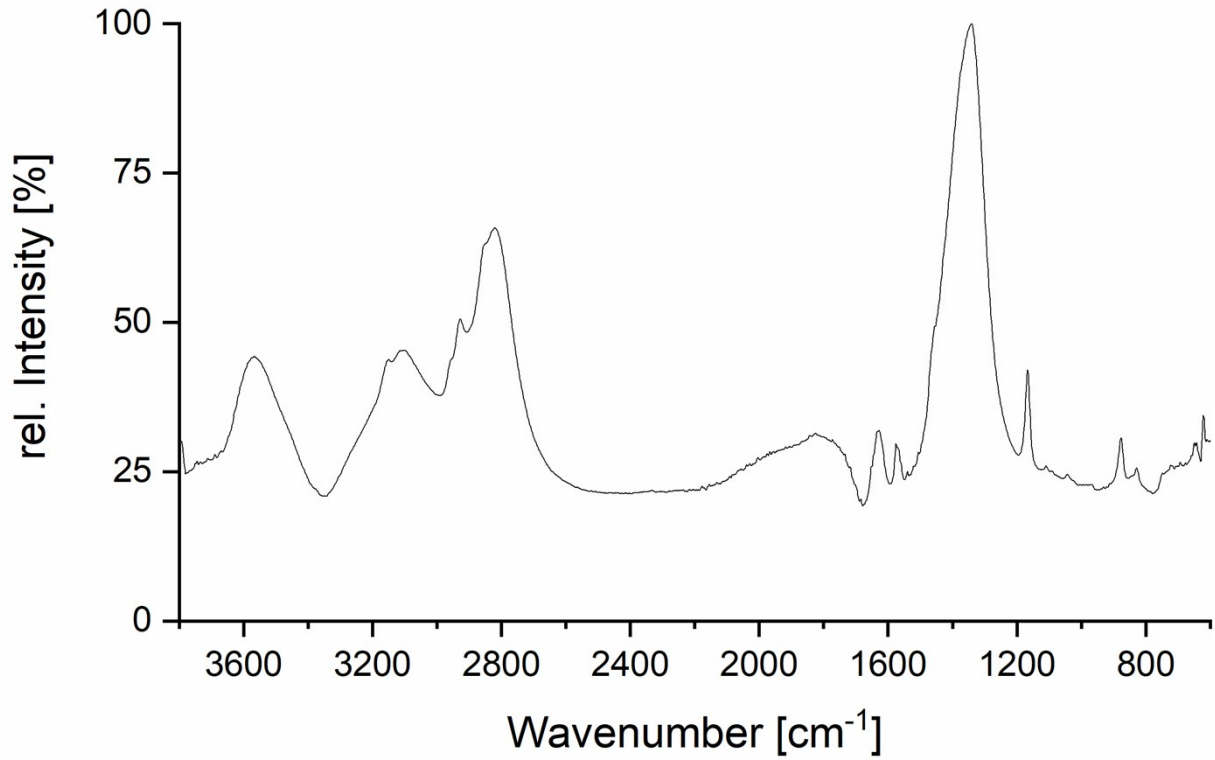


Fig. S13. IR difference spectrum of [OMIM][NO_3] (Fig. S12) and aqueous H_2O_2 (Fig. S8).

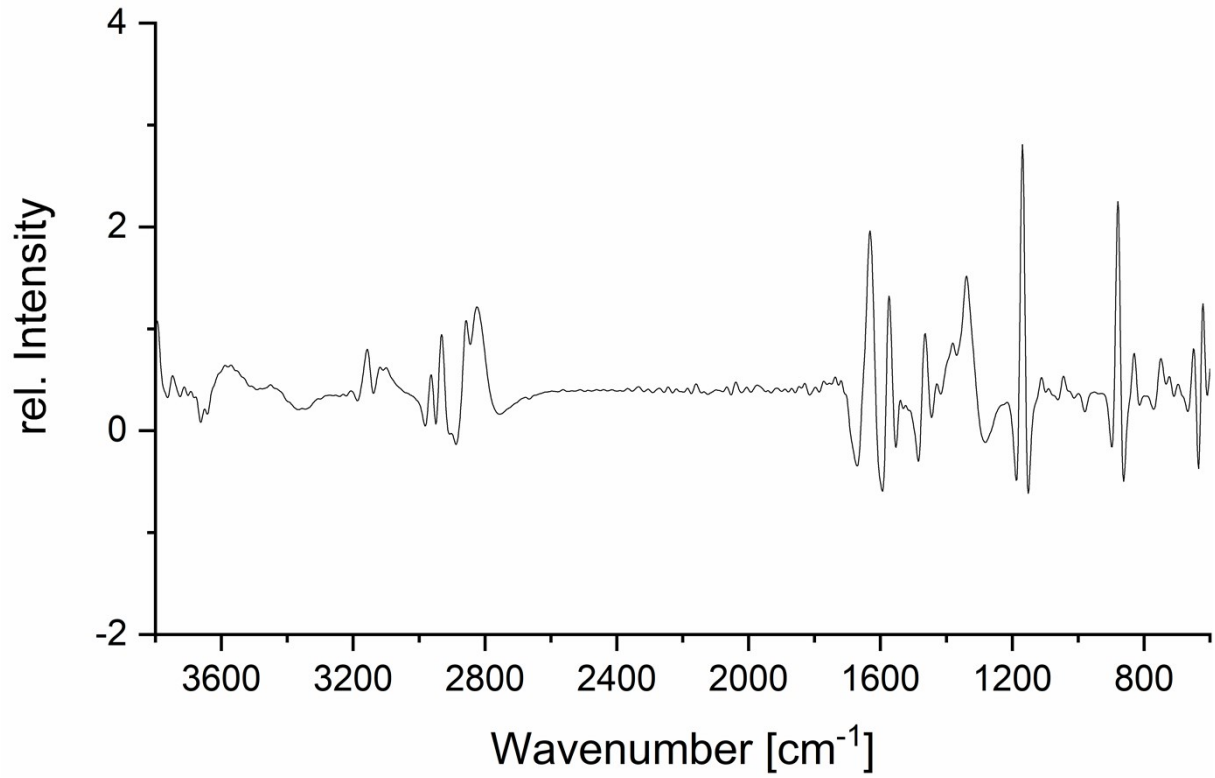


Fig. S14. Second derivative of the IR difference spectrum, shown in Fig. S13.

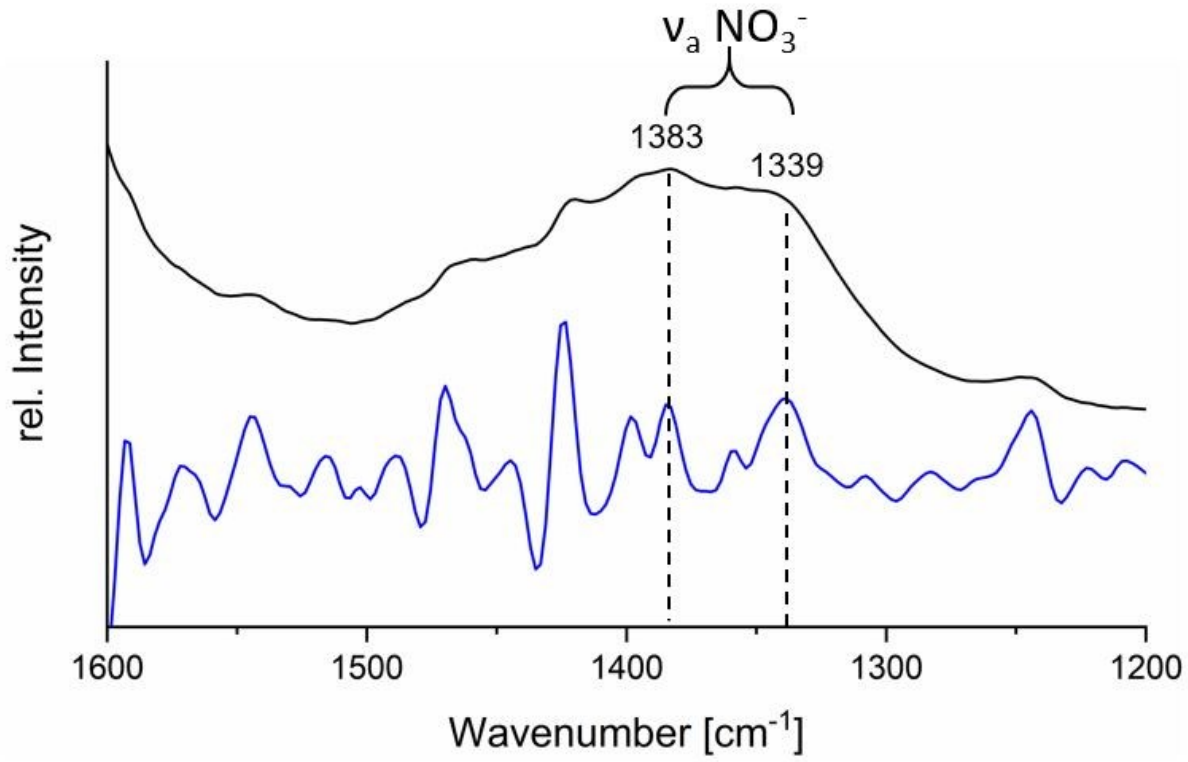


Fig. S15. Splitting of the asymmetric nitrate stretching for a solution of [OMMIM][NO_3] in 50 wt. % H_2O_2. Top: IR spectrum. Bottom: 2nd derivative of the IR spectrum.

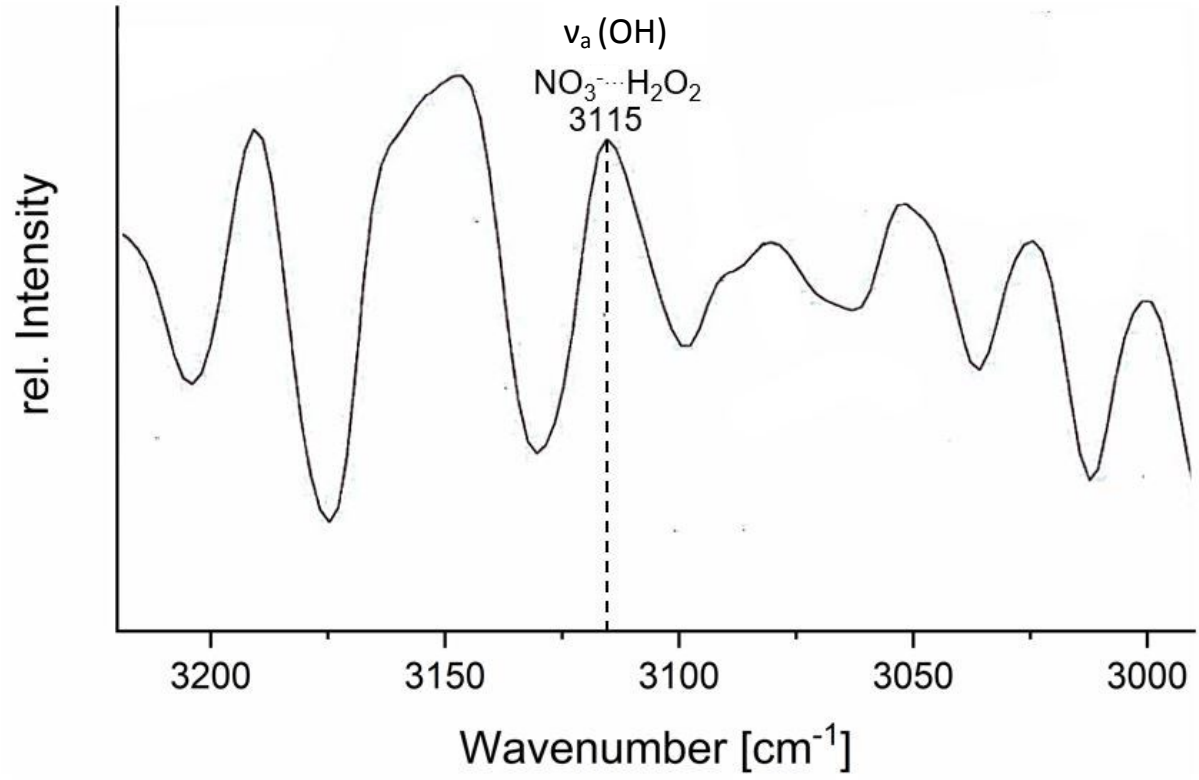


Fig. S16. Second derivative spectrum of a solution of [OMMIM][NO_3] in 50 wt.% aq. H_2O_2 in the OH stretching region.

Force field study of hydrogen peroxide in various systems

Infrared and Raman spectra of H_2O_2 have been widely studied [6,7,8] and normal coordinate calculations of the H_2O_2 and D_2O_2 have been reported by several publications.[8,9,10] All coordinated H_2O_2 molecules in the studied aqueous systems belong to the $\boldsymbol{C_2}$ point group and the irreducible representation is 4***A*** + 2***B***. If we consider the molecules as having non-planar symmetry ($\boldsymbol{C_2}$), then all the 6 fundamentals should appear both in the IR and Raman spectra as well. This is in good agreement with our experimental observations (see Table S5). A clear trend was observed for the OH stretching modes (ν_1 and ν_5, Table S5). Both experimental frequencies exhibit the following trend: H_2O_2 (gas) >> H_2O_2/H_2O (liquid) > KNO_3/H_2O_2 > [OMIM][NO_3]/H_2O_2 > [OMMIM][NO_3]/H_2O_2 . It is clear that the lower the OH stretching is, the stronger is the $[NO_3]^{-}\cdots H_2O_2$ hydrogen bond. Both, the two OOH bendings (ν_3 and ν_6) and the O-O stretching (ν_2) frequencies are shifted up compared to those of gaseous H_2O_2 upon formation of hydrogen bonds.

Table S5. Summary of fundamental modes (cm^{-1}) of H_2O_2 in different systems.

H_2O_2 (gas) [d]	H_2O_2/H_2O (liq) [a]	KNO_3/H_2O_2 [b]	$[OMIM][NO_3]/H_2O_2$ [b]	$[OMMIM][NO_3]/H_2O_2$ [b]	Assignments
3606	3177	3169	3157	3158	A, OH sym stretch (ν_1)
3608	3147	3129	3118	3115	B, OH asym stretch (ν_5)
1394	1445	1458	1396	1398	A, OH sym deform (ν_3)
1266	1367	(1350)[c]	(1356)[c]	(1358)[c]	B, OH asym deform (ν_6)
86	877	877	879	879	A, O-O stretch (ν_2)
351	237	616	661	649	A, HOOH torsion (ν_4)
-	-	213	231	211	$NO_3\cdots H_2O_2$ stretching (external mode)

[a] Infrared spectral data after subtraction of liquid H_2O spectrum.

[b] Infrared spectral data after subtraction of liquid H_2O_2/H_2O (liquid) spectrum.

[c] Band positions are uncertain due to the overlap with $[NO_3]^-$ antisymmetric stretching bands.

[d] Fundamental frequencies of gaseous H_2O_2 were taken from Ref. 8

Table S6. Calculated internal and external force constants of H_2O_2 in different systems and estimating OH and O-O relative bond orders.

Force constants	Descriptions	H_2O_2 gas	H_2O_2/ H_2O (liq)	KNO_3 / H_2O_2	[OMIM] $[NO_3]$/ H_2O_2	[OMMIM] $[NO_3]$/ H_2O_2	Unit [a]
K(OH) (fr)	Stretching, diagonal	7.531	5.415	5.434	5.387	5.379	x
F(OH, OH) (frr)	Stretch–stretch, interaction	-0.141	-0.117	-0.032	-0.039	-0.038	x
K(O-O) (f_R)	Stretching, diagonal	3.798	3.915	3.970	3.938	3.938	x
H(OOH) (fα)	Deformation, diagonal	0.953	1.115	1.133	1.079	1.183	y
h(OH, OH) (fαα)	Def.-def. interaction	0.151	0.168	0.243	0.179	0.179	y
τ(HOOH) (fχ)	Torsion, diagonal	0.025	0.014	0.097	0.111	0.108	y
T(NO_3···H_2O_2) [b]	Translation of H_2O_2	-	-	0.513	0.603	0.503	x
n(OH) [c]	OH bond order	1.00	0.719	0.722	0.715	0.714	-
n(OO) [c]	O-O bond order	1.00	1.031	1.045	1.037	1.037	-

[a] Units: x ≡ $10^2 Nm^{-1}$ (Ncm^{-1}); y ≡ 10^{-18} Nm rad^{-2}.

[b] External translational force constants were calculated by using molecular weights of NO_3^- and H_2O_2.

[c] Relative bond orders were calculated on the basis fitted OH and O-O stretching force constants. The bond orders of gaseous H_2O_2 were set as 1.00.

Six force constants were obtained from six experimental frequencies, which are listed in Table S 6. The stretch-stretch interaction force constants F(OH,OO)= 0.304 Ncm^{-1} and the stretch-bend term f(OH, OOH)= -0.422 10^{-8} $Nrad^{-1}$ was constrained to the values of gaseous H_2O_2.[8]

The HOOH torsion mode (ν_4) exhibit strong correlation with the φ dihedral angle in agreement with the DFT calculations. In case of H_2O_2(gas) and H_2O_2/H_2O(liquid) the dihedral angles are close to 120° and rather low torsion frequencies were detected at 315 and 237 cm^{-1}, respectively. In the cases when H_2O_2 is hydrogen bonded to the NO_3^- counter ion, the calculated torsion angles are close to ~40° and this mode is shifted up to ~600 cm^{-1} as a consequence of the formed strain structure of H_2O_2. The

major results of normal coordinate calculation are summarized in Table S6. The OH stretching force constants are about 30% smaller in all aqueous systems comparing to gaseous H_2O_2. The existence of strong hydrogen bonds is clearly reflected by the relatively low OH bond orders (n) comparing to those of H_2O_2 (gas) with n=1.00 value set as reference.

It can be seen that most of the force constants of neat H_2O_2/H_2O (liquid) are out of the trend with those of NO_3^- containing adducts. In spite of the fact that highest OH stretching frequencies were recorded for H_2O_2/H_2O (liquid) solution, the fitted OH stretching force constant is the lowest 5.415 Ncm^{-1}. This effect can be partly explained by the big difference in torsion angle of H_2O_2 (φ = 121.2°) comparing to NO_3^- systems (φ = 40-47°). This geometrical difference modifies some of the G-matrix elements leading to decreasing the K(OH) force constant.

Weakening of the (OH) bonds by formation of hydrogen bonds leads to strengthening of the O-O bonds. The O-O bond orders are increased about 3-4% in hydrogen bonded H_2O_2. It is interesting to discuss the translational (stretching) vibrations between $[NO_3]^-\cdots H_2O_2$. The calculated (DFT) and observed frequencies are just over ~200 cm^{-1} (see Table S 5) and the calculated external force constants (T) are between 0.5-0.6 Ncm^{-1} (Table S 6). It can be seen that $[OMIM][NO_3]\cdots H_2O_2$ exhibits the highest frequency (231 cm^{-1}) and force constant (0.603 Ncm^{-1}) in this series. The enhancement of this bonding can be explained with the presence of the C2-H proton in the imidazolium ring, which is forming an additional hydrogen bond with the oxygen atom of the hydrogen peroxide. In the $C2\text{-}H\cdots O_2H_2$ interaction the H···O distance is 2.572 Å, short enough to form a hydrogen bond. As a comparison, the DFT-calculated (M06GD3-SMD level of theory, vide infra) distance is 2.34 Å and the OH···O distance in the crystalline H_2O_2 is 2.78 Å obtained by X-Ray diffraction.[11] The three NO_3^- containing systems exhibit a clear trend in the OH stretching force constants as KNO_3/H_2O_2 > $[OMIM][NO_3]/H_2O_2$ > $[OMMIM][NO_3]/H_2O_2$. The very small difference between $[OMIM][NO_3]/H_2O_2$ and $[OMMIM][NO_3]/H_2O_2$ adducts a good explanation of their similar catalytic activity. In the KNO_3/H_2O_2 solution the hydrogen peroxide forms the weakest hydrogen bonds with $[NO_3]^-$ and this is most likely the explanation of its inactivity as catalyst.

The refined OH stretching force constants of the above system exhibit a clear correlation with the OH bond lengths ($1/r^3$) illustrated by Fig. S17.

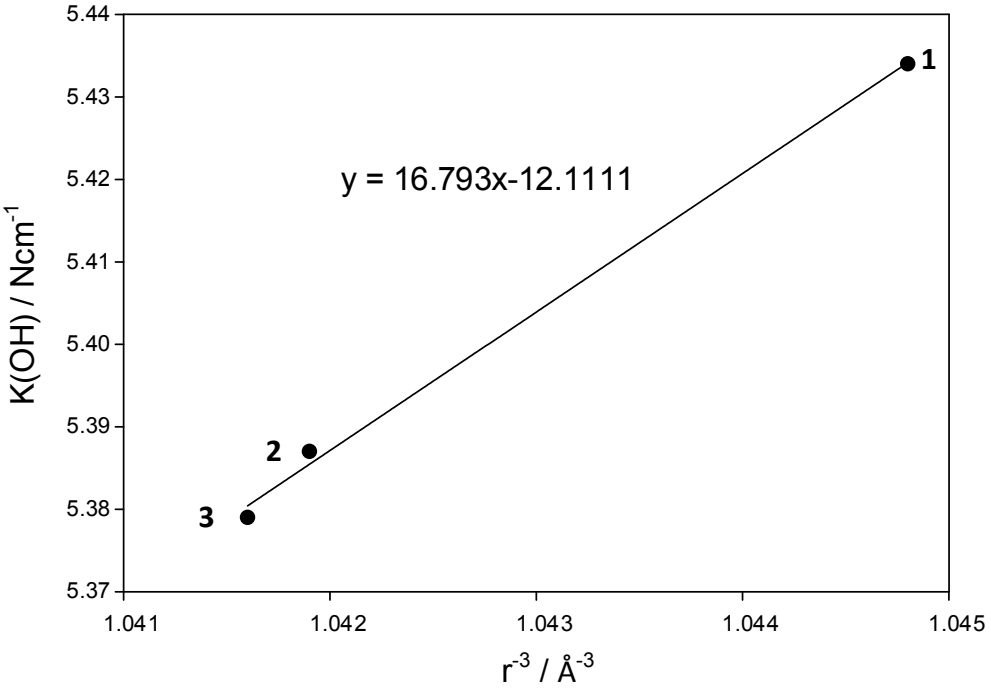


Fig. S17. Correlation between OH stretching force constants of hydrogen bonded H_2O_2 to $[NO_3]^-$ in (1) KNO_3/H_2O_2, (2) $[OMIM][NO_3]/H_2O_2$, (3) $[OMMIM][NO_3]/H_2O_2$ to the inverse of third power of the averaged OH bond lengths (r^{-3}).

5. DFT calculations: xyz coordinates, images and absolute energies

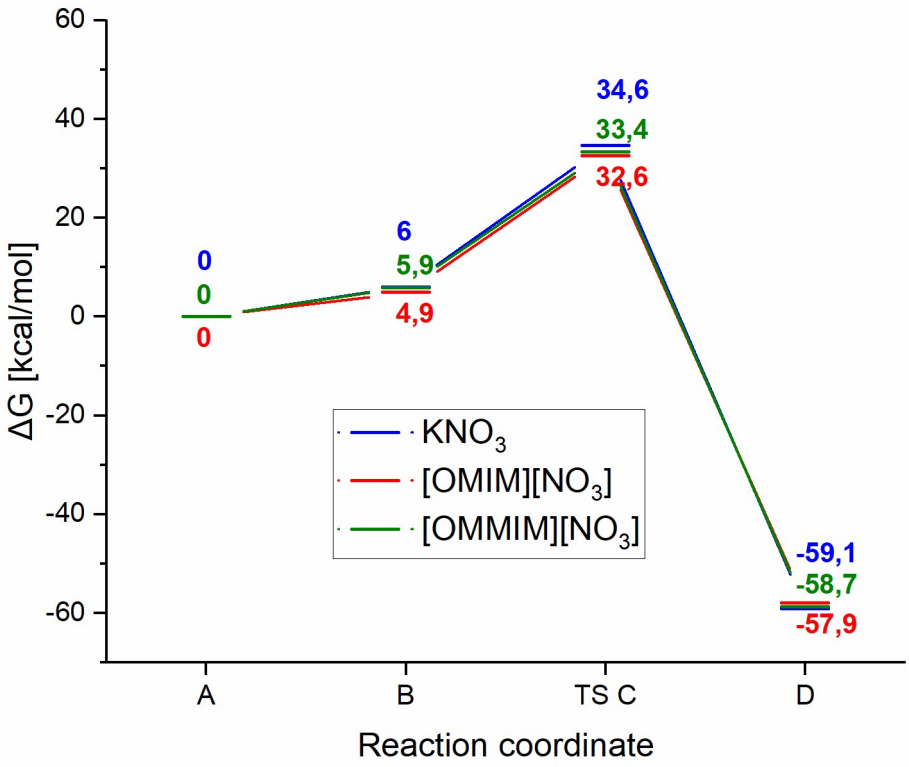
5.1. Computational details

All calculations have been performed using the Gaussian 09 and 16 software.[12] The DFT level of theory chosen consist of the hybrid functional B3LYP[13,14,15,16] or M06[17] with the dispersion correction GD3[18] and the basis set 6-311+G**.[19,20] This combination is very common for metal-free systems. No PCM solvation effects have been applied, because a micelle cannot be compared to a “normal” solvation situation. Therefore, we chose the gas-phase settings which have been applied previously for theoretic H-bond investigation in ionic liquids.[21,22] Additionally, for the M06DG3 calculations the solvation model by density (SMD)[23] in water was applied for the reason that the majority of the solvent molecules are water molecules and hydrogen peroxide is part of the calculated structures.

All the reported ΔG values are unscaled and calculated for 298.15 K. The frequency calculations have been also applied to characterize if an optimized structure is a ground state (number of imaginary frequencies=0) or a transition state (number of imaginary frequencies=1). The determination of frequencies of all the calculated ground states have also been used to identify the IR and Raman active signals of the vibrational spectra. Besides the imaginary frequency, we utilized IRC calculations to ensure that the transition state ensures the connection of the relevant minima.[24,25]

5.2. Energetic DFT calculations

Free energy diagram for the epoxidation of COE with nitrate catalysts. Calculated with the M06GD3/6-311+G** SMD (water) level of theory.



Scheme S1. Free energy surface for the oxidation of cyclooctene in nitrate catalysis. Blue= KNO_3, red= [OMIM][NO_3], green = [OMMIM][NO_3].

The free energy calculations reveal that is not feasible to calculate the reaction pathway for a 'naked' nitrate ion (Table S7). The negative charge has to be compensated by an alkali cation, likely potassium, as solutions of KNO_3 in aq. H_2O_2 have been investigated by vibrational spectroscopy.

The activation energy (of transition state C) is higher for the epoxidation of ethylene with KNO_3 involving the sophisticated M06GD3-SMD level of theory compared to [OMMIM][NO_3] and [OMIM][NO_3]. This is in good agreement with the spectroscopic results of the H_2O_2-activation. As the effect is drastically oppositional for the B3LYP (gas-phase) calculations, it can be concluded, that the this functional is not suitable for the comparison of homogeneous and micellar systems. Nevertheless, it might be a fast method to estimate the relative energy differences of micellar systems as the transition state energies for the ethylene epoxidation are identical (36.4 kcal/mol). Calculations with cyclooctene are slightly lower in transition state energies than those for ethylene with M06-GD3-SMD, while the difference is larger for the gas-phase calculations.

Table S7. Free energy evaluation (kcal/mol) of the H_2O_2 activation with nitrate.

System/Olefin/ Level of Theory	H_2O_2/nitrate complex A	Olefin/H_2O_2/ nitrate complex B	Transition State C	H_2O/nitrate complex D
'Naked' $[NO_3]^-$/Ethene				
gas-phase[a]	ΔG= 0.0	ΔG= +4.6	$\Delta G^{\#}$= +45.6	ΔG= -41.1
'Naked' $[NO_3]^-$/COE				
gas-phase[a]	ΔG= 0.0	ΔG= +5.2	$\Delta G^{\#}$= +42.3	ΔG= -45.2
KNO_3/Ethene				
gas-phase[a]	ΔG= 0.0	ΔG= +5.2	$\Delta G^{\#}$= +29.9	ΔG= -45.4
solvent[b]	ΔG= 0.0	ΔG= +6.0	$\Delta G^{\#}$= +34.6	ΔG= -59.1
KNO_3/COE				
gas-phase[a]	ΔG= 0.0	no convergence	$\Delta G^{\#}$= +25.9	ΔG= -49.4
solvent[b]	ΔG= 0.0	ΔG= +5.5	$\Delta G^{\#}$= +23.4	ΔG= -63.7
[OMIM][NO_3]/Ethene				
gas-phase[a]	ΔG= 0.0	ΔG= +7.5	$\Delta G^{\#}$= +36.4	ΔG= -44.0
solvent[b c]	ΔG= 0.0	ΔG= +4.9	$\Delta G^{\#}$= +32.6	ΔG= -57.9
[OMIM][NO_3]/COE gas-phase[a]	ΔG= 0.0	ΔG= +4.8	$\Delta G^{\#}$= +29.8	ΔG= -48.9
[OMMIM][NO_3]/Ethene				
gas-phase[a]	ΔG= 0.0	ΔG= +5.9	$\Delta G^{\#}$= +36.4	ΔG= -44.6
solvent[b]	ΔG= 0.0	ΔG= +5.9	$\Delta G^{\#}$= +33.4	ΔG= -58.7
[OMMIM][NO_3]/COE				
gas-phase[a]	ΔG= 0.0	ΔG= +3.8	$\Delta G^{\#}$= +33.7	ΔG= -48.7

Note: Complex A is chosen as the zero point to complete the full catalytic cycle.
a: B3LYP/6-311++G** (gas-phase)

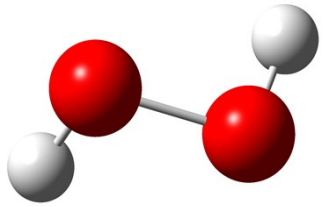
b: M06GD3/6-311+G** with SMD for water

c: Structural isomers with the energetic most favorable geometry taken (see discussion below)

5.3. Calculated structures

5.3.1. Substrates and small products

H_2O_2 (charge=0, multiplicity=1)



B3LYP/6-311++G** (gas-phase)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.727259	-0.052098
2	1	0	0.827608	0.902617	0.416788
3	8	0	0.000000	-0.727259	-0.052098
4	1	0	-0.827608	-0.902617	0.416788

Sum of electronic and thermal Enthalpies= -151.571439

Sum of electronic and thermal Free Energies= -151.597284

HF= -151.6020644 / NImag=0

M06GD3/6-311++G** (SMD, water)

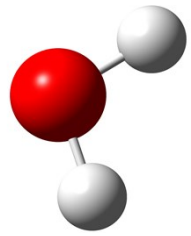
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.000000	-0.711153	-0.069199
2	1	0	-0.711286	-0.925414	0.553592
3	8	0	0.000000	0.711153	-0.069199
4	1	0	0.711286	0.925414	0.553592

Sum of electronic and thermal Enthalpies= -151.507854

Sum of electronic and thermal Free Energies= -151.533604

HF=-151.5387944 / NImag=0

H_2O (charge=0, multiplicity=1)



B3LYP/6-311++G** (gas-phase)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.000000	0.763339	-0.468462
2	8	0	0.000000	0.000000	0.117115
3	1	0	0.000000	-0.763339	-0.468462

Sum of electronic and thermal Enthalpies= -76.433399

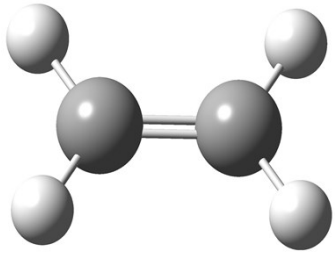
Sum of electronic and thermal Free Energies= -76.454822

HF= -76.4584627 / NImag=0

M06GD3/6-311++G** (SMD, water)

Not required

Ethene (charge=0, multiplicity=1)



B3LYP/6-311++G** (gas-phase)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	-0.664413	0.000000	-0.000004
2	6	0	0.664413	0.000000	0.000003
3	1	0	-1.235177	0.922705	0.000011
4	1	0	-1.235177	-0.922706	-0.000022
5	1	0	1.235177	-0.922705	-0.000009
6	1	0	1.235177	0.922706	0.000023

Sum of electronic and thermal Enthalpies= -78.560741

Sum of electronic and thermal Free Energies= -78.586906

HF= -78.6155126 / NImag=0

M06GD3/6-311++G** (SMD, water)

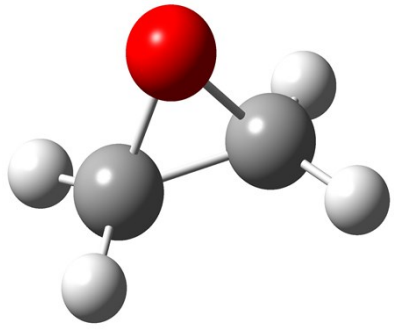
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.662179	0.000000	0.000004
2	6	0	0.662179	0.000000	-0.000003
3	1	0	-1.234853	-0.923967	-0.000011
4	1	0	-1.234853	0.923968	0.000022
5	1	0	1.234853	0.923967	0.000010
6	1	0	1.234853	-0.923968	-0.000024

Sum of electronic and thermal Enthalpies= -78.482075

Sum of electronic and thermal Free Energies= -78.508255

HF=-78.5363479 / NImag=0

Ethene oxide (charge=0, multiplicity=1)



B3LYP/6-311++G** (gas-phase)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.665642	-0.484920	0.000000
2	6	0	0.000000	0.822855	0.000000
3	8	0	0.762535	-0.387516	0.000000
4	1	0	-1.102377	-0.864178	0.919979
5	1	0	-1.102377	-0.864178	-0.919979
6	1	0	0.049164	1.400440	0.919350
7	1	0	0.049164	1.400440	-0.919350

Sum of electronic and thermal Enthalpies= -153.774812

Sum of electronic and thermal Free Energies= -153.803006

HF= -153.8360401 / NImag=0

M06GD3/6-311++G** (SMD, water)

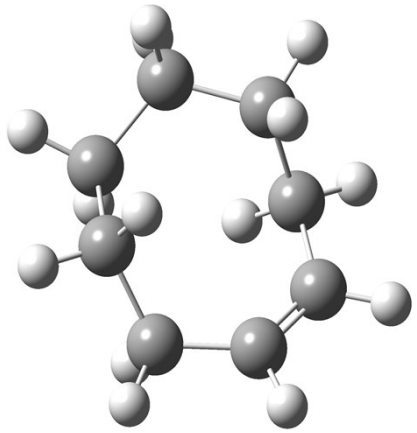
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.662216	-0.477174	0.000000
2	6	0	0.000000	0.815884	0.000000
3	8	0	0.758458	-0.388201	0.000000
4	1	0	-1.098565	-0.855263	0.921539
5	1	0	-1.098565	-0.855263	-0.921539
6	1	0	0.051383	1.391937	0.921016
7	1	0	0.051383	1.391937	-0.921016

Sum of electronic and thermal Enthalpies= -153.679237

Sum of electronic and thermal Free Energies= -153.707400

HF=-153.7404598 / NImag=0

Cis-Cyclooctene (charge=0, multiplicity=1)



B3LYP/6-311++G** (gas-phase)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.972835	-0.003794	-0.119322
2	6	0	1.201350	-1.230123	0.402955
3	6	0	-1.352841	1.335766	-0.034262
4	6	0	-0.056419	-1.681955	-0.373684
5	6	0	-1.937800	0.145993	-0.198907
6	6	0	-1.417509	-1.214641	0.212268
7	1	0	2.537767	-0.290721	-1.014268
8	1	0	0.922143	-1.067228	1.450075
9	1	0	0.012123	-1.388283	-1.426661
10	1	0	-1.888014	2.207712	-0.404412
11	1	0	-2.912575	0.141971	-0.681592
12	1	0	2.724833	0.252188	0.636993
13	1	0	1.914222	-2.061534	0.426819
14	1	0	-0.074007	-2.776529	-0.369098
15	1	0	-2.174024	-1.951503	-0.072006
16	1	0	-1.352961	-1.271297	1.307251
17	6	0	1.155879	1.258278	-0.459267
18	1	0	0.716384	1.150183	-1.454799
19	1	0	1.852369	2.099848	-0.530848
20	6	0	0.015777	1.601398	0.543299
21	1	0	0.154397	1.034110	1.469901

```
    22          1           0        0.079714    2.655556    0.824166
Sum of electronic and thermal Enthalpies=            -313.129140
Sum of electronic and thermal Free Energies=         -313.170539
HF= -313.3410823 / NImag=0
```

M06GD3/6-311++G** (SMD, water)

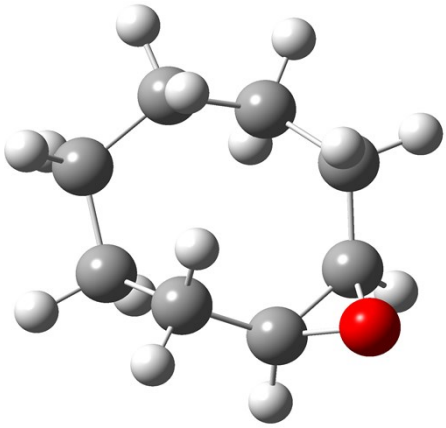
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.960588	-0.072873	-0.109561
2	6	0	-1.240603	1.169064	0.407067
3	6	0	1.396905	-1.279797	-0.024758
4	6	0	-0.016190	1.645502	-0.382032
5	6	0	1.935052	-0.071571	-0.192364
6	6	0	1.351230	1.254222	0.210180
7	1	0	-2.552429	0.195578	-0.995669
8	1	0	-0.943449	1.014799	1.453369
9	1	0	-0.078473	1.314554	-1.428255
10	1	0	1.963973	-2.137422	-0.387689
11	1	0	2.913503	-0.028349	-0.671120
12	1	0	-2.688575	-0.379033	0.654829
13	1	0	-1.980368	1.978629	0.440574
14	1	0	-0.041708	2.740855	-0.417759
15	1	0	2.075680	2.028427	-0.064818
16	1	0	1.271983	1.306658	1.306911
17	6	0	-1.082614	-1.267328	-0.471997
18	1	0	-0.629913	-1.097672	-1.457150
19	1	0	-1.728960	-2.144328	-0.593906
20	6	0	0.040577	-1.573289	0.540553
21	1	0	-0.121216	-0.991249	1.458267
22	1	0	-0.002661	-2.625022	0.839882

Sum of electronic and thermal Enthalpies= -312.866932

Sum of electronic and thermal Free Energies= -312.908144

HF=-313.0772259 / NImag=0

Cis-cyclooctene oxide (charge=0, Multiplicity=1)



B3LYP/6-311++G** (gas-phase)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.169206	-0.582858	0.042241
2	6	0	1.805647	0.831244	-0.454538
3	6	0	-1.385600	-0.897479	0.267610
4	6	0	0.787573	1.667840	0.358035
5	6	0	-1.558831	0.550415	0.452420
6	6	0	-0.669939	1.612918	-0.164440
7	1	0	2.835537	-0.494171	0.908288
8	1	0	1.451459	0.774486	-1.489869
9	1	0	0.822201	1.394105	1.419522
10	1	0	-1.771700	-1.534713	1.065416
11	1	0	-2.066426	0.860275	1.366179
12	1	0	2.770424	-1.051541	-0.745931
13	1	0	2.747293	1.388031	-0.508039
14	1	0	1.109388	2.712478	0.315499
15	1	0	-1.150459	2.580447	0.013360
16	1	0	-0.665075	1.476109	-1.249342
17	6	0	1.024348	-1.540693	0.429957
18	1	0	0.706862	-1.318697	1.455258
19	1	0	1.434933	-2.553827	0.469330
20	6	0	-0.226487	-1.507578	-0.486126
21	1	0	-0.038875	-0.942084	-1.400748
22	1	0	-0.503504	-2.518078	-0.800851

```
    23            8             0        -2.419696    -0.196960    -0.436129
Sum of electronic and thermal Enthalpies=            -388.350691
Sum of electronic and thermal Free Energies=         -388.393119
HF= -388.568453 / NImag=0
```

M06GD3/6-311++G** (SMD, water)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.151559	-0.587924	0.035769
2	6	0	1.798361	0.816732	-0.450992
3	6	0	-1.374330	-0.885890	0.263703
4	6	0	0.783761	1.626849	0.367591
5	6	0	-1.541328	0.549857	0.448774
6	6	0	-0.652722	1.589559	-0.175968
7	1	0	2.828527	-0.507858	0.897298
8	1	0	1.442484	0.767381	-1.489130
9	1	0	0.797476	1.311163	1.421221
10	1	0	-1.752141	-1.525008	1.065501
11	1	0	-2.038879	0.862672	1.368426
12	1	0	2.737293	-1.071100	-0.758388
13	1	0	2.740176	1.376960	-0.501214
14	1	0	1.109219	2.672549	0.372887
15	1	0	-1.128573	2.564762	-0.022196
16	1	0	-0.627861	1.431990	-1.261127
17	6	0	0.999633	-1.506194	0.435935
18	1	0	0.670460	-1.240768	1.450752
19	1	0	1.388208	-2.526776	0.520543
20	6	0	-0.224103	-1.475593	-0.494485
21	1	0	-0.026945	-0.887826	-1.397693
22	1	0	-0.489884	-2.483502	-0.830395
23	8	0	-2.411819	-0.188628	-0.427305

Sum of electronic and thermal Enthalpies= -388.072585

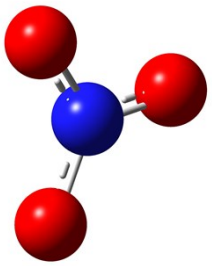
Sum of electronic and thermal Free Energies= -388.114613

HF=-388.2891407 / NImag=0

5.4. Structures along the pathway for the ‘naked’ nitrate system without cation

B3LYP, gas-phase only

Nitrate anion (charge=-1, multiplicity=1)



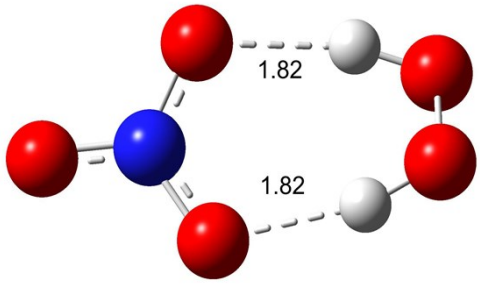
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.000000	0.000000	0.000895
2	8	0	0.000000	1.260263	-0.000261
3	8	0	-1.091420	-0.630132	-0.000261
4	8	0	1.091420	-0.630132	-0.000261

Sum of electronic and thermal Enthalpies= -280.439625

Sum of electronic and thermal Free Energies= -280.468195

HF= -280.4575651 / NImag=0

Complex A1: nitrate + H_2O_2 (complex charge=-1, complex multiplicity=1)



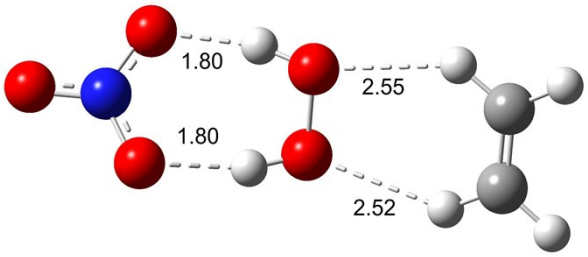
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	2.140689	-0.655567	0.323779
2	1	0	1.233287	-0.969793	0.101584
3	8	0	2.143063	0.654665	-0.322823
4	1	0	1.236628	0.971605	-0.101432
5	8	0	-0.554881	1.073781	0.207882
6	7	0	-1.195863	0.000200	-0.000214
7	8	0	-2.436457	-0.000157	0.001011
8	8	0	-0.554773	-1.073123	-0.209681

Sum of electronic and thermal Enthalpies= -432.045067

Sum of electronic and thermal Free Energies= -432.084497

HF= -432.0961791 / NImag=0

Complex B1a: nitrate + H_2O_2 + ethene (complex charge=-1, complex multiplicity=1)



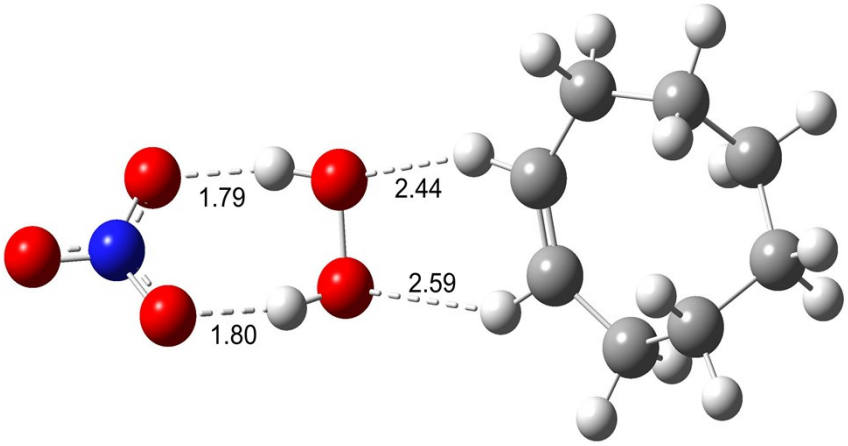
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.750170	-0.578975	0.649845
2	1	0	0.098612	-0.907533	0.267493
3	8	0	-0.768195	0.791168	0.143633
4	1	0	0.181221	1.041031	0.246561
5	8	0	1.978887	1.043014	0.281259
6	7	0	2.522204	-0.034837	-0.107822
7	8	0	3.746440	-0.088639	-0.293105
8	8	0	1.797780	-1.056782	-0.304974
9	6	0	-4.116339	-0.681593	-0.020806
10	6	0	-4.134173	0.585262	-0.426117
11	1	0	-3.184626	-1.138093	0.297693
12	1	0	-5.017904	-1.289043	0.003015
13	1	0	-5.050270	1.071822	-0.752246
14	1	0	-3.217332	1.165372	-0.439499

Sum of electronic and thermal Enthalpies= -510.607974

Sum of electronic and thermal Free Energies= -510.663986

HF= -510.7157876 / NImag=0

Complex B1: nitrate + H_2O_2 + cyclooctene (complex charge=-1, complex multiplicity=1)



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-1.996468	-0.698182	-0.994376
2	1	0	-2.716295	-0.934906	-0.361612
3	8	0	-1.983878	0.757188	-0.865374
4	1	0	-2.950219	0.949247	-0.797158
5	8	0	-4.702665	0.907689	-0.422685
6	7	0	-5.065747	-0.048973	0.326912
7	8	0	-6.216680	-0.084665	0.784670
8	8	0	-4.236490	-0.967972	0.601790
9	6	0	1.455348	-0.692948	-0.228546
10	6	0	1.340703	0.618661	0.019420
11	1	0	0.509371	-1.143488	-0.525535
12	1	0	0.323183	0.983538	-0.115986
13	6	0	2.268432	1.753184	0.392517
14	1	0	2.166391	2.493328	-0.415829
15	1	0	1.835223	2.252791	1.270003
16	6	0	2.575790	-1.712887	-0.212719
17	1	0	2.114689	-2.648257	0.126217
18	1	0	2.871248	-1.917948	-1.254133
19	6	0	3.766231	1.538346	0.643535
20	1	0	4.221326	2.528740	0.757746
21	1	0	3.912810	1.038111	1.606630
22	6	0	3.842172	-1.492728	0.630313

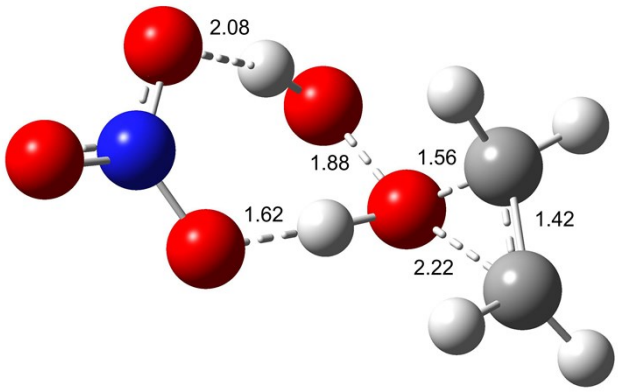
23	1	0	3.556766	-1.064823	1.596784
24	1	0	4.275194	-2.474413	0.858053
25	6	0	4.494581	0.754568	-0.469523
26	1	0	3.835710	0.668912	-1.339862
27	1	0	5.376189	1.308514	-0.810825
28	6	0	4.940729	-0.645351	-0.025993
29	1	0	5.340497	-1.188072	-0.892396
30	1	0	5.773669	-0.545991	0.683294

Sum of electronic and thermal Enthalpies= -745.176143

Sum of electronic and thermal Free Energies= -745.246750

HF= -745.4411775 / NImag=0

Transition State C1a (charge=-1, multiplicity=1) – oxidation of ethene



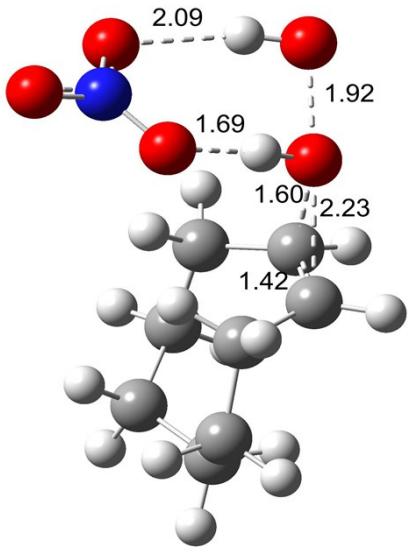
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.309705	-1.591926	0.002897
2	6	0	2.062501	-0.413749	0.759506
3	8	0	1.511343	0.439364	-0.417981
4	8	0	0.871855	2.202920	-0.356845
5	8	0	-2.900902	-0.753276	-0.008071
6	8	0	-0.847239	-0.681299	-0.722942
7	8	0	-1.544741	0.768789	0.756352
8	1	0	0.041120	1.949720	0.084787
9	1	0	0.589832	0.046397	-0.603117
10	1	0	2.922175	0.159336	1.098729
11	1	0	1.273959	-0.453638	1.508596
12	1	0	3.204953	-1.669750	-0.600960
13	1	0	1.505577	-2.290989	-0.185350
14	7	0	-1.784769	-0.217001	0.016970

Sum of electronic and thermal Enthalpies= -510.550927

Sum of electronic and thermal Free Energies= -510.598621

HF=-510.655824 / NImag=1 (-236.8785 cm^{-1})

Transition State C1 (charge=-1, multiplicity=1) – oxidation of cyclooctene



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.451502	-0.514640	0.090562
2	6	0	-2.713019	-0.556015	1.448915
3	6	0	-1.135712	0.669700	-1.403905
4	6	0	-1.859050	0.675692	1.818405
5	6	0	-0.621655	1.431521	-0.321870
6	6	0	-0.518216	0.859722	1.083809
7	1	0	-3.626965	0.531857	-0.183912
8	1	0	-2.088785	-1.456396	1.507679
9	1	0	-2.472967	1.580173	1.704989
10	1	0	-1.400784	1.209834	-2.307454
11	1	0	-0.915680	2.481384	-0.315758
12	1	0	-4.444963	-0.962948	0.215974
13	1	0	-3.465814	-0.666941	2.238766
14	1	0	-1.632115	0.602956	2.888868
15	1	0	0.116592	1.542822	1.654435
16	1	0	0.020109	-0.090755	1.054975
17	6	0	-2.773242	-1.235362	-1.087416
18	1	0	-3.383621	-1.063304	-1.983427
19	1	0	-2.786757	-2.318906	-0.908966
20	6	0	-1.308449	-0.813252	-1.382863

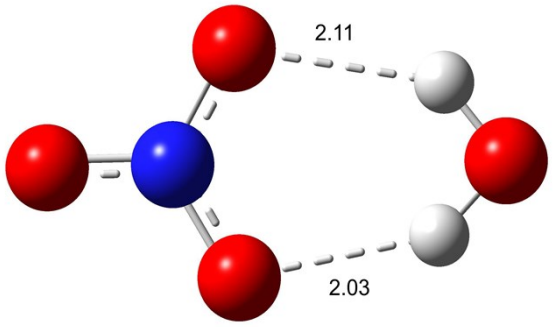
21	1	0	-0.640517	-1.260257	-0.644737
22	1	0	-1.016292	-1.252126	-2.343560
23	8	0	0.851118	1.572819	-0.920328
24	1	0	1.265809	0.655190	-0.864531
25	8	0	2.413537	2.457166	-0.252542
26	1	0	2.744818	1.672477	0.220080
27	8	0	1.835575	-0.925953	-0.688668
28	8	0	3.151186	-0.254699	0.921907
29	7	0	2.719514	-1.184790	0.201458
30	8	0	3.120634	-2.351300	0.337449

Sum of electronic and thermal Enthalpies= -745.128281

Sum of electronic and thermal Free Energies= -745.189143

HF=-745.3897467 / NImag=1 (-310.5527)

Complex D1 nitrate + H_2O (complex charge=-1, complex multiplicity=1)



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	2.535067	-0.006181	0.000669
2	1	0	1.927445	0.750725	-0.000250
3	1	0	1.860062	-0.707277	0.000856
4	8	0	-0.135008	-1.086878	-0.000892
5	7	0	-0.782842	0.000918	-0.000191
6	8	0	-2.031005	-0.012980	0.001088
7	8	0	-0.157506	1.099805	-0.000774

Sum of electronic and thermal Enthalpies= -356.895507

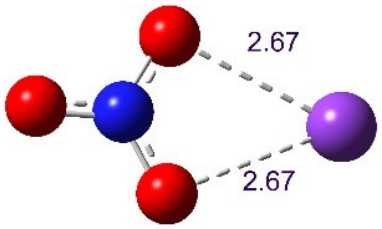
Sum of electronic and thermal Free Energies= -356.933824

HF=-356.9412275 / NImag=0

5.5. Structures along the pathway for the KNO_3 system

All structure graphics are taken from the M06GD3-SMD (water) calculation

KNO_3 (charge=0, multiplicity=1)



B3LYP/6-311++G** (gas-phase)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-1.141225	-0.000100	-0.000037
2	8	0	-0.473334	-1.092448	-0.000131
3	8	0	-0.472223	1.092017	-0.000131
4	8	0	-2.360509	0.000589	0.000167
5	19	0	1.812479	-0.000030	0.000054

Sum of electronic and thermal Enthalpies= -880.379336

Sum of electronic and thermal Free Energies= -880.414920

HF= -880.400413 / NImag=0

M06GD3/6-311++G** (SMD, water)

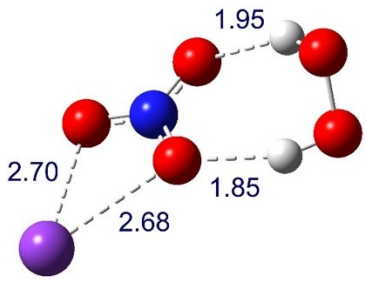
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-1.180868	-0.000033	-0.000123
2	8	0	-0.543815	-1.076999	-0.000675
3	8	0	-0.542117	1.076159	-0.000677
4	8	0	-2.412969	0.000921	0.000844
5	19	0	1.908278	-0.000022	0.000259

Sum of electronic and thermal Enthalpies= -880.248050

Sum of electronic and thermal Free Energies= -880.284506

HF= 880.2692652 / NImag=0

Complex A2: $KNO_3 + H_2O_2$ (complex charge=0, complex multiplicity=1)



B3LYP/6-311++G** (gas-phase)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-1.853189	0.870829	0.819153
2	1	0	-1.866216	1.581814	1.473708
3	8	0	-1.680128	1.600126	-0.426950
4	1	0	-0.718230	1.436727	-0.605630
5	8	0	0.678818	0.447403	-0.884002
6	7	0	1.601752	0.171787	-0.018421
7	8	0	1.503459	-0.935677	0.584965
8	8	0	2.511580	0.954142	0.191532
9	19	0	-0.942744	-1.458717	-0.158775

Sum of electronic and thermal Enthalpies= -1031.974399

Sum of electronic and thermal Free Energies= -1032.020976

HF=-1032.0283169 / NImag=0

M06GD3/6-311++G** (SMD, water)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.019914	0.871757	-0.060371
2	8	0	0.007795	-0.382652	0.017816
3	8	0	-1.064677	1.478309	-0.076407
4	8	0	1.090186	1.484623	-0.120228
5	8	0	2.621922	-1.195877	-0.511520
6	1	0	1.649146	-1.156245	-0.387305
7	8	0	3.095198	-0.401238	0.574548
8	1	0	2.663970	0.460590	0.405504

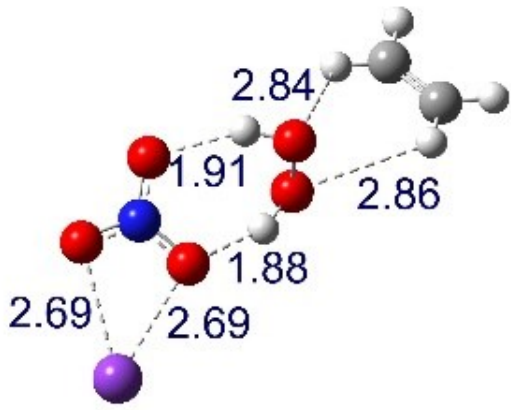
9	19	0	-2.655574	-0.698524	0.070038

Sum of electronic and thermal Enthalpies= -1031.764295

Sum of electronic and thermal Free Energies= -1031.811074

HF=-1031.8187666 / NImag=0

Complex B2a: KNO_3 + H_2O_2 + ethene (complex charge=0, complex multiplicity=1)



B3LYP/6-311++G** (gas-phase)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.103751	0.074496	1.108716
2	6	0	-3.793704	-0.496432	0.122389
3	8	0	-0.483806	1.458425	-1.259236
4	8	0	-0.387241	2.114523	0.035117
5	8	0	3.382182	0.344252	0.496174
6	7	0	2.309533	-0.212114	0.335897
7	8	0	1.245267	0.221215	0.934557
8	8	0	2.171110	-1.222064	-0.410623
9	1	0	0.360635	1.604853	0.444894
10	1	0	-0.082054	2.114125	-1.844845
11	1	0	-2.533401	0.986311	0.956737
12	1	0	-3.099410	-0.344001	2.110659
13	1	0	-4.381495	-1.395649	0.278944
14	1	0	-3.827929	-0.059889	-0.871534
15	19	0	-0.454655	-1.169481	-0.483194

Sum of electronic and thermal Enthalpies= -1110.539162

Sum of electronic and thermal Free Energies= -1110.599587

HF= -1110.6499645 / NImag=0

M06GD3/6-311++G** (SMD, water)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

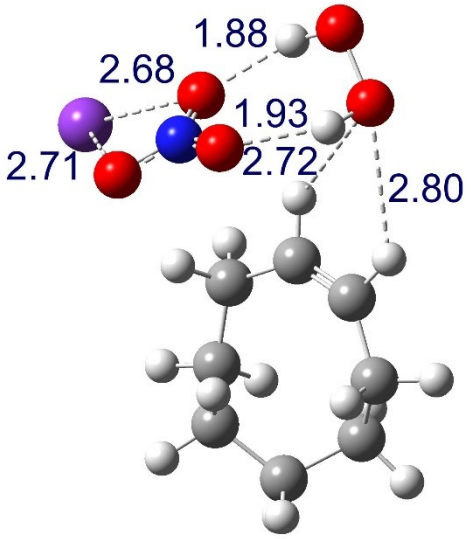
1	8	0	1.826206	0.359443	0.912833
2	1	0	1.216319	1.092014	0.685288
3	8	0	1.656804	-0.531345	-0.188832
4	1	0	0.695429	-0.722338	-0.155217
5	8	0	-1.112493	-0.268413	0.089290
6	7	0	-1.349524	0.958485	-0.036312
7	8	0	-2.526614	1.326485	-0.189930
8	8	0	-0.427845	1.780958	-0.006755
9	6	0	5.076030	0.115936	-0.587305
10	6	0	5.128453	-1.009550	0.109222
11	1	0	4.158636	0.693251	-0.675362
12	1	0	5.948901	0.511916	-1.100343
13	1	0	6.046374	-1.585336	0.197753
14	1	0	4.256222	-1.406661	0.623221
15	19	0	-3.654241	-1.119346	-0.072921

Sum of electronic and thermal Enthalpies= -1110.246509

Sum of electronic and thermal Free Energies= -1110.309726

HF= -1110.357405 / NImag=0

Complex B2: KNO_3 + H_2O_2 + cyclooctene (complex charge=0, complex multiplicity=1)



B3LYP/6-311++G** (gas-phase)

Did not converge

M06GD3/6-311++G** (SMD, water)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	3.052209	-2.697091	-0.861614
2	1	0	3.021418	-1.716584	-0.845775
3	8	0	1.734621	-3.051147	-0.443577
4	1	0	1.662362	-2.610046	0.428363
5	8	0	1.969113	-1.104381	1.596313
6	7	0	2.139914	-0.032365	1.006575
7	8	0	1.882621	1.049277	1.562524
8	8	0	2.564205	-0.017233	-0.175469
9	6	0	-1.534185	-1.543285	-0.271672
10	6	0	-0.762133	-0.513529	-0.635045
11	1	0	-1.005751	-2.499466	-0.280199
12	1	0	0.259602	-0.807117	-0.889097
13	6	0	-0.908078	0.979162	-0.720933
14	1	0	-0.251373	1.379706	0.073527
15	1	0	-0.447111	1.295718	-1.669668
16	6	0	-2.963716	-1.705399	0.162151

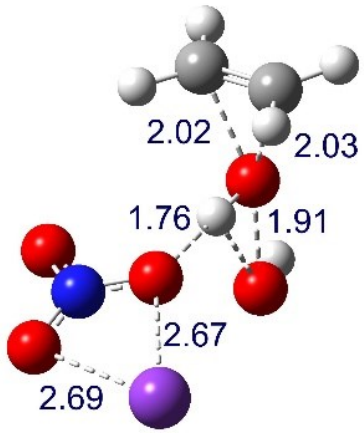
17	1	0	-3.244557	-2.730401	-0.108765
18	1	0	-3.000070	-1.695691	1.264474
19	6	0	-2.256552	1.662007	-0.574698
20	1	0	-2.075878	2.742331	-0.615721
21	1	0	-2.882652	1.437507	-1.447840
22	6	0	-4.027920	-0.757311	-0.383324
23	1	0	-3.772918	-0.482980	-1.415573
24	1	0	-4.977138	-1.302586	-0.449602
25	6	0	-2.997807	1.300337	0.714347
26	1	0	-2.325121	0.738464	1.378587
27	1	0	-3.267001	2.207070	1.267979
28	6	0	-4.256937	0.487224	0.460177
29	1	0	-4.699127	0.189928	1.421373
30	1	0	-5.001394	1.123492	-0.039094
31	19	0	2.402586	2.635083	-0.581601

Sum of electronic and thermal Enthalpies= -1344.638545

Sum of electronic and thermal Free Energies= -1344.710495

HF=-1344.90575 / NImag=0

Transition state C2a: Epoxidation of ethene with KNO_3 (complex charge=0, complex multiplicity=1)



B3LYP/6-311++G** (gas-phase)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.018265	-0.280949	0.685626
2	6	0	2.849867	0.362512	-0.517979
3	8	0	1.516197	-1.115845	-0.197858
4	8	0	-0.045509	-2.239810	-0.415889
5	8	0	-1.811462	1.602879	-0.347840
6	8	0	-0.239889	0.643109	0.813075
7	8	0	0.177948	2.487319	-0.279263
8	1	0	0.484974	-2.957470	-0.772845
9	1	0	0.852358	-0.477105	0.176345
10	1	0	3.354889	0.015580	-1.409549
11	1	0	2.250669	1.263561	-0.585800
12	1	0	3.693394	-1.119850	0.787115
13	1	0	2.593513	0.129136	1.592939
14	7	0	-0.620483	1.612865	0.046041
15	19	0	-2.151236	-1.034447	0.121359

Sum of electronic and thermal Enthalpies= -1110.506431

Sum of electronic and thermal Free Energies= -1110.560159

HF= -1110.6146521 / NImag=1 (-401.6980 cm^{-1})

M06GD3/6-311++G** (SMD, water)

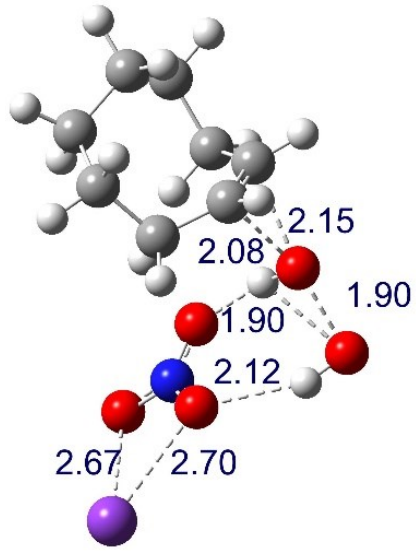
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.565494	-1.630113	-0.754792
2	6	0	-2.799496	-0.408351	-1.313256
3	8	0	-2.249948	-0.190808	0.624525
4	8	0	-1.652406	0.653781	2.235933
5	8	0	0.405587	-0.069204	-0.080191
6	7	0	0.768906	1.078162	-0.457448
7	8	0	-0.066453	1.943761	-0.700909
8	8	0	1.988811	1.299617	-0.572803
9	19	0	2.842360	-1.111740	0.264205
10	1	0	-2.535296	0.971244	2.454476
11	1	0	-1.294506	-0.103502	0.382663
12	1	0	-3.789739	0.032219	-1.306453
13	1	0	-2.022329	0.118382	-1.858090
14	1	0	-3.363630	-2.198082	-0.291119
15	1	0	-1.596472	-2.110720	-0.843388

Sum of electronic and thermal Enthalpies= -1110.207301

Sum of electronic and thermal Free Energies= -1110.264138

HF= -1110.3146393 / NImag=1 (-562.8986 cm^{-1})

Transition state C2: Epoxidation of cyclooctene with KNO_3 (complex charge=0, complex multiplicity=1)



B3LYP/6-311++G** (gas-phase)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.233609	-0.037388	0.220213
2	6	0	3.640783	-1.303759	-0.442799
3	6	0	1.652489	1.504569	0.191990
4	6	0	2.726629	-1.080400	-1.663735
5	6	0	1.355702	0.983410	-1.052648
6	6	0	1.325843	-0.479611	-1.392155
7	1	0	4.274607	0.768666	-0.521962
8	1	0	3.109079	-1.905689	0.303847
9	1	0	3.258729	-0.466856	-2.402025
10	1	0	1.788068	2.578280	0.270395
11	1	0	1.327101	1.675021	-1.887807
12	1	0	5.275765	-0.235124	0.491535
13	1	0	4.471857	-1.928803	-0.785546
14	1	0	2.562494	-2.051694	-2.142333
15	1	0	0.711841	-0.606644	-2.287145
16	1	0	0.830067	-1.045696	-0.601252
17	6	0	3.530844	0.467668	1.493673

18	1	0	4.005419	1.406806	1.800566
19	1	0	3.701797	-0.243223	2.309492
20	6	0	1.997859	0.676668	1.385727
21	1	0	1.496006	-0.289580	1.335128
22	1	0	1.644755	1.167033	2.296884
23	8	0	-0.383834	1.579635	-0.297597
24	1	0	-0.575965	0.777614	0.239208
25	8	0	-2.282934	1.919999	-0.221034
26	1	0	-2.113112	2.832920	0.028422
27	8	0	-0.831989	-0.903264	1.223789
28	8	0	-2.048069	-1.536297	-0.470674
29	7	0	-1.943057	-1.248934	0.756779
30	8	0	-2.968797	-1.258908	1.479753
31	19	0	-4.043404	0.184908	-0.521071

Sum of electronic and thermal Enthalpies= -1345.082688

Sum of electronic and thermal Free Energies= -1345.150285

HF=-1345.3478261 / NImag=1 (-344.8743 cm^{-1})

M06GD3/6-311++G** (SMD, water)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.160810	0.096392	-0.166754
2	6	0	-3.606492	-1.320536	0.037415
3	6	0	-1.572638	1.465404	0.267991
4	6	0	-2.698354	-1.521107	1.250301
5	6	0	-1.317346	0.586699	1.292269
6	6	0	-1.298058	-0.897528	1.163942
7	1	0	-4.140588	0.632897	0.793166
8	1	0	-3.080815	-1.654043	-0.869527
9	1	0	-3.216128	-1.155966	2.150261
10	1	0	-1.712874	2.514137	0.519900
11	1	0	-1.227157	1.000168	2.294026
12	1	0	-5.221965	0.035274	-0.436436
13	1	0	-4.450162	-2.011415	0.153305
14	1	0	-2.559358	-2.598572	1.401566
15	1	0	-0.671219	-1.307995	1.961963
16	1	0	-0.817447	-1.197497	0.225730

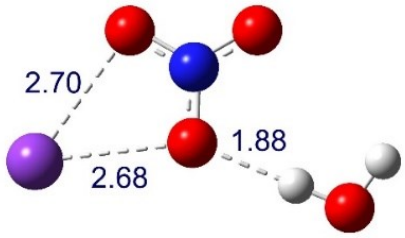
17	6	0	-3.470571	0.934874	-1.239958
18	1	0	-3.909077	1.942256	-1.233604
19	1	0	-3.690777	0.512361	-2.228987
20	6	0	-1.946546	1.038684	-1.106402
21	1	0	-1.482296	0.077111	-1.344769
22	1	0	-1.562739	1.755964	-1.839836
23	8	0	0.413479	1.453237	0.551108
24	1	0	0.561605	0.746968	-0.120754
25	8	0	2.264540	1.842879	0.290921
26	1	0	2.061230	2.731355	-0.007562
27	8	0	0.811679	-0.634895	-1.394653
28	8	0	1.915770	-1.463586	0.264892
29	7	0	1.880275	-1.058921	-0.921149
30	8	0	2.925442	-1.037044	-1.589685
31	19	0	3.986075	0.095127	0.581901

Sum of electronic and thermal Enthalpies= -1344.586252

Sum of electronic and thermal Free Energies= -1344.652661

HF= -1344.8507522 / NImag=1 (-388.1353 cm^{-1})

Complex D2: $KNO_3 + H_2O$ (complex charge=0, complex multiplicity=1)



B3LYP/6-311++G** (gas-phase)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-1.449645	0.025895	-0.028217
2	8	0	-0.565270	0.684121	-0.697007
3	8	0	-1.081596	-1.075301	0.485233
4	8	0	-2.585401	0.451100	0.095189
5	8	0	1.738667	1.631943	0.321475
6	1	0	0.809378	1.687756	0.017170
7	19	0	1.435815	-0.943018	-0.107975
8	1	0	2.006455	2.513421	0.592750

Sum of electronic and thermal Enthalpies= -956.834238

Sum of electronic and thermal Free Energies= -956.877151

HF= -956.8829296 / NImag=0

M06GD3/6-311++G** (SMD, water)

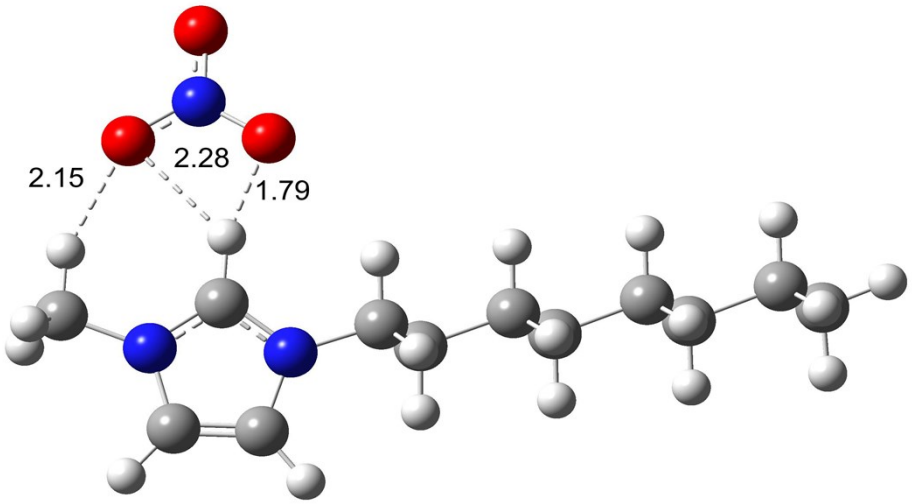
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.423528	0.868995	0.010136
2	8	0	0.403239	-0.387178	0.060577
3	8	0	-0.664498	1.476941	-0.046594
4	8	0	1.492428	1.476631	0.018257
5	8	0	3.037787	-1.469126	-0.037328
6	1	0	2.137496	-1.099323	-0.004017
7	19	0	-2.255996	-0.687522	-0.002865
8	1	0	3.610086	-0.698870	0.028204

Sum of electronic and thermal Enthalpies= -956.659150

Sum of electronic and thermal Free Energies= -956.706076
HF=-956.7076075 / NImag=0

5.6. Structures along the pathway for the [OMIM][NO_3] system

NO_3^-/$OMIM^+$ (Complex charge=0, Complex Multiplicity=1)



B3LYP/6-311++G** (gas-phase)

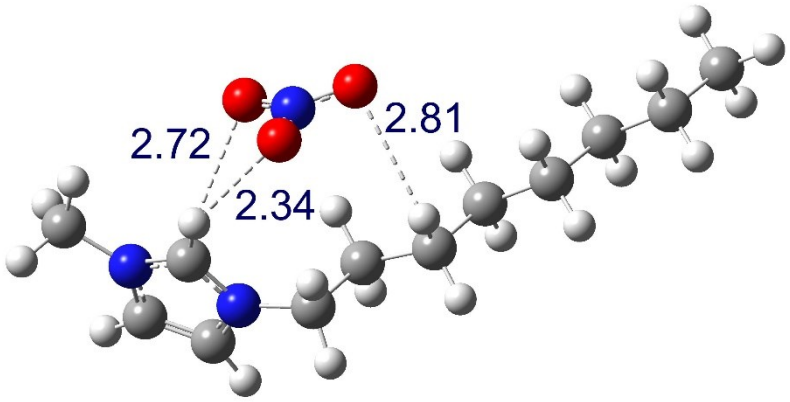
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.263548	-2.781258	0.136754
2	6	0	-3.491448	-2.696180	-0.443497
3	6	0	-2.875324	-0.650615	0.139874
4	7	0	-1.900190	-1.495021	0.495463
5	1	0	-1.632940	-3.633030	0.323870
6	1	0	-4.129493	-3.460123	-0.853149
7	7	0	-3.853146	-1.359777	-0.433017
8	6	0	-5.101488	-0.782635	-0.952282
9	1	0	-5.944531	-1.157503	-0.370673
10	1	0	-5.025845	0.301318	-0.861242
11	6	0	-0.632143	-1.060502	1.114180
12	6	0	0.533494	-1.058998	0.123463
13	1	0	-0.435379	-1.722835	1.960822
14	1	0	-0.811054	-0.055237	1.498148
15	6	0	1.824749	-0.546352	0.771598
16	1	0	0.689701	-2.071094	-0.268833

17	1	0	0.268800	-0.422393	-0.727091
18	6	0	3.017478	-0.538488	-0.191490
19	1	0	1.656146	0.468744	1.149232
20	1	0	2.068614	-1.165186	1.644960
21	1	0	3.193239	-1.556927	-0.561669
22	1	0	2.766249	0.067787	-1.070566
23	6	0	4.304728	0.000197	0.442660
24	6	0	5.502845	0.003646	-0.513099
25	1	0	4.550893	-0.598999	1.329051
26	1	0	4.127540	1.020564	0.804825
27	6	0	6.788312	0.552290	0.116549
28	1	0	5.684586	-1.018036	-0.871956
29	1	0	5.255277	0.597972	-1.402178
30	6	0	7.981028	0.551769	-0.843884
31	1	0	6.607050	1.573488	0.472795
32	1	0	7.035843	-0.040017	1.006086
33	1	0	8.880311	0.947011	-0.363517
34	1	0	8.208728	-0.460683	-1.192360
35	1	0	7.778970	1.167052	-1.726274
36	1	0	-2.828735	0.440944	0.297951
37	7	0	-3.100447	2.793320	0.059374
38	8	0	-2.235942	2.084282	0.683758
39	8	0	-3.006323	4.017107	0.035746
40	8	0	-4.045470	2.187812	-0.529080
41	1	0	-5.217707	-1.063319	-1.999323

Sum of electronic and thermal Enthalpies= -860.805606

Sum of electronic and thermal Free Energies= -860.884898

HF=-861.1811028 / NImag=0



M06GD3/6-311++G** (SMD, water)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.271329	-2.067874	-0.395765
2	6	0	-4.350156	-1.431114	-0.910763
3	6	0	-3.309874	-0.026809	0.425846
4	7	0	-2.643645	-1.177153	0.448239
5	1	0	-2.893461	-3.067420	-0.544461
6	1	0	-5.114399	-1.760497	-1.596589
7	7	0	-4.354079	-0.155898	-0.385550
8	6	0	-5.340781	0.879306	-0.660106
9	1	0	-6.281141	0.641939	-0.160838
10	1	0	-4.957261	1.830402	-0.291781
11	6	0	-1.335892	-1.363794	1.079970
12	6	0	-0.214810	-1.211835	0.071746
13	1	0	-1.327401	-2.350075	1.552110
14	1	0	-1.255598	-0.609756	1.868762
15	6	0	1.126616	-1.046056	0.758385
16	1	0	-0.202570	-2.078836	-0.603134
17	1	0	-0.415611	-0.331098	-0.555571
18	6	0	2.271750	-0.888226	-0.224411
19	1	0	1.080704	-0.158099	1.408330

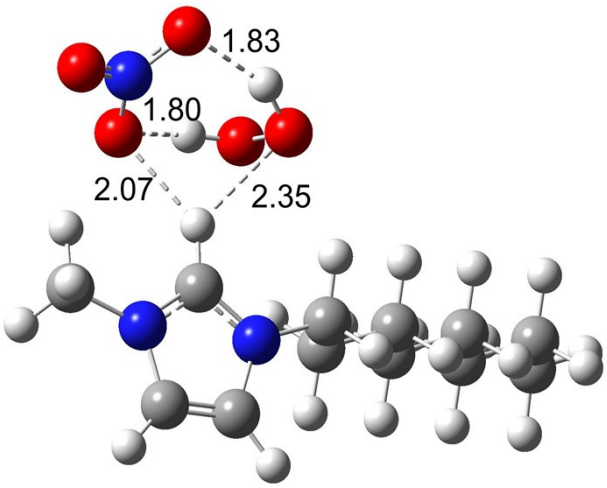
20	1	0	1.319126	-1.902447	1.421674
21	1	0	2.404670	-1.822883	-0.790086
22	1	0	2.008809	-0.117725	-0.965747
23	6	0	3.575886	-0.504836	0.448903
24	6	0	4.739612	-0.388450	-0.517101
25	1	0	3.819153	-1.243829	1.228346
26	1	0	3.438293	0.454468	0.972939
27	6	0	6.037615	0.027160	0.152024
28	1	0	4.886902	-1.351542	-1.030522
29	1	0	4.488187	0.338250	-1.305598
30	6	0	7.191363	0.131396	-0.826321
31	1	0	5.888370	0.991434	0.658708
32	1	0	6.282356	-0.695643	0.943659
33	1	0	8.121476	0.434081	-0.334841
34	1	0	7.374978	-0.829999	-1.320908
35	1	0	6.975854	0.866818	-1.610713
36	1	0	-3.033350	0.865330	0.972431
37	7	0	-0.671078	2.185300	0.159780
38	8	0	-1.099336	2.136103	1.329128
39	8	0	0.554299	2.176102	-0.055503
40	8	0	-1.472965	2.229880	-0.792565
41	1	0	-5.502467	0.941495	-1.736386

Sum of electronic and thermal Enthalpies= -860.254757

Sum of electronic and thermal Free Energies= -860.332879

HF= -860.6279937 / NImag=0

Complex A3: NO_3^-/$OMIM^+$/H_2O_2 (Complex Charge=0, Complex Multiplicity=1)



B3LYP/6-311++G** (gas-phase)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.618269	-3.109879	-0.369260
2	6	0	2.826769	-3.189629	0.251724
3	6	0	2.355945	-1.053270	-0.053031
4	7	0	1.343861	-1.767769	-0.554481
5	1	0	0.942330	-3.882066	-0.693215
6	1	0	3.402389	-4.043374	0.564894
7	7	0	3.269896	-1.894087	0.443673
8	6	0	4.542134	-1.488164	1.063870
9	1	0	5.369228	-1.761119	0.408149
10	1	0	4.522851	-0.407558	1.210036
11	6	0	0.113871	-1.191259	-1.142727
12	6	0	-1.043620	-1.152404	-0.143500
13	1	0	-0.132059	-1.797527	-2.017848
14	1	0	0.373238	-0.184854	-1.472212
15	6	0	-2.300524	-0.536535	-0.768905
16	1	0	-1.262800	-2.165932	0.214649
17	1	0	-0.736210	-0.556729	0.721299
18	6	0	-3.488562	-0.492287	0.198846
19	1	0	-2.067667	0.479265	-1.106930
20	1	0	-2.583717	-1.106935	-1.663387

21	1	0	-3.715013	-1.509698	0.544058
22	1	0	-3.204355	0.078710	1.091100
23	6	0	-4.749235	0.124737	-0.417188
24	6	0	-5.945948	0.155113	0.539871
25	1	0	-5.022995	-0.436697	-1.320085
26	1	0	-4.524786	1.145808	-0.749862
27	6	0	-7.208179	0.770832	-0.074759
28	1	0	-6.169717	-0.866736	0.873852
29	1	0	-5.674038	0.716785	1.442889
30	6	0	-8.400898	0.791852	0.885496
31	1	0	-6.986627	1.793171	-0.404025
32	1	0	-7.477772	0.212199	-0.979495
33	1	0	-9.283381	1.235881	0.416625
34	1	0	-8.669191	-0.219892	1.206110
35	1	0	-8.175053	1.373892	1.784549
36	1	0	2.430619	0.025867	-0.037124
37	7	0	4.246557	2.167289	0.170653
38	8	0	3.758016	2.939289	-0.689310
39	8	0	5.458851	1.979252	0.270332
40	8	0	3.443200	1.536290	0.959126
41	1	0	4.643225	-1.994284	2.023819
42	8	0	1.287561	1.800308	-1.076041
43	1	0	2.064662	2.404647	-1.136150
44	8	0	0.839141	2.018431	0.293774
45	1	0	1.700359	1.965944	0.773709

Sum of electronic and thermal Enthalpies= -1012.399575

Sum of electronic and thermal Free Energies= -1012.486048

HF=-1012.8088191 / NImag=0

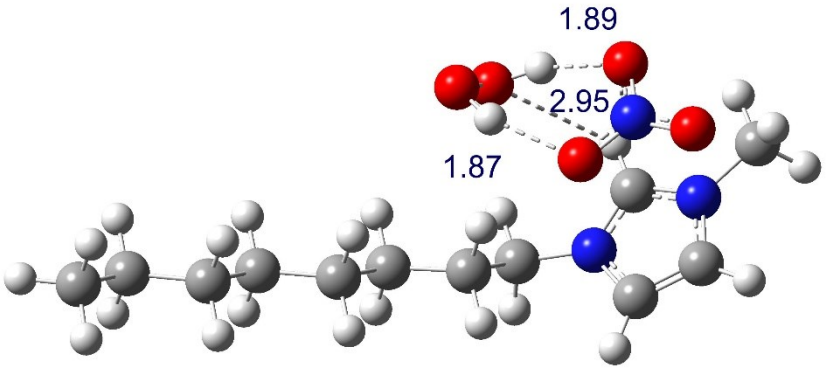
M06GD3/6-311++G** (SMD, water)

Discussion of four different isomers of this complex

Complex	Free energy (M06GD3, 6-311++G**, SMD)
A3a	ΔG= +0.0
A3b	ΔG= -0.2
A3c	ΔG= +0.8
A3d	ΔG= +0.3

The four structural isomers are all energetically very similar (within a frame of 1 kcal/mol) and may all be present in the catalytic mixture [OMIM][NO_3] in 50 wt.% H_2O_2. However, structure A3d seems to be the most feasible structure as it contains the FIR-detected imidazolium H-2 to H_2O_2 H-bonds. This leads to the shortest H-bonds between the nitrate and H2O2 with 1.86 and 1.78 Å.

A3a



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.346135	-1.929689	-1.095223
2	6	0	-3.613236	-1.454978	-1.151699
3	6	0	-2.838428	-1.079414	0.872242
4	7	0	-1.884107	-1.697510	0.183290
5	1	0	-1.735450	-2.413168	-1.841132
6	1	0	-4.334622	-1.436020	-1.953648

7	7	0	-3.905663	-0.936506	0.091378
8	6	0	-5.165291	-0.311905	0.474531
9	1	0	-5.969017	-1.047276	0.416871
10	1	0	-5.076764	0.055893	1.496177
11	6	0	-0.526644	-1.965303	0.669625
12	6	0	0.514333	-1.250979	-0.164952
13	1	0	-0.368919	-3.048369	0.663944
14	1	0	-0.497470	-1.625702	1.709073
15	6	0	1.879841	-1.299258	0.492605
16	1	0	0.561262	-1.700022	-1.166210
17	1	0	0.209041	-0.206231	-0.300883
18	6	0	2.941996	-0.596948	-0.331829
19	1	0	1.817379	-0.829658	1.486453
20	1	0	2.174850	-2.345113	0.665958
21	1	0	3.020633	-1.082251	-1.316698
22	1	0	2.620564	0.437907	-0.528113
23	6	0	4.304003	-0.582572	0.335988
24	6	0	5.369032	0.109784	-0.493573
25	1	0	4.619244	-1.616401	0.546522
26	1	0	4.223299	-0.085348	1.315088
27	6	0	6.729451	0.144222	0.179646
28	1	0	5.458239	-0.394370	-1.468648
29	1	0	5.047335	1.139534	-0.715078
30	6	0	7.781361	0.835070	-0.666221
31	1	0	6.637552	0.651873	1.150589
32	1	0	7.046388	-0.884271	0.404827
33	1	0	8.757665	0.857256	-0.171663
34	1	0	7.908315	0.325304	-1.628834
35	1	0	7.494301	1.871552	-0.880444
36	1	0	-2.768775	-0.763301	1.903093
37	7	0	-2.760245	1.874562	-0.679169
38	8	0	-2.925953	2.161353	0.526493
39	8	0	-3.706432	1.951719	-1.471018
40	8	0	-1.638477	1.497030	-1.078466
41	1	0	-5.375495	0.518810	-0.201268
42	8	0	-0.625926	1.267950	1.868250
43	1	0	-1.542475	1.557866	1.668844

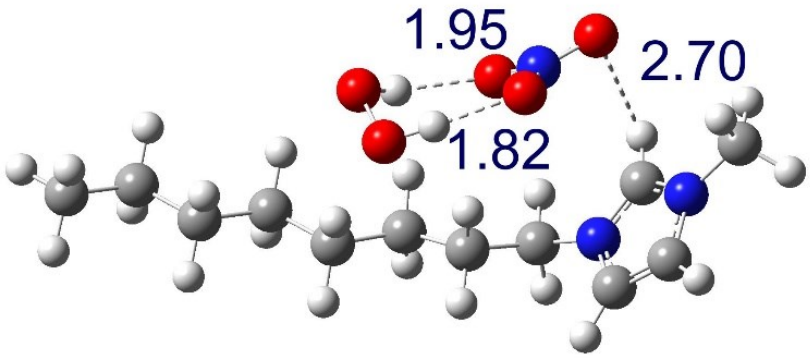
44	8	0	0.147211	2.092031	0.995803
45	1	0	-0.262062	1.908845	0.121353

Sum of electronic and thermal Enthalpies= -1011.776892

Sum of electronic and thermal Free Energies= -1011.859190

HF=-1012.1839201 / NImag=0

A3b



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.897169	-1.931163	1.080295
2	6	0	4.066758	-1.283877	1.301319
3	6	0	3.349538	-0.721039	-0.698920
4	7	0	2.470901	-1.573077	-0.180803
5	1	0	2.337368	-2.615635	1.697773
6	1	0	4.733909	-1.285000	2.148787
7	7	0	4.334630	-0.537561	0.174786
8	6	0	5.451925	0.381169	0.005129
9	1	0	6.376945	-0.122162	0.287021
10	1	0	5.501394	0.683135	-1.040370
11	6	0	1.185382	-1.924920	-0.792125
12	6	0	0.026521	-1.494401	0.082605
13	1	0	1.172172	-3.003001	-0.978056
14	1	0	1.156357	-1.415476	-1.760071

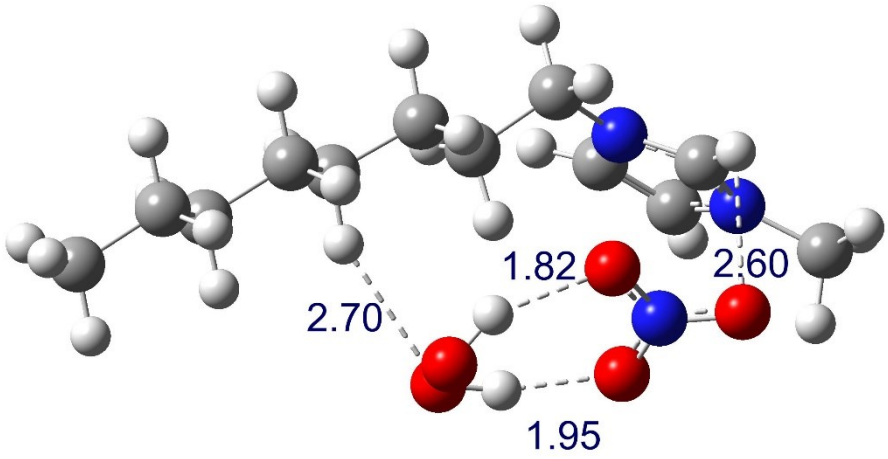
15	6	0	-1.275073	-1.466724	-0.696397
16	1	0	-0.059092	-2.164677	0.948560
17	1	0	0.231972	-0.488684	0.474677
18	6	0	-2.471770	-1.166278	0.188117
19	1	0	-1.196468	-0.697309	-1.480771
20	1	0	-1.425021	-2.421918	-1.221495
21	1	0	-2.679252	-2.031505	0.835420
22	1	0	-2.219322	-0.336328	0.863676
23	6	0	-3.716316	-0.798915	-0.596869
24	6	0	-4.890467	-0.429875	0.289560
25	1	0	-3.998679	-1.631001	-1.260679
26	1	0	-3.482823	0.051233	-1.257705
27	6	0	-6.138546	-0.053541	-0.488579
28	1	0	-5.120700	-1.268506	0.965322
29	1	0	-4.599314	0.411008	0.939770
30	6	0	-7.297535	0.323521	0.413501
31	1	0	-5.902827	0.781695	-1.163712
32	1	0	-6.426426	-0.894056	-1.136332
33	1	0	-8.192160	0.593141	-0.156796
34	1	0	-7.564986	-0.507411	1.077310
35	1	0	-7.038353	1.179138	1.048561
36	1	0	3.278013	-0.261035	-1.673926
37	1	0	5.302772	1.259296	0.635989
38	7	0	1.779969	1.937551	-0.521509
39	8	0	0.810252	1.467955	-1.148723
40	8	0	1.703655	2.094928	0.717945
41	8	0	2.824972	2.229564	-1.115018
42	1	0	-0.939302	1.734081	-0.318913
43	8	0	-1.495040	2.158788	0.366945
44	8	0	-0.908510	1.695089	1.584218
45	1	0	0.047167	1.888253	1.449894

Sum of electronic and thermal Enthalpies= -1011.775285

Sum of electronic and thermal Free Energies= -1011.857963

HF=-1012.1819549 / NImag=0

A3c



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.897098	-1.929488	1.081231
2	6	0	4.067172	-1.282676	1.300990
3	6	0	3.349697	-0.722091	-0.699806
4	7	0	2.470654	-1.572892	-0.180228
5	1	0	2.336969	-2.612592	1.699925
6	1	0	4.734582	-1.282983	2.148255
7	7	0	4.335106	-0.538008	0.173364
8	6	0	5.453287	0.379360	0.002060
9	1	0	6.378240	-0.125372	0.281635
10	1	0	5.500911	0.682031	-1.043325
11	6	0	1.184875	-1.925062	-0.790836
12	6	0	0.026215	-1.494134	0.083969
13	1	0	1.171641	-3.003222	-0.976312
14	1	0	1.155516	-1.416072	-1.759010
15	6	0	-1.275304	-1.466443	-0.695175
16	1	0	-0.059561	-2.164195	0.950066
17	1	0	0.231943	-0.488382	0.475826
18	6	0	-2.472256	-1.165909	0.188932
19	1	0	-1.196563	-0.697040	-1.479539
20	1	0	-1.425157	-2.421670	-1.220246
21	1	0	-2.679471	-2.030718	0.836877
22	1	0	-2.220380	-0.335293	0.863869
23	6	0	-3.716777	-0.799626	-0.596624
24	6	0	-4.891115	-0.429858	0.289258

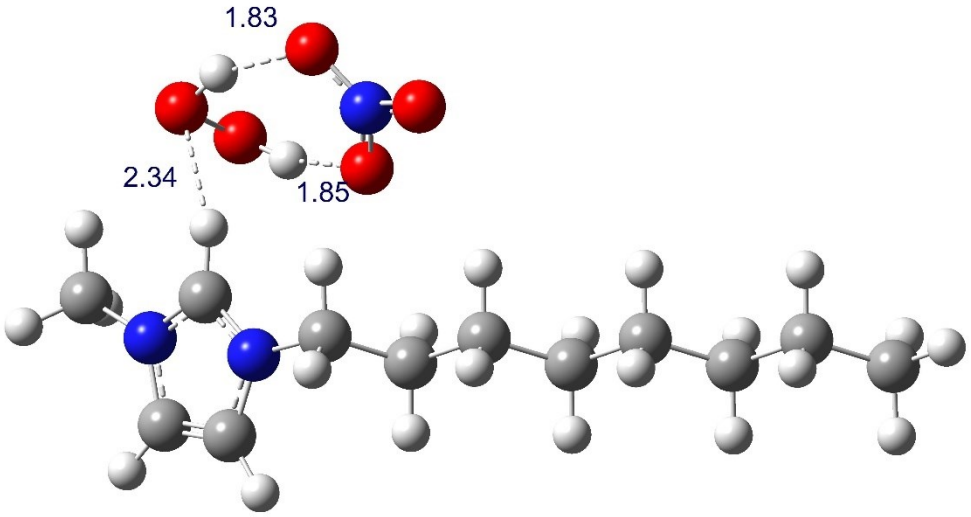
25	1	0	-3.998793	-1.632392	-1.259722
26	1	0	-3.483339	0.049966	-1.258200
27	6	0	-6.139159	-0.054460	-0.489390
28	1	0	-5.121364	-1.267780	0.965888
29	1	0	-4.600039	0.411761	0.938550
30	6	0	-7.298207	0.323550	0.412205
31	1	0	-5.903441	0.780033	-1.165440
32	1	0	-6.426949	-0.895720	-1.136217
33	1	0	-8.192839	0.592428	-0.158433
34	1	0	-7.565612	-0.506624	1.076979
35	1	0	-7.039127	1.179934	1.046273
36	1	0	3.278205	-0.263846	-1.675664
37	1	0	5.306545	1.257267	0.633775
38	7	0	1.780670	1.937428	-0.520189
39	8	0	0.810360	1.469271	-1.147683
40	8	0	1.704752	2.093475	0.719398
41	8	0	2.825798	2.228920	-1.113655
42	1	0	-0.937239	1.737082	-0.320120
43	8	0	-1.495093	2.159690	0.365427
44	8	0	-0.909455	1.696024	1.583107
45	1	0	0.046261	1.889678	1.450052

Sum of electronic and thermal Enthalpies= -1011.775303

Sum of electronic and thermal Free Energies= -1011.857945

HF=-1012.181955 / NImag=0

A3d



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.131838	-2.889241	-0.184966
2	6	0	3.380399	-2.874872	0.338318
3	6	0	2.915213	-0.839989	-0.359295
4	7	0	1.862363	-1.609316	-0.621185
5	1	0	1.415916	-3.688395	-0.296264
6	1	0	3.978628	-3.655958	0.780028
7	7	0	3.853071	-1.586334	0.217845
8	6	0	5.157095	-1.118632	0.669931
9	1	0	5.301674	-0.097466	0.320303
10	6	0	0.592344	-1.159481	-1.198646
11	6	0	-0.542495	-1.269553	-0.204240
12	1	0	0.397173	-1.764778	-2.089634
13	1	0	0.737770	-0.123690	-1.519523
14	6	0	-1.831900	-0.720064	-0.783970
15	1	0	-0.679415	-2.320881	0.083984
16	1	0	-0.276529	-0.719018	0.708305
17	6	0	-2.996659	-0.821371	0.182546
18	1	0	-1.681489	0.332527	-1.067516
19	1	0	-2.076061	-1.257132	-1.712981
20	1	0	-3.147264	-1.874613	0.465155
21	1	0	-2.743435	-0.290244	1.113033
22	6	0	-4.288020	-0.260243	-0.382479

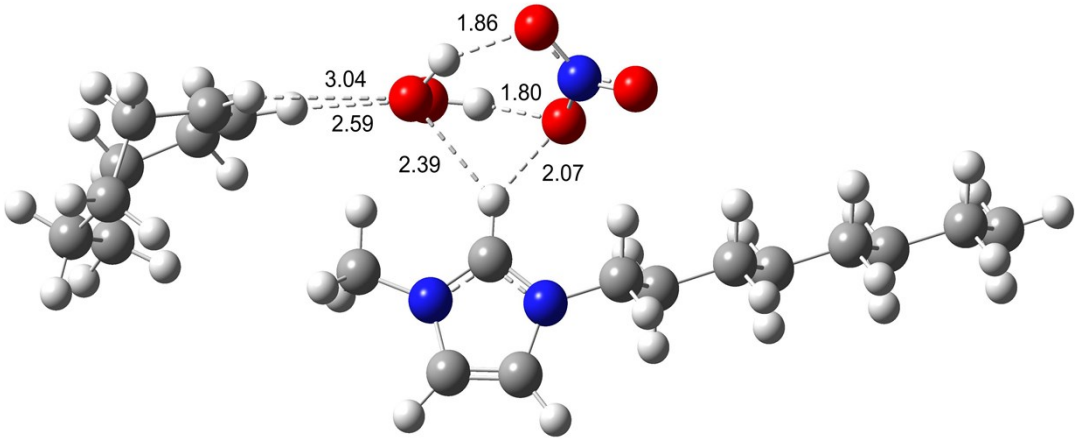
23	6	0	-5.455882	-0.357631	0.581066
24	1	0	-4.538787	-0.789772	-1.314832
25	1	0	-4.134407	0.792847	-0.664718
26	6	0	-6.748469	0.206960	0.019187
27	1	0	-5.611255	-1.411007	0.862515
28	1	0	-5.204359	0.169842	1.514581
29	6	0	-7.904015	0.102126	0.995389
30	1	0	-6.590025	1.258132	-0.261476
31	1	0	-6.996989	-0.320789	-0.912846
32	1	0	-8.830694	0.512466	0.581683
33	1	0	-8.095788	-0.943076	1.266281
34	1	0	-7.685275	0.645493	1.922475
35	1	0	3.007993	0.215435	-0.581683
36	7	0	0.913088	2.502357	-0.443661
37	8	0	1.000078	1.636329	0.452244
38	8	0	-0.137130	2.629528	-1.081574
39	8	0	1.892775	3.236525	-0.697398
40	1	0	5.199218	-1.145493	1.759788
41	8	0	3.520282	1.825706	1.633857
42	1	0	2.597236	1.596545	1.383409
43	8	0	4.143202	2.030939	0.365232
44	1	0	3.514237	2.637595	-0.084966
45	1	0	5.931908	-1.765783	0.257962

Sum of electronic and thermal Enthalpies= -1011.772905

Sum of electronic and thermal Free Energies= -1011.858694

HF=-1012.1794433 / NImag=0

Complex B3 (NO_3^-/$OMIM^+$/H_2O_2/cyclooctene) – Complex charge: 0, Complex multiplicity =1



B3LYP/6-311++G** (gas-phase) only - not calculated for M06GD3-SMD

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.661877	3.516345	-0.488408
2	6	0	0.670337	3.401715	-0.743328
3	6	0	0.025587	1.596768	0.354718
4	7	0	-1.045808	2.381741	0.200594
5	1	0	-1.357845	4.301922	-0.726366
6	1	0	1.351913	4.066785	-1.244668
7	7	0	1.080862	2.195529	-0.207152
8	6	0	2.439414	1.634012	-0.254367
9	1	0	2.471065	0.757393	0.389376
10	6	0	-2.421975	2.052345	0.644826
11	6	0	-3.207682	1.285737	-0.419150
12	1	0	-2.900467	3.002342	0.892996
13	1	0	-2.343857	1.455855	1.554379
14	6	0	-4.623655	0.958040	0.068890
15	1	0	-3.252027	1.870023	-1.346762
16	1	0	-2.673697	0.355708	-0.634015
17	6	0	-5.430488	0.146793	-0.951201
18	1	0	-4.550834	0.397979	1.007253
19	1	0	-5.159779	1.888708	0.297856
20	1	0	-5.484432	0.698899	-1.898991

21	1	0	-4.895623	-0.785681	-1.169023
22	6	0	-6.849953	-0.183340	-0.476448
23	6	0	-7.655744	-1.008286	-1.486047
24	1	0	-7.386887	0.749881	-0.261317
25	1	0	-6.793740	-0.728165	0.474066
26	6	0	-9.077524	-1.336415	-1.016295
27	1	0	-7.707375	-0.466308	-2.439780
28	1	0	-7.121111	-1.943436	-1.697194
29	6	0	-9.874012	-2.163653	-2.029569
30	1	0	-9.026193	-1.877127	-0.063598
31	1	0	-9.612805	-0.402176	-0.806490
32	1	0	-10.882593	-2.378706	-1.665666
33	1	0	-9.970893	-1.635053	-2.983385
34	1	0	-9.383091	-3.120934	-2.231427
35	1	0	0.025875	0.629011	0.838387
36	7	0	-1.379561	-0.885789	2.613791
37	8	0	-1.230815	-0.942083	1.337783
38	8	0	-2.390518	-0.346277	3.079052
39	8	0	-0.480683	-1.354347	3.349931
40	1	0	2.681240	1.350452	-1.278563
41	8	0	1.303988	-1.710642	0.695146
42	1	0	0.321337	-1.653075	0.773575
43	8	0	1.706076	-0.801717	1.760073
44	1	0	1.165646	-1.123907	2.517302
45	1	0	4.736810	-0.715749	1.523948
46	6	0	5.395761	-1.023322	0.714113
47	6	0	4.811015	-1.738581	-0.252608
48	1	0	3.750766	-1.941805	-0.112826
49	1	0	3.146324	2.382796	0.102141
50	6	0	5.369543	-2.343436	-1.515565
51	1	0	5.384489	-3.435147	-1.388168
52	1	0	4.629022	-2.172429	-2.309715
53	6	0	6.831052	-0.565791	0.867469
54	1	0	6.983577	-0.332867	1.925354
55	1	0	7.533353	-1.372955	0.641449
56	6	0	7.207044	0.689396	0.039781
57	1	0	7.970987	1.254243	0.586302

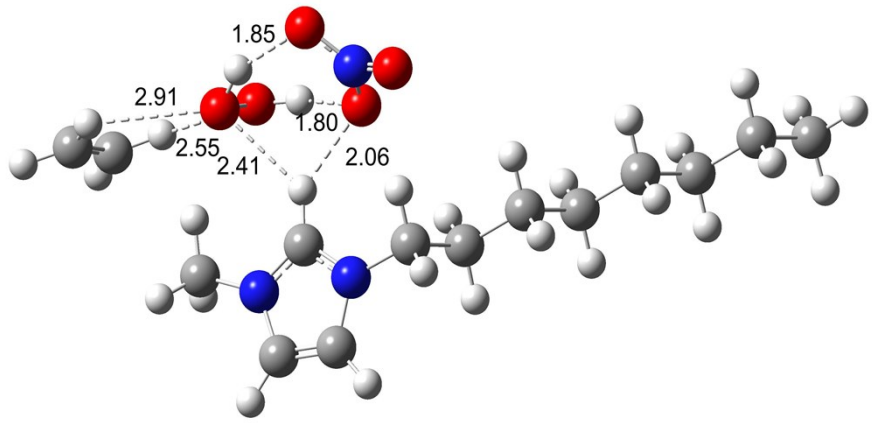
58	1	0	6.330797	1.346449	-0.023151
59	6	0	6.740787	-1.889173	-2.035396
60	1	0	6.930297	-2.450668	-2.956277
61	1	0	7.529455	-2.197607	-1.343950
62	6	0	7.753899	0.426874	-1.370961
63	1	0	8.721104	-0.085845	-1.284625
64	1	0	7.973359	1.399289	-1.828477
65	6	0	6.867242	-0.374579	-2.339190
66	1	0	5.868639	0.077553	-2.382704
67	1	0	7.291740	-0.254172	-3.341327

Sum of electronic and thermal Enthalpies= -1325.533035

Sum of electronic and thermal Free Energies= -1325.648908

HF=-1326.1560842 / NImag=0

Complex B3e (NO_3^-/$OMIM^+$/H_2O_2/ethene) – Complex charge=0, multiplicity =1



B3LYP/6-311++G** (gas-phase)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.269483	3.335026	-0.441984
2	6	0	-2.529253	3.338753	0.073704
3	6	0	-1.948827	1.240676	-0.299638
4	7	0	-0.925506	2.016489	-0.672013
5	1	0	-0.601683	4.147216	-0.671228
6	1	0	-3.163536	4.152983	0.378573
7	7	0	-2.936072	2.020079	0.153609
8	6	0	-4.224066	1.530054	0.667701
9	1	0	-4.304969	0.470192	0.436228
10	6	0	0.377719	1.529071	-1.185055
11	6	0	1.396746	1.313208	-0.066317
12	1	0	0.722972	2.272614	-1.906889
13	1	0	0.197115	0.592310	-1.712816
14	6	0	2.727573	0.792799	-0.622358
15	1	0	1.555547	2.250045	0.482257
16	1	0	0.985850	0.581545	0.635400
17	6	0	3.772289	0.548698	0.472277
18	1	0	2.540031	-0.138574	-1.167049
19	1	0	3.128052	1.509143	-1.352020
20	1	0	3.950710	1.482003	1.022809
21	1	0	3.367832	-0.164764	1.200721
22	6	0	5.104775	0.017677	-0.068454

23	6	0	6.152905	-0.224938	1.023024
24	1	0	5.506240	0.726746	-0.804302
25	1	0	4.924831	-0.917212	-0.613375
26	6	0	7.486408	-0.758648	0.487010
27	1	0	6.332516	0.710945	1.568735
28	1	0	5.751367	-0.933195	1.759333
29	6	0	8.527859	-0.996209	1.584341
30	1	0	7.307538	-1.694711	-0.055627
31	1	0	7.887312	-0.052273	-0.250288
32	1	0	9.465216	-1.377798	1.170014
33	1	0	8.755135	-0.069910	2.121681
34	1	0	8.169175	-1.724271	2.318820
35	1	0	-1.958256	0.159559	-0.341963
36	7	0	-0.747734	-1.960985	-1.549410
37	8	0	-0.703194	-1.479357	-0.357745
38	8	0	0.156037	-1.682627	-2.345709
39	8	0	-1.723144	-2.675938	-1.877530
40	1	0	-4.266760	1.676374	1.746889
41	8	0	-3.053023	-1.918057	0.953120
42	1	0	-2.100215	-1.893238	0.694920
43	8	0	-3.677590	-1.530686	-0.304892
44	1	0	-3.225812	-2.125145	-0.947362
45	1	0	-6.511169	-1.499851	0.363828
46	6	0	-6.934032	-1.301896	1.343291
47	1	0	-7.977748	-1.004853	1.382346
48	6	0	-6.199798	-1.438409	2.444318
49	1	0	-6.616523	-1.257666	3.430837
50	1	0	-5.161254	-1.748191	2.390574
51	1	0	-5.031903	2.079052	0.184542

Sum of electronic and thermal Enthalpies= -1090.960890

Sum of electronic and thermal Free Energies= -1091.062146

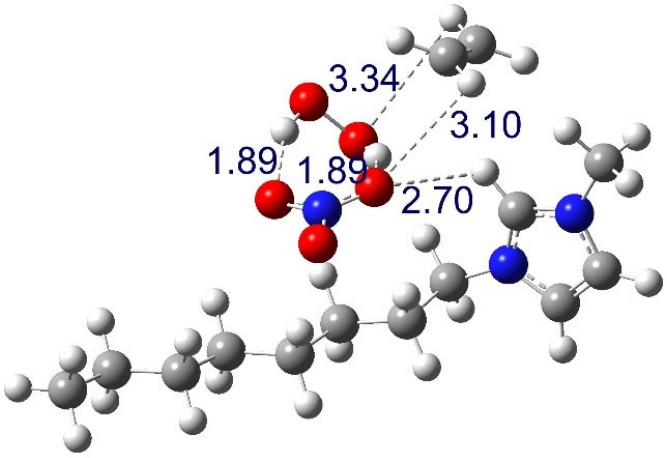
HF=-1091.4268962 / NImag=0

M06GD3/6-311++G** (SMD, water)

Discussion of three different isomers of this complex

Complex	Free energy (M06GD3, 6-311++G**, SMD)
B3a	ΔG= +6.4
B3b	ΔG= +6.0
B3c (best)	ΔG= +4.9

B3a



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.107436	-2.894980	-0.164643
2	6	0	4.167243	-2.494736	0.578532
3	6	0	3.083745	-0.696791	-0.079082
4	7	0	2.452989	-1.755970	-0.577633
5	1	0	2.758198	-3.877478	-0.441622
6	1	0	4.941730	-3.054367	1.078482
7	7	0	4.132521	-1.117620	0.621889
8	6	0	5.121248	-0.263468	1.267702
9	1	0	6.006758	-0.175077	0.636517
10	1	0	4.685181	0.721297	1.433073
11	6	0	1.175770	-1.703872	-1.292563
12	6	0	0.003102	-1.873042	-0.349005
13	1	0	1.197242	-2.479213	-2.063430
14	1	0	1.135663	-0.733314	-1.795972

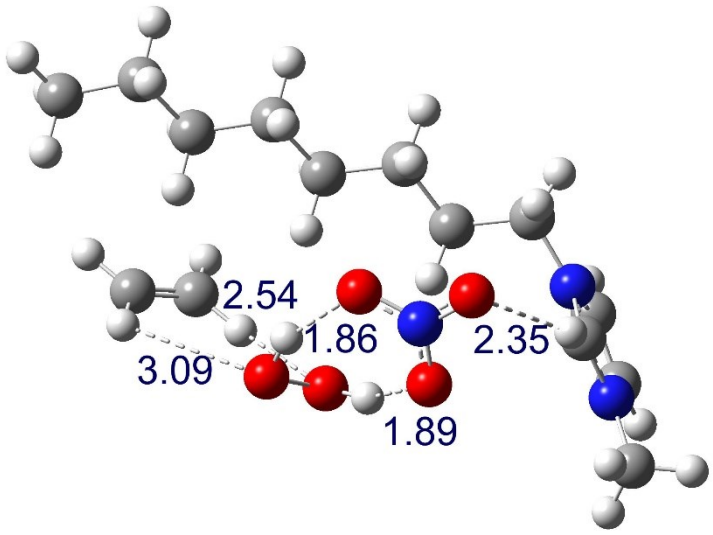
15	6	0	-1.300358	-1.475120	-1.016494
16	1	0	-0.039246	-2.909422	0.012707
17	1	0	0.169216	-1.235783	0.531236
18	6	0	-2.476278	-1.493152	-0.058070
19	1	0	-1.187950	-0.456895	-1.421394
20	1	0	-1.500990	-2.128269	-1.878526
21	1	0	-2.660765	-2.520084	0.291419
22	1	0	-2.212951	-0.913591	0.840030
23	6	0	-3.746354	-0.916618	-0.655795
24	6	0	-4.840755	-0.715552	0.375298
25	1	0	-4.109563	-1.568684	-1.464932
26	1	0	-3.516466	0.052224	-1.126659
27	6	0	-6.126822	-0.159058	-0.208001
28	1	0	-5.052132	-1.670446	0.881970
29	1	0	-4.469850	-0.033494	1.158030
30	6	0	-7.197703	0.058725	0.843215
31	1	0	-5.907890	0.788489	-0.721084
32	1	0	-6.497517	-0.844489	-0.983646
33	1	0	-8.121271	0.459374	0.413350
34	1	0	-7.447844	-0.881277	1.349682
35	1	0	-6.856033	0.763082	1.611132
36	1	0	2.797399	0.336601	-0.225498
37	7	0	-0.721357	1.330736	1.124420
38	8	0	0.494505	1.249528	0.848159
39	8	0	-1.135470	0.929604	2.218734
40	8	0	-1.519309	1.805586	0.288409
41	1	0	5.396420	-0.705531	2.225114
42	8	0	0.687346	1.751739	-1.907262
43	1	0	0.883526	1.456402	-0.991212
44	8	0	0.070136	3.018640	-1.681379
45	1	0	-0.674653	2.778372	-1.088568
46	1	0	3.572797	3.390868	-1.473540
47	6	0	3.760693	2.841938	-0.553938
48	6	0	3.069458	3.077867	0.551178
49	1	0	4.545568	2.088257	-0.590947
50	1	0	3.251314	2.528965	1.473133
51	1	0	2.284831	3.829852	0.587110

Sum of electronic and thermal Enthalpies= -1090.263068

Sum of electronic and thermal Free Energies= -1090.357171

HF=-1090.7264197 / NImag=0

B3b



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.701871	-0.759579	-2.016576
2	6	0	-4.664357	0.143727	-1.713030
3	6	0	-3.779533	-0.562212	0.173540
4	7	0	-3.172760	-1.200429	-0.822759
5	1	0	-3.345670	-1.133042	-2.963913
6	1	0	-5.330080	0.716070	-2.339297
7	7	0	-4.694616	0.253760	-0.338822
8	6	0	-5.586469	1.111728	0.428957
9	1	0	-6.605256	0.724558	0.386225
10	1	0	-5.242857	1.133238	1.462771
11	6	0	-1.972889	-2.025984	-0.666416
12	6	0	-0.723872	-1.209477	-0.929244
13	1	0	-2.058627	-2.878163	-1.346178
14	1	0	-1.982893	-2.406232	0.359908
15	6	0	0.524930	-1.911290	-0.433418
16	1	0	-0.644819	-0.983875	-2.001873
17	1	0	-0.824270	-0.242957	-0.415988
18	6	0	1.775291	-1.076462	-0.637800
19	1	0	0.404521	-2.124862	0.640235
20	1	0	0.636572	-2.886081	-0.930738

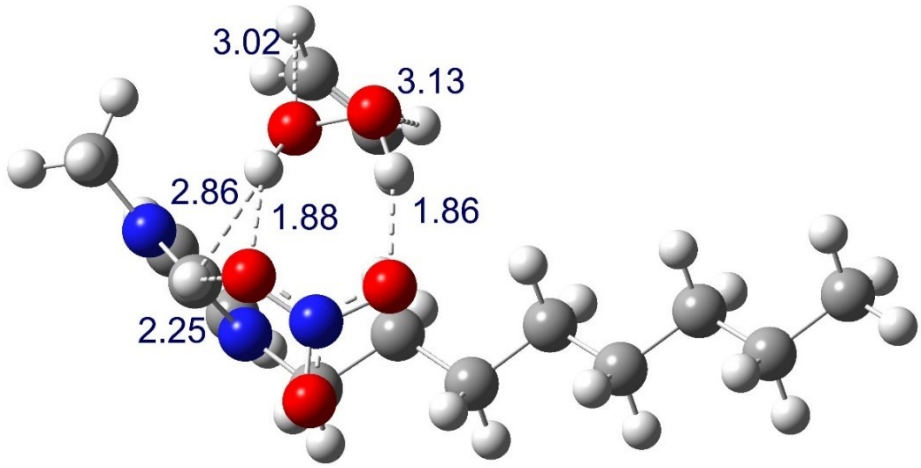
21	1	0	1.972632	-0.959280	-1.714782
22	1	0	1.597216	-0.059715	-0.253273
23	6	0	2.998597	-1.652734	0.050788
24	6	0	4.225201	-0.776208	-0.108242
25	1	0	3.206655	-2.660814	-0.340498
26	1	0	2.778981	-1.781355	1.122786
27	6	0	5.469606	-1.314540	0.571383
28	1	0	4.433253	-0.628927	-1.180118
29	1	0	4.002749	0.227359	0.289322
30	6	0	6.655588	-0.384611	0.399852
31	1	0	5.262922	-1.466483	1.640546
32	1	0	5.707530	-2.307580	0.163762
33	1	0	7.558251	-0.768570	0.885594
34	1	0	6.886421	-0.236911	-0.662423
35	1	0	6.442263	0.603152	0.827098
36	1	0	-3.553889	-0.686585	1.224494
37	1	0	-5.558894	2.118940	0.012856
38	7	0	-1.048325	0.256957	2.153791
39	8	0	0.197441	0.222051	2.109645
40	8	0	-1.662946	1.236588	1.676619
41	8	0	-1.679312	-0.681691	2.656769
42	1	0	1.035092	1.678257	1.238971
43	8	0	1.071316	2.528631	0.749266
44	8	0	0.037443	2.372425	-0.223125
45	1	0	-0.737127	2.126907	0.328905
46	1	0	1.917113	2.320532	-1.930886
47	6	0	2.940909	2.120043	-2.238226
48	6	0	3.975853	2.480936	-1.494505
49	1	0	3.071189	1.600970	-3.184897
50	1	0	3.847601	2.995382	-0.544899
51	1	0	4.999873	2.269999	-1.794951

Sum of electronic and thermal Enthalpies= -1090.263143

Sum of electronic and thermal Free Energies= -1090.357830

HF=-1090.7263597 / NImag=0

B3c



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.112542	1.453186	1.767335
2	6	0	4.169254	1.404380	0.920994
3	6	0	2.983397	-0.425243	0.629889
4	7	0	2.394096	0.291873	1.582842
5	1	0	2.804219	2.199161	2.483156
6	1	0	4.980431	2.094163	0.749033
7	7	0	4.072653	0.218585	0.224750
8	6	0	4.940947	-0.195764	-0.867749
9	1	0	4.622135	-1.178549	-1.213708
10	6	0	1.051709	0.020529	2.104973
11	6	0	0.012490	0.623020	1.183672
12	1	0	0.999581	0.435284	3.115238
13	1	0	0.939731	-1.066984	2.175873
14	6	0	-1.406112	0.292787	1.596820
15	1	0	0.154889	1.712227	1.141026
16	1	0	0.192284	0.240043	0.167417
17	6	0	-2.416151	0.812342	0.589282
18	1	0	-1.512133	-0.798524	1.689663
19	1	0	-1.618904	0.710502	2.591695
20	1	0	-2.387542	1.912863	0.574282
21	1	0	-2.116149	0.488858	-0.420769

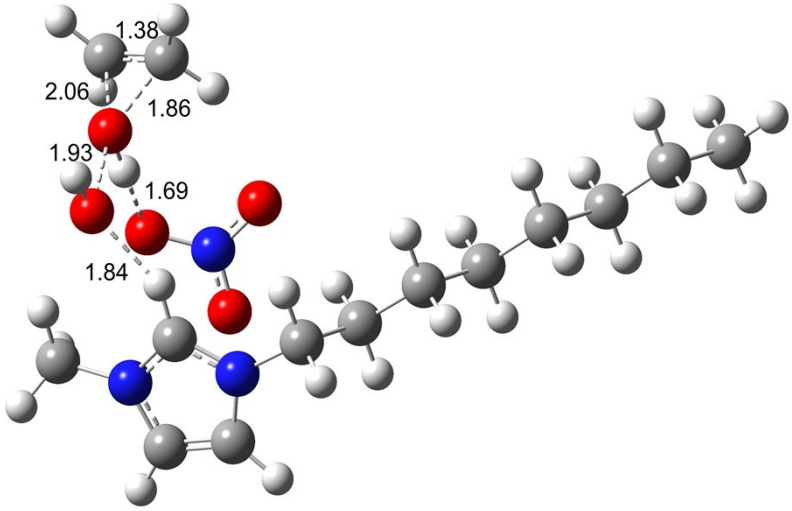
22	6	0	-3.830364	0.338212	0.862771
23	6	0	-4.843303	0.873206	-0.131742
24	1	0	-4.126804	0.630444	1.882269
25	1	0	-3.847566	-0.763282	0.845607
26	6	0	-6.257077	0.382414	0.123990
27	1	0	-4.830881	1.974253	-0.110465
28	1	0	-4.538361	0.588166	-1.151005
29	6	0	-7.253984	0.927443	-0.880240
30	1	0	-6.266085	-0.716809	0.101349
31	1	0	-6.558485	0.666439	1.142551
32	1	0	-8.269897	0.567616	-0.688680
33	1	0	-7.279485	2.023472	-0.853225
34	1	0	-6.984168	0.631780	-1.901221
35	1	0	2.632540	-1.381225	0.260498
36	7	0	-0.025996	-2.722684	-0.041131
37	8	0	-0.921994	-2.053864	-0.594121
38	8	0	-0.246800	-3.287265	1.035692
39	8	0	1.102570	-2.814173	-0.574707
40	1	0	4.861348	0.525089	-1.684073
41	8	0	0.130128	-0.651417	-2.782953
42	1	0	-0.407189	-0.992903	-2.034192
43	8	0	1.445778	-0.591331	-2.227203
44	1	0	1.544186	-1.474510	-1.811432
45	1	0	5.973358	-0.243892	-0.520022
46	1	0	0.541203	2.225909	-1.609801
47	6	0	1.444169	2.711207	-1.243928
48	6	0	2.592843	2.643563	-1.900106
49	1	0	1.353577	3.258030	-0.307774
50	1	0	2.687989	2.102178	-2.838132
51	1	0	3.491282	3.132489	-1.529823

Sum of electronic and thermal Enthalpies= -1090.266649

Sum of electronic and thermal Free Energies= -1090.359650

HF=-1090.7299121 / NImag=0

Transition state C3e, Charge=0, Multiplicity=1 – Oxidation of ethene



B3LYP/6-311++G** (gas-phase)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.576400	3.170664	-0.285881
2	6	0	2.862248	3.004832	-0.693697
3	6	0	2.387158	1.375175	0.720006
4	7	0	1.298697	2.144262	0.598612
5	1	0	0.842618	3.907793	-0.559606
6	1	0	3.455053	3.567870	-1.392926
7	7	0	3.350317	1.885433	-0.051165
8	6	0	4.659900	1.255948	-0.261501
9	1	0	4.786493	0.489026	0.502932
10	6	0	-0.001849	1.871648	1.236027
11	6	0	-1.071674	1.437427	0.231602
12	1	0	-0.301676	2.773358	1.777694
13	1	0	0.177098	1.086286	1.972311
14	6	0	-2.381527	1.064646	0.935146
15	1	0	-1.253480	2.248976	-0.482339
16	1	0	-0.695748	0.586122	-0.343223
17	6	0	-3.480953	0.637698	-0.044374
18	1	0	-2.190273	0.244544	1.638848
19	1	0	-2.740000	1.910387	1.537780
20	1	0	-3.690778	1.464029	-0.735530

21	1	0	-3.107993	-0.188194	-0.661141
22	6	0	-4.780611	0.213080	0.648135
23	6	0	-5.885697	-0.207177	-0.327150
24	1	0	-5.146008	1.037476	1.274927
25	1	0	-4.568572	-0.618227	1.332937
26	6	0	-7.180471	-0.649300	0.364199
27	1	0	-6.106385	0.626317	-1.006806
28	1	0	-5.517615	-1.024621	-0.960449
29	6	0	-8.280747	-1.063510	-0.617175
30	1	0	-6.960370	-1.485168	1.039429
31	1	0	-7.546854	0.166093	1.000200
32	1	0	-9.189076	-1.373081	-0.092624
33	1	0	-8.547696	-0.237462	-1.284088
34	1	0	-7.957438	-1.900968	-1.243536
35	1	0	2.522361	0.480369	1.337643
36	7	0	1.593835	-0.690712	-1.510528
37	8	0	2.772763	-1.105335	-1.233359
38	8	0	1.457758	0.334987	-2.196544
39	8	0	0.603971	-1.314523	-1.063548
40	1	0	4.665112	0.784673	-1.243691
41	8	0	3.122002	-2.548227	1.003668
42	1	0	2.988943	-1.955239	0.205813
43	8	0	3.586615	-0.912893	1.908057
44	1	0	3.767948	-1.380006	2.730224
45	1	0	3.843037	-4.861991	0.248805
46	6	0	3.106621	-4.214453	-0.208229
47	1	0	3.310364	-3.832316	-1.200118
48	6	0	1.941454	-3.877960	0.445266
49	1	0	1.168865	-3.310101	-0.059832
50	1	0	1.688658	-4.340169	1.390685
51	1	0	5.437072	2.016972	-0.183179

Sum of electronic and thermal Enthalpies= -1090.921872

Sum of electronic and thermal Free Energies= -1091.016096

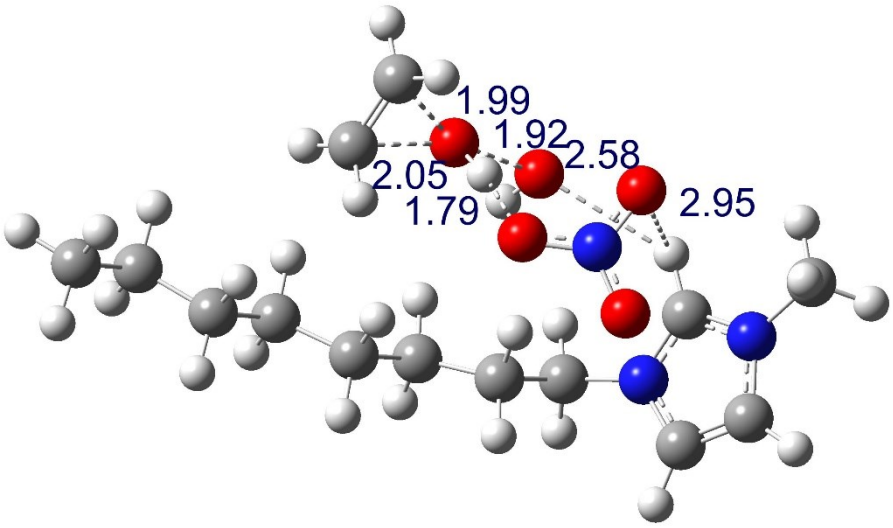
HF=-1091.3846904 / NImag=1 (-425.9677 cm^{-1})

M06GD3/6-311++G** (SMD, water)

Discussion of two different isomers of this transition state

Complex	Free energy (M06GD3, 6-311++G**, SMD)
TS C3a	ΔG= +33.6
TS C3b (best)	ΔG= +32.6

TS C3a



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.530153	-2.208408	-0.507306
2	6	0	-4.556446	-1.369843	-0.789085
3	6	0	-3.323591	-0.430305	0.770362
4	7	0	-2.782987	-1.611758	0.484278
5	1	0	-3.266677	-3.174807	-0.908234
6	1	0	-5.376048	-1.452265	-1.485411
7	7	0	-4.415740	-0.271368	0.030242
8	6	0	-5.245421	0.924041	-0.008988
9	1	0	-6.293551	0.641001	0.092679
10	1	0	-4.958633	1.577468	0.814222

11	6	0	-1.488901	-2.083283	0.986044
12	6	0	-0.380016	-1.736152	0.015835
13	1	0	-1.569248	-3.160975	1.153398
14	1	0	-1.329308	-1.599708	1.954701
15	6	0	0.996235	-1.917682	0.624404
16	1	0	-0.484854	-2.338345	-0.897836
17	1	0	-0.494120	-0.685799	-0.282927
18	6	0	2.097763	-1.522159	-0.342016
19	1	0	1.070023	-1.290000	1.527527
20	1	0	1.138326	-2.955122	0.960587
21	1	0	2.147620	-2.247888	-1.167626
22	1	0	1.832528	-0.558307	-0.805241
23	6	0	3.456805	-1.394397	0.318562
24	6	0	4.549157	-0.960617	-0.640618
25	1	0	3.734813	-2.350029	0.789340
26	1	0	3.384823	-0.663406	1.140443
27	6	0	5.880886	-0.705171	0.041846
28	1	0	4.677245	-1.723878	-1.423844
29	1	0	4.231068	-0.044270	-1.163712
30	6	0	6.960846	-0.272791	-0.930543
31	1	0	5.743669	0.065534	0.814864
32	1	0	6.196172	-1.614156	0.574098
33	1	0	7.915597	-0.085300	-0.429051
34	1	0	7.132152	-1.040580	-1.694514
35	1	0	6.672785	0.648347	-1.451435
36	1	0	-2.935780	0.276773	1.491674
37	7	0	-1.560103	1.591213	-1.160819
38	8	0	-2.166641	2.381408	-0.422698
39	8	0	-2.177385	0.826911	-1.916403
40	8	0	-0.305762	1.551683	-1.135472
41	1	0	-5.092776	1.440101	-0.958652
42	8	0	-0.566459	1.054639	2.155337
43	1	0	-0.065891	0.288429	2.459482
44	8	0	0.964508	1.848016	1.308354
45	1	0	0.414670	1.762096	0.490482
46	6	0	2.105450	3.284088	0.533231
47	6	0	2.676825	2.090287	0.201593

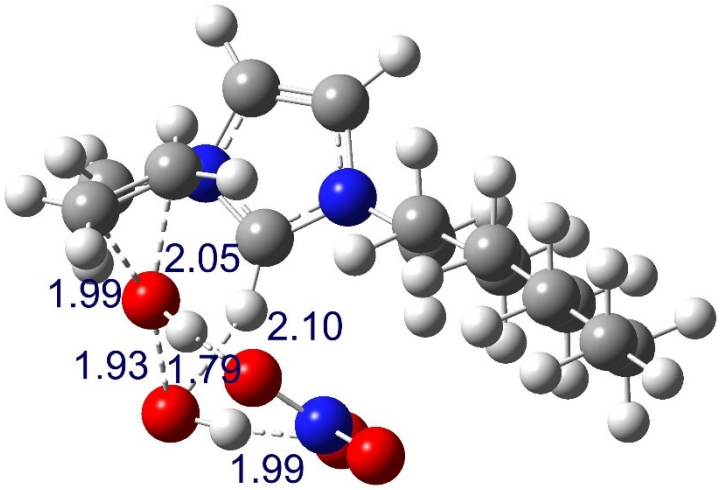
48	1	0	2.399022	3.817537	1.429808
49	1	0	1.429274	3.789661	-0.148699
50	1	0	3.423615	1.628404	0.839167
51	1	0	2.452576	1.605967	-0.744066

Sum of electronic and thermal Enthalpies= -1090.225208

Sum of electronic and thermal Free Energies= -1090.313928

HF=-1090.6852445 / NImag=1 (-562.6558 cm^{-1})

TS C3b



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	2.461026	-1.768917	-0.550771
2	6	0	3.177259	-0.654613	-0.670324
3	7	0	4.244538	-0.753795	0.117130
4	6	0	4.189469	-1.955226	0.793254
5	6	0	3.068062	-2.589660	0.377764
6	6	0	5.219333	0.302559	0.346841
7	6	0	1.119751	-1.965310	-1.106735
8	6	0	0.072070	-1.483216	-0.127565
9	6	0	-1.340111	-1.680744	-0.639377
10	6	0	-2.375691	-1.137306	0.329339
11	6	0	-3.789065	-1.176599	-0.219936

12	6	0	-4.799983	-0.509125	0.693071
13	6	0	-6.218586	-0.552114	0.154119
14	6	0	-7.211702	0.137503	1.069113
15	8	0	2.167853	1.885573	0.377484
16	8	0	2.424720	2.240026	-1.501519
17	6	0	1.747667	0.897941	2.127685
18	6	0	1.998886	2.223434	2.331565
19	8	0	-0.329204	1.291719	-1.883380
20	7	0	-1.059763	1.803446	-1.016281
21	8	0	-2.284691	1.855207	-1.176572
22	8	0	-0.551449	2.258077	0.036454
23	1	0	2.649438	-3.548447	0.641582
24	1	0	4.958940	-2.245997	1.490812
25	1	0	6.223090	-0.122959	0.339019
26	1	0	1.008854	-3.029886	-1.332726
27	1	0	1.069708	-1.407164	-2.047061
28	1	0	0.206722	-2.000427	0.833959
29	1	0	0.246418	-0.413901	0.057088
30	1	0	-1.447552	-1.172072	-1.609786
31	1	0	-1.526559	-2.748294	-0.827587
32	1	0	-2.328509	-1.701143	1.273391
33	1	0	-2.118904	-0.097521	0.588637
34	1	0	-4.085962	-2.221068	-0.401839
35	1	0	-3.808610	-0.680251	-1.202992
36	1	0	-4.771900	-0.985342	1.685815
37	1	0	-4.502976	0.539936	0.852296
38	1	0	-6.238996	-0.083917	-0.840553
39	1	0	-6.514899	-1.599851	0.001420
40	1	0	-8.231455	0.099584	0.672930
41	1	0	-7.223377	-0.331027	2.060585
42	1	0	-6.948968	1.192911	1.209122
43	1	0	2.925844	0.216518	-1.273707
44	1	0	5.128778	1.042996	-0.447346
45	1	0	1.203864	2.047860	0.209710
46	1	0	1.557495	1.905663	-1.782406
47	1	0	5.027727	0.773575	1.313624
48	1	0	1.186721	2.940892	2.393700

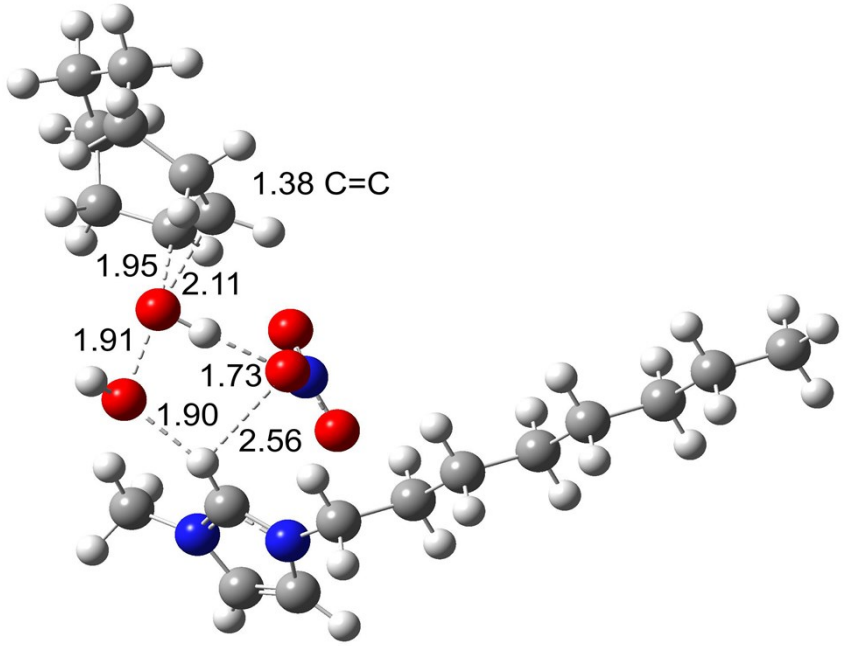
49	1	0	2.997623	2.579717	2.556286
50	1	0	0.731594	0.535780	2.002521
51	1	0	2.543261	0.158743	2.160343

Sum of electronic and thermal Enthalpies= -1090.226274

Sum of electronic and thermal Free Energies= -1090.315548

HF= -1090.68591 / NImag=1 (-554.8950 cm^{-1})

Transition state C3, Charge=0, Multiplicity=1 – Oxidation of cyclooctene



B3LYP/6-311++G** (gas-phase) only - not calculated by M06GD3-SMD

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.708328	4.225251	-0.002881
2	6	0	0.572525	4.807322	0.461669
3	6	0	-0.010790	3.072676	-0.780471
4	7	0	1.322814	3.147645	-0.780787
5	1	0	2.740977	4.473317	0.165735
6	1	0	0.430772	5.654792	1.109159
7	7	0	-0.489209	4.076857	-0.040293
8	6	0	-1.912715	4.286232	0.247134
9	1	0	-2.480120	3.563178	-0.342920
10	6	0	2.213911	2.150408	-1.398665

11	6	0	3.067760	1.414602	-0.364816
12	1	0	2.832401	2.661859	-2.142404
13	1	0	1.563943	1.448600	-1.921817
14	6	0	3.871056	0.275903	-1.002473
15	1	0	3.754855	2.121653	0.115307
16	1	0	2.405157	1.033581	0.415700
17	6	0	4.747350	-0.470122	0.010135
18	1	0	3.177647	-0.433943	-1.470334
19	1	0	4.504052	0.667727	-1.810367
20	1	0	5.442809	0.238340	0.478471
21	1	0	4.112390	-0.852066	0.818391
22	6	0	5.542254	-1.627897	-0.603837
23	6	0	6.412672	-2.376601	0.411330
24	1	0	6.178089	-1.244503	-1.412860
25	1	0	4.846076	-2.334783	-1.073504
26	6	0	7.206106	-3.539453	-0.195467
27	1	0	7.110176	-1.670867	0.881371
28	1	0	5.776718	-2.757617	1.220788
29	6	0	8.069318	-4.282618	0.828199
30	1	0	6.509289	-4.244428	-0.665253
31	1	0	7.843588	-3.159350	-1.003291
32	1	0	8.619043	-5.106788	0.364957
33	1	0	8.801993	-3.612459	1.289036
34	1	0	7.455758	-4.702575	1.631516
35	1	0	-0.646560	2.347611	-1.288478
36	7	0	-0.311460	0.799212	1.650714
37	8	0	-0.345704	0.460095	0.411308
38	8	0	0.568698	1.597275	2.026874
39	8	0	-1.154632	0.332641	2.436602
40	1	0	-2.089733	4.122584	1.310870
41	8	0	-2.785768	0.147236	-0.758305
42	1	0	-1.901104	0.289517	-0.324663
43	8	0	-2.418280	1.789381	-1.671829
44	1	0	-2.934025	1.514529	-2.436841
45	6	0	-3.507956	-1.034266	0.609159
46	1	0	-2.986327	-0.639254	1.476338
47	6	0	-2.755337	-1.885395	-0.175743

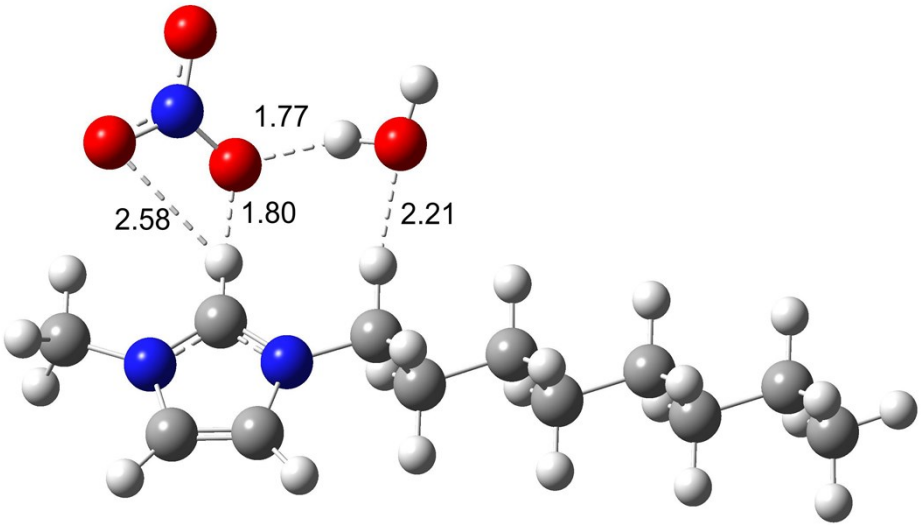
48	1	0	-1.711857	-1.962245	0.116316
49	1	0	-2.191839	5.304939	-0.025754
50	6	0	-4.989782	-0.779677	0.576587
51	1	0	-5.153391	0.176454	1.079168
52	1	0	-5.338857	-0.646623	-0.448747
53	6	0	-3.136338	-2.754563	-1.336340
54	1	0	-2.731495	-2.286521	-2.243020
55	1	0	-2.564414	-3.685686	-1.223046
56	6	0	-5.820137	-1.875756	1.292081
57	1	0	-6.686504	-1.399108	1.762400
58	1	0	-5.230931	-2.301461	2.112791
59	6	0	-4.609868	-3.121234	-1.564019
60	1	0	-5.181305	-2.237145	-1.858443
61	1	0	-4.630731	-3.781588	-2.436846
62	6	0	-6.343198	-3.004196	0.392030
63	1	0	-7.051377	-2.579742	-0.331883
64	1	0	-6.929732	-3.684554	1.020343
65	6	0	-5.303523	-3.836821	-0.376310
66	1	0	-4.546468	-4.213434	0.322574
67	1	0	-5.818305	-4.723748	-0.759206

Sum of electronic and thermal Enthalpies= -1325.500403

Sum of electronic and thermal Free Energies= -1325.609071

HF=-1326.1204197 / NImag=1 (-380.2685 cm^{-1})

Complex D3 (NO_3^-, $OMIM^+$,H_2O) – Complex charge=0, Multiplicity =1



B3LYP/6-311++G** (gas-phase):

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.093009	-2.903602	-0.608214
2	6	0	3.282712	-2.993335	0.045781
3	6	0	2.631281	-0.877614	0.101000
4	7	0	1.705403	-1.577057	-0.566361
5	1	0	1.503716	-3.656696	-1.101961
6	1	0	3.924803	-3.837755	0.227371
7	7	0	3.600479	-1.719523	0.479796
8	6	0	4.798719	-1.327023	1.235363
9	1	0	5.678872	-1.741373	0.743863
10	1	0	4.855360	-0.237335	1.231890
11	6	0	0.453708	-1.013694	-1.119320
12	6	0	-0.720281	-1.134382	-0.145447
13	1	0	0.253286	-1.549746	-2.049895
14	1	0	0.638039	0.034959	-1.361820
15	6	0	-1.994886	-0.518327	-0.734469
16	1	0	-0.890696	-2.187808	0.109305
17	1	0	-0.459739	-0.616755	0.783841
18	6	0	-3.191624	-0.591751	0.220460
19	1	0	-1.789246	0.525963	-0.991670
20	1	0	-2.248164	-1.031272	-1.671753
21	1	0	-3.380035	-1.638312	0.494546

22	1	0	-2.939921	-0.071234	1.152785
23	6	0	-4.471311	0.014868	-0.366434
24	6	0	-5.671230	-0.045707	0.585111
25	1	0	-4.723236	-0.505539	-1.299696
26	1	0	-4.279685	1.059204	-0.642498
27	6	0	-6.952234	0.557213	-0.003053
28	1	0	-5.860781	-1.090314	0.865660
29	1	0	-5.421570	0.478158	1.516844
30	6	0	-8.146076	0.495580	0.954140
31	1	0	-6.762941	1.600374	-0.283605
32	1	0	-7.202887	0.033300	-0.933597
33	1	0	-9.041491	0.934160	0.504972
34	1	0	-8.383402	-0.538102	1.225475
35	1	0	-7.938838	1.040595	1.880457
36	1	0	2.601711	0.203892	0.306975
37	7	0	3.649767	2.483775	0.268064
38	8	0	3.737866	3.621469	-0.187667
39	8	0	4.653065	1.764078	0.483697
40	8	0	2.486302	1.988940	0.533933
41	1	0	4.728119	-1.708084	2.255052
42	8	0	0.403096	2.229471	-1.196760
43	1	0	0.393523	3.030365	-1.728298
44	1	0	1.142310	2.353978	-0.559879

Sum of electronic and thermal Enthalpies= -937.256999

Sum of electronic and thermal Free Energies= -937.341292

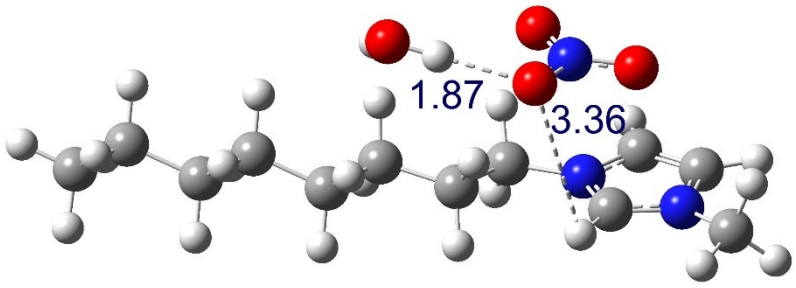
HF=-937.6605529 / NImag=0

M06GD3/6-311++G** (SMD, water):

Discussion of two different isomers of this complex

Complex	Free energy (M06GD3, 6-311++G**, SMD)
D3a	ΔG= -57.7
D3b (best)	ΔG= -57.9

D3a



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.625879	-1.404361	-1.132454
2	6	0	4.661374	-1.026332	-0.346713
3	6	0	2.811905	-0.835768	0.827923
4	7	0	2.478476	-1.289071	-0.377664
5	1	0	3.593045	-1.746133	-2.154996
6	1	0	5.720426	-0.965194	-0.541309
7	7	0	4.132935	-0.690844	0.878953
8	6	0	4.869106	-0.087167	1.979833
9	1	0	5.153028	0.932165	1.711253
10	1	0	4.230391	-0.070129	2.862250
11	6	0	1.127701	-1.546857	-0.897830
12	6	0	0.031546	-1.130967	0.051530
13	1	0	1.061882	-2.614427	-1.131464
14	1	0	1.051588	-0.992323	-1.839278
15	6	0	-1.324388	-1.229965	-0.622316
16	1	0	0.053219	-1.756359	0.954616
17	1	0	0.183855	-0.090912	0.375286
18	6	0	-2.461134	-0.898536	0.326180
19	1	0	-1.343954	-0.536716	-1.478850
20	1	0	-1.467516	-2.236517	-1.041991
21	1	0	-2.529140	-1.674422	1.103448
22	1	0	-2.227423	0.039373	0.852971
23	6	0	-3.799056	-0.754502	-0.373362

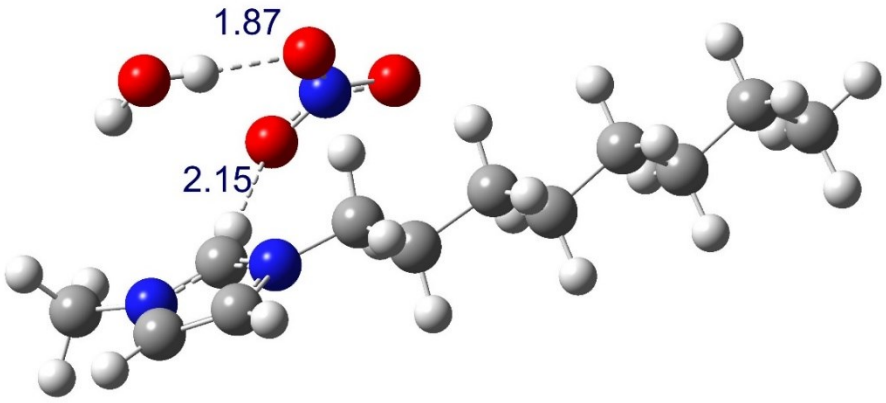
24	6	0	-4.926888	-0.382534	0.570209
25	1	0	-4.046948	-1.692487	-0.894262
26	1	0	-3.714598	0.014531	-1.157807
27	6	0	-6.269797	-0.237758	-0.122911
28	1	0	-5.006904	-1.141101	1.364642
29	1	0	-4.675909	0.562181	1.078711
30	6	0	-7.383199	0.138151	0.835319
31	1	0	-6.185849	0.520087	-0.915086
32	1	0	-6.516225	-1.180979	-0.631399
33	1	0	-8.346924	0.240992	0.326490
34	1	0	-7.500498	-0.621016	1.618001
35	1	0	-7.167434	1.090923	1.333512
36	1	0	2.139527	-0.619006	1.644591
37	7	0	1.800412	2.005745	-0.374053
38	8	0	1.357456	1.624669	-1.470245
39	8	0	3.022731	2.032605	-0.162089
40	8	0	1.006941	2.345522	0.532783
41	1	0	5.762513	-0.677387	2.184294
42	8	0	-1.681617	2.417943	-0.397824
43	1	0	-1.768444	1.684206	-1.015627
44	1	0	-0.756852	2.363499	-0.092101

Sum of electronic and thermal Enthalpies= -936.668370

Sum of electronic and thermal Free Energies= -936.752003

HF=-937.0694563 / NImag=0

D3b



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.523119	-2.165963	-0.549510
2	6	0	4.567557	-1.724631	0.191532
3	6	0	2.884868	-0.338758	0.496174
4	7	0	2.480026	-1.290035	-0.342357
5	1	0	3.421168	-3.020401	-1.199497
6	1	0	5.565384	-2.112031	0.322945
7	7	0	4.144650	-0.584892	0.840183
8	6	0	4.968627	0.272918	1.679814
9	1	0	4.336795	1.045075	2.118229
10	6	0	1.165792	-1.327250	-0.996255
11	6	0	0.023298	-1.272602	-0.005775
12	1	0	1.138798	-2.245303	-1.588589
13	1	0	1.117204	-0.478745	-1.688230
14	6	0	-1.302714	-1.075035	-0.715942
15	1	0	0.007715	-2.191617	0.595052
16	1	0	0.179371	-0.442129	0.697391
17	6	0	-2.472757	-0.978195	0.245126
18	1	0	-1.250708	-0.153325	-1.315974
19	1	0	-1.472327	-1.895625	-1.428680
20	1	0	-2.606901	-1.939515	0.763855
21	1	0	-2.238300	-0.239272	1.027201
22	6	0	-3.764994	-0.579801	-0.442347
23	6	0	-4.951742	-0.511701	0.499960

24	1	0	-3.983043	-1.289443	-1.255755
25	1	0	-3.624309	0.400813	-0.924367
26	6	0	-6.239522	-0.090140	-0.185043
27	1	0	-5.097820	-1.493550	0.976924
28	1	0	-4.728273	0.190860	1.318215
29	6	0	-7.416010	-0.029421	0.769597
30	1	0	-6.090658	0.891007	-0.658363
31	1	0	-6.457795	-0.790801	-1.003861
32	1	0	-8.338915	0.275724	0.266188
33	1	0	-7.597714	-1.007228	1.231678
34	1	0	-7.227920	0.685316	1.579754
35	1	0	2.293158	0.504928	0.835127
36	7	0	0.159880	2.131680	-0.033918
37	8	0	0.922833	2.162600	0.949835
38	8	0	-1.068655	2.178483	0.121742
39	8	0	0.638633	2.041379	-1.185288
40	1	0	5.424587	-0.321375	2.472164
41	8	0	3.475512	2.084504	-1.348422
42	1	0	3.822523	2.207266	-0.458731
43	1	0	2.507114	2.073686	-1.231063
44	1	0	5.749261	0.736154	1.074117

Sum of electronic and thermal Enthalpies= -936.669124

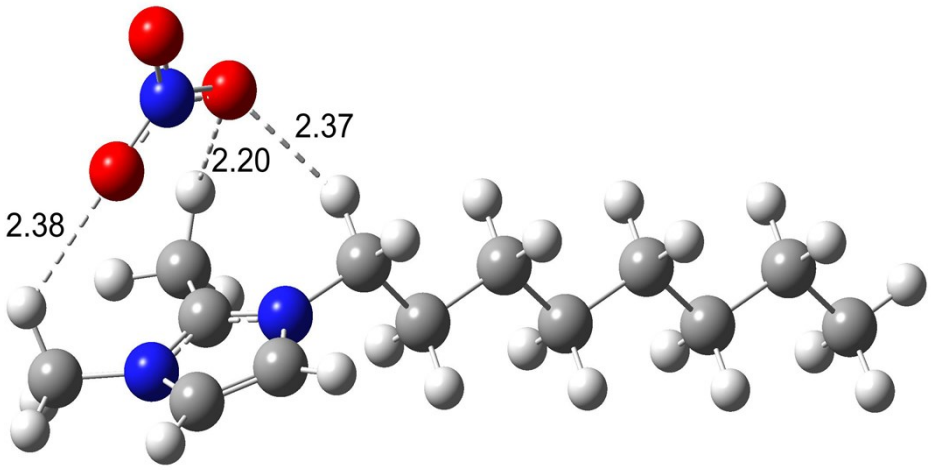
Sum of electronic and thermal Free Energies= -936.752358

HF= HF=-937.070078 / NImag=0

5.7. Structures along the pathway for the [OMMIM][NO_3] system

Complex NO_3^- / $OMMIM^+$ - Complex charge=0, Multiplicity=1

B3LYP (gas-phase):



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.198024	-1.340238	-1.634066
2	6	0	3.312593	-1.967859	-1.187796
3	6	0	2.393072	-0.910607	0.537978
4	7	0	1.632509	-0.694086	-0.549108
5	1	0	1.767327	-1.283387	-2.618086
6	1	0	4.048430	-2.552872	-1.710305
7	7	0	3.409199	-1.711571	0.167604
8	6	0	4.590505	-1.997104	0.983410
9	1	0	5.203700	-2.722513	0.451975
10	1	0	5.145218	-1.069041	1.126869
11	6	0	0.431845	0.158516	-0.605178
12	6	0	-0.857830	-0.606149	-0.298751
13	1	0	0.405011	0.583288	-1.610173
14	1	0	0.605093	0.993119	0.073410
15	6	0	-2.089516	0.304204	-0.371554
16	1	0	-0.967788	-1.437160	-1.005382
17	1	0	-0.791007	-1.053435	0.699519
18	6	0	-3.401667	-0.434174	-0.083017

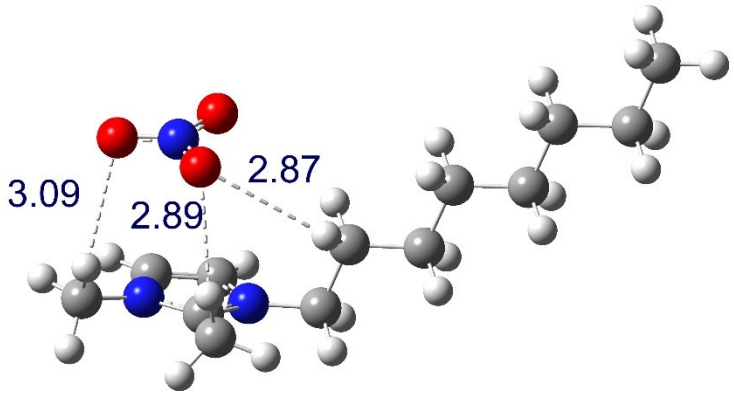
19	1	0	-1.971334	1.130805	0.339157
20	1	0	-2.143382	0.764095	-1.366222
21	1	0	-3.521070	-1.255642	-0.801055
22	1	0	-3.343534	-0.902003	0.908200
23	6	0	-4.636156	0.472809	-0.141534
24	6	0	-5.950145	-0.264393	0.140048
25	1	0	-4.691252	0.945733	-1.130406
26	1	0	-4.517596	1.291054	0.579950
27	6	0	-7.185624	0.641902	0.088899
28	1	0	-6.071288	-1.080102	-0.584712
29	1	0	-5.893998	-0.741599	1.127232
30	6	0	-8.494121	-0.103065	0.368288
31	1	0	-7.065733	1.455403	0.814516
32	1	0	-7.241258	1.120055	-0.896591
33	1	0	-9.354550	0.570083	0.322078
34	1	0	-8.658152	-0.901851	-0.361966
35	1	0	-8.484611	-0.561377	1.362315
36	7	0	3.784739	2.113280	0.000461
37	8	0	2.569000	2.288779	0.319859
38	8	0	4.418795	2.990876	-0.590603
39	8	0	4.333908	1.004721	0.297630
40	1	0	4.294130	-2.423043	1.941468
41	6	0	2.133065	-0.363459	1.890317
42	1	0	1.172582	-0.714782	2.278030
43	1	0	2.920068	-0.654287	2.582066
44	1	0	2.131970	0.728793	1.808072

Sum of electronic and thermal Enthalpies= -900.104136

Sum of electronic and thermal Free Energies= -900.185057

HF= -900.5093038 / NImag=0

M06GD3 – SMD solvent:



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.622583	-0.732468	-1.665807
2	6	0	-3.790351	-0.257649	-1.180454
3	6	0	-2.703485	-1.221477	0.492841
4	7	0	-1.966693	-1.347083	-0.616957
5	1	0	-2.194212	-0.703197	-2.655256
6	1	0	-4.601133	0.270181	-1.656690
7	7	0	-3.830571	-0.581767	0.159566
8	6	0	-4.873750	-0.194587	1.096925
9	1	0	-5.340413	-1.081098	1.530689
10	1	0	-4.449137	0.422487	1.891629
11	6	0	-0.592607	-1.847994	-0.692195
12	6	0	0.405538	-0.765598	-0.341984
13	1	0	-0.445274	-2.206972	-1.715052
14	1	0	-0.502287	-2.710041	-0.025144
15	6	0	1.833902	-1.262274	-0.446287
16	1	0	0.250660	0.090998	-1.013850
17	1	0	0.206425	-0.405148	0.677455
18	6	0	2.845436	-0.190033	-0.086672
19	1	0	1.968723	-2.131740	0.214782
20	1	0	2.024654	-1.622141	-1.468525
21	1	0	2.705093	0.678445	-0.748333
22	1	0	2.643693	0.171265	0.933423
23	6	0	4.283021	-0.666015	-0.176862
24	6	0	5.290176	0.408633	0.187761
25	1	0	4.485787	-1.026078	-1.197480

26	1	0	4.421750	-1.535675	0.484168
27	6	0	6.731457	-0.061431	0.105458
28	1	0	5.152805	1.277843	-0.474423
29	1	0	5.084089	0.771242	1.207071
30	6	0	7.721072	1.026554	0.474683
31	1	0	6.865633	-0.929271	0.767100
32	1	0	6.935183	-0.422843	-0.912765
33	1	0	8.757142	0.678616	0.413573
34	1	0	7.621278	1.891054	-0.192575
35	1	0	7.550122	1.381917	1.497976
36	7	0	-2.230247	2.263904	0.025317
37	8	0	-1.781595	1.663927	1.020005
38	8	0	-1.494977	2.479670	-0.955954
39	8	0	-3.417273	2.639209	0.008938
40	1	0	-5.622731	0.380234	0.553824
41	6	0	-2.355478	-1.660495	1.850444
42	1	0	-1.495871	-2.330970	1.838252
43	1	0	-2.111110	-0.790955	2.471795
44	1	0	-3.201618	-2.176985	2.311855

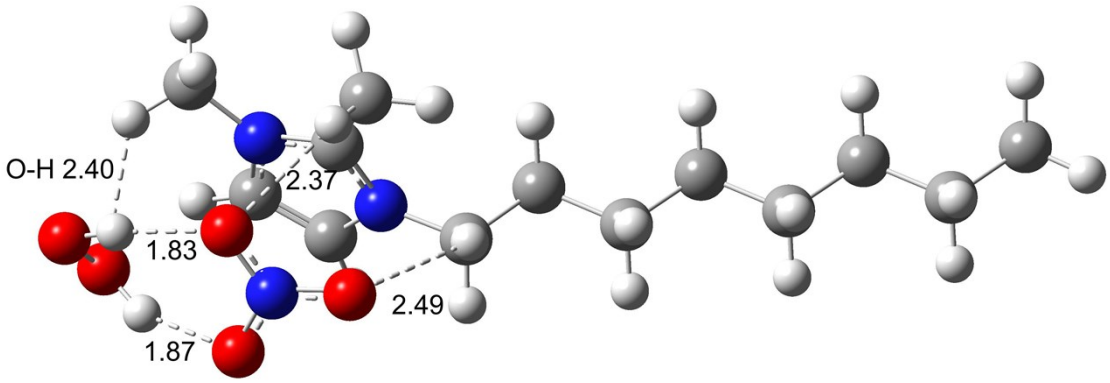
Sum of electronic and thermal Enthalpies= -899.531745

Sum of electronic and thermal Free Energies= -899.610326

HF= -899.9342393 / NImag=0

Complex A4 – H_2O_2 / NO_3^- / $OMMIM^+$ - Complex charge=0, Multiplicity=1

B3LYP (gas-phase):



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.555645	-1.143576	-1.555936
2	6	0	2.682338	-1.753234	-1.113994
3	6	0	1.659833	-0.855268	0.645728
4	7	0	0.931755	-0.584805	-0.453412
5	1	0	1.166084	-1.020314	-2.550805
6	1	0	3.476237	-2.247120	-1.644636
7	7	0	2.731149	-1.567647	0.254173
8	6	0	3.838947	-2.005491	1.109668
9	1	0	4.761518	-1.888186	0.544782
10	1	0	3.892181	-1.358835	1.981441
11	6	0	-0.282751	0.249384	-0.513628
12	6	0	-1.566787	-0.542272	-0.257699
13	1	0	-0.291043	0.699122	-1.507536
14	1	0	-0.145425	1.070641	0.189139
15	6	0	-2.811119	0.349122	-0.348989
16	1	0	-1.641103	-1.360460	-0.983157
17	1	0	-1.519548	-1.008956	0.732964
18	6	0	-4.117551	-0.411218	-0.093423
19	1	0	-2.722037	1.171771	0.370977
20	1	0	-2.851143	0.816304	-1.340831
21	1	0	-4.206992	-1.232368	-0.815992
22	1	0	-4.075237	-0.880624	0.897771
23	6	0	-5.363926	0.477156	-0.179185

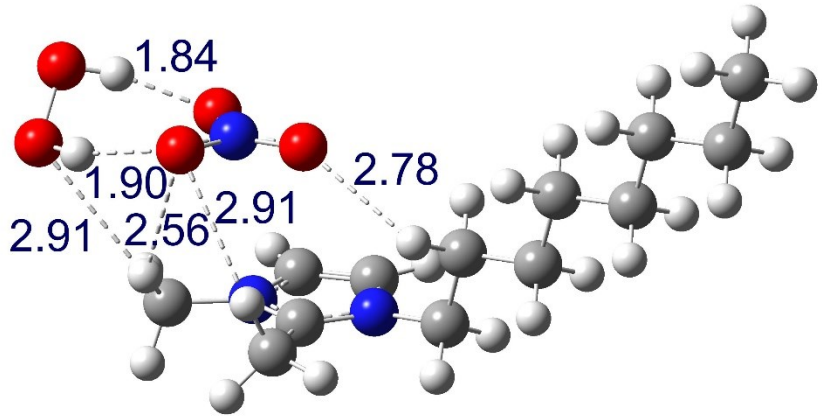
24	6	0	-6.672305	-0.277801	0.080307
25	1	0	-5.406704	0.945496	-1.170828
26	1	0	-5.271424	1.299739	0.541301
27	6	0	-7.919429	0.609983	-0.003245
28	1	0	-6.766380	-1.100270	-0.640747
29	1	0	-6.629725	-0.747018	1.071947
30	6	0	-9.222104	-0.150856	0.259778
31	1	0	-7.824779	1.432484	0.715958
32	1	0	-7.963346	1.077124	-0.994581
33	1	0	-10.091056	0.508918	0.188272
34	1	0	-9.360151	-0.960886	-0.463405
35	1	0	-9.225575	-0.596656	1.259484
36	7	0	3.150701	1.890435	0.147933
37	8	0	2.002672	2.306323	0.392680
38	8	0	3.615954	1.929895	-1.017982
39	8	0	3.849381	1.390715	1.087492
40	1	0	3.690692	-3.043534	1.413678
41	6	0	1.378102	-0.412074	2.034962
42	1	0	0.355369	-0.053252	2.126916
43	1	0	1.520188	-1.235550	2.737822
44	1	0	2.058424	0.407352	2.288730
45	1	0	4.893349	0.591857	-1.311541
46	8	0	5.377476	-0.227206	-1.067577
47	8	0	6.161491	0.229272	0.074020
48	1	0	5.473235	0.712209	0.586884

Sum of electronic and thermal Enthalpies= -1051.700487

Sum of electronic and thermal Free Energies= -1051.790031

HF= -1052.1389092 / NImag=0

M06GD3 – SMD solvent:



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.526055	-2.188235	-1.487239
2	6	0	-2.813733	-1.821576	-1.309442
3	6	0	-1.793963	-1.693415	0.654565
4	7	0	-0.910516	-2.123480	-0.252906
5	1	0	-0.985697	-2.498988	-2.367516
6	1	0	-3.638009	-1.743333	-2.000339
7	7	0	-2.966679	-1.526556	0.028896
8	6	0	-4.202285	-1.086654	0.664484
9	1	0	-4.597503	-1.876104	1.307087
10	6	0	0.522316	-2.341961	-0.041147
11	6	0	1.313295	-1.057325	-0.156717
12	1	0	0.839499	-3.068359	-0.795132
13	1	0	0.657612	-2.807926	0.939347
14	6	0	2.799836	-1.309628	0.002727
15	1	0	1.109885	-0.596836	-1.134015
16	1	0	0.966813	-0.346206	0.606446
17	6	0	3.620217	-0.036290	-0.084006
18	1	0	2.986646	-1.801557	0.969307
19	1	0	3.135698	-2.017254	-0.770226
20	1	0	3.417114	0.463154	-1.043749
21	1	0	3.288710	0.663901	0.698019
22	6	0	5.111709	-0.277602	0.053240
23	6	0	5.933370	0.995908	-0.018492
24	1	0	5.442846	-0.970758	-0.735653

25	1	0	5.312505	-0.787973	1.008071
26	6	0	7.427246	0.756431	0.108597
27	1	0	5.727370	1.511043	-0.969853
28	1	0	5.607007	1.686536	0.774853
29	6	0	8.231715	2.040113	0.042533
30	1	0	7.629432	0.236719	1.056197
31	1	0	7.750912	0.070608	-0.687514
32	1	0	9.307141	1.856758	0.132500
33	1	0	8.062274	2.561440	-0.907252
34	1	0	7.943494	2.726072	0.848116
35	7	0	-2.326548	1.520114	-0.275995
36	8	0	-3.132959	1.473775	-1.230545
37	8	0	-1.169071	1.113782	-0.423103
38	8	0	-2.700120	1.963145	0.830778
39	1	0	-4.016935	-0.189917	1.259398
40	8	0	-5.297066	3.037373	-0.487577
41	1	0	-4.623510	2.515790	-0.978568
42	8	0	-5.492454	2.245668	0.684725
43	1	0	-4.578434	2.158463	1.030587
44	1	0	-4.924704	-0.860106	-0.118820
45	6	0	-1.552519	-1.418111	2.077847
46	1	0	-0.589653	-1.817242	2.397401
47	1	0	-1.556508	-0.335651	2.254527
48	1	0	-2.341344	-1.862701	2.690898

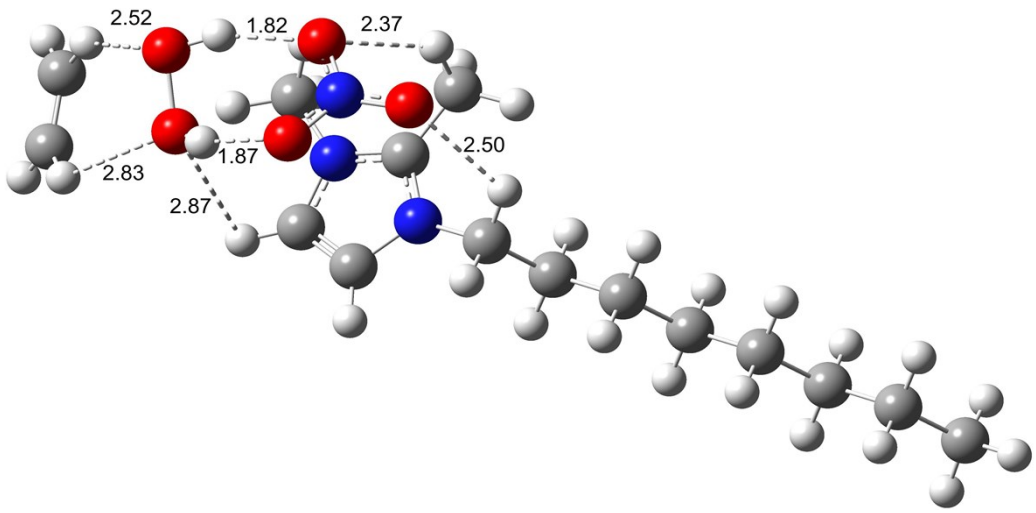
Sum of electronic and thermal Enthalpies= -1051.050133

Sum of electronic and thermal Free Energies= -1051.137399

HF= -1051.4856333 / NImag=0

Complex B4a ethene / H_2O_2 / NO_3^- / OMMIM$^+$ - Complex charge=0, Multiplicity=1

B3LYP (gas-phase):



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	2.172263	-1.061295	0.508338
2	6	0	2.163366	-1.437172	-0.820276
3	6	0	1.001283	-0.984360	-1.351679
4	7	0	0.316074	-0.329558	-0.342047
5	6	0	1.042416	-0.388223	0.788887
6	6	0	0.710342	0.215318	2.103954
7	6	0	-0.963782	0.379909	-0.522010
8	6	0	-2.178350	-0.481060	-0.168599
9	6	0	-3.495047	0.272475	-0.390797
10	6	0	-4.732641	-0.562157	-0.041452
11	6	0	-6.052567	0.185963	-0.260058
12	6	0	-7.291694	-0.644882	0.091282
13	6	0	-8.613048	0.101362	-0.126122
14	6	0	-9.845624	-0.735416	0.228295
15	6	0	3.286603	-1.277834	1.436700
16	8	0	4.720640	0.333907	-0.982404
17	8	0	5.455012	1.032247	0.064738
18	8	0	3.043314	2.084234	0.932460
19	7	0	2.308114	2.386979	-0.062739
20	8	0	2.773736	2.304198	-1.226133
21	8	0	1.128254	2.733022	0.130928

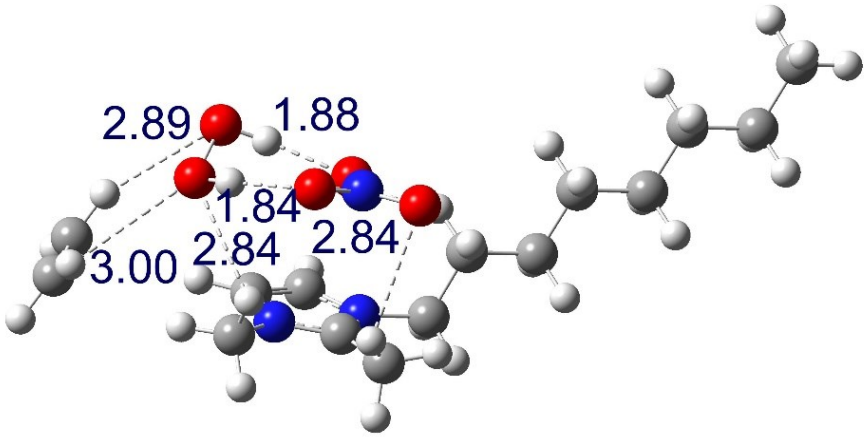
22	6	0	6.780049	-2.547354	-0.790216
23	6	0	7.126647	-1.999982	0.372042
24	1	0	0.620789	-1.032087	-2.356483
25	1	0	3.000584	-1.940706	-1.268646
26	1	0	4.175857	-1.496795	0.851370
27	1	0	3.463371	-0.361605	1.995943
28	1	0	-0.993607	0.689820	-1.567612
29	1	0	-0.910636	1.296295	0.065090
30	1	0	-2.165322	-1.394063	-0.774887
31	1	0	-2.109121	-0.801899	0.877202
32	1	0	-3.494181	1.190722	0.209161
33	1	0	-3.557492	0.593585	-1.437985
34	1	0	-4.732262	-1.480167	-0.642915
35	1	0	-4.668263	-0.884031	1.005855
36	1	0	-6.117080	0.507191	-1.307521
37	1	0	-6.050900	1.104978	0.339789
38	1	0	-7.294124	-1.564416	-0.508541
39	1	0	-7.227646	-0.966400	1.139069
40	1	0	-8.610877	1.020042	0.472921
41	1	0	-8.677966	0.421838	-1.173003
42	1	0	-10.769666	-0.175091	0.061936
43	1	0	-9.895058	-1.644604	-0.379261
44	1	0	-9.827793	-1.041134	1.279201
45	1	0	3.059478	-2.105494	2.111542
46	1	0	-0.342408	0.484826	2.154808
47	1	0	0.929697	-0.485777	2.912091
48	1	0	1.309813	1.121750	2.237880
49	1	0	4.163695	1.058771	-1.341997
50	1	0	4.719102	1.504118	0.518991
51	1	0	6.268563	-1.961717	-1.547116
52	1	0	7.008038	-3.581929	-1.029004
53	1	0	7.652931	-2.569012	1.132939
54	1	0	6.901963	-0.960268	0.587888

Sum of electronic and thermal Enthalpies= -1130.261904

Sum of electronic and thermal Free Energies= -1130.367479

HF= -1130.7570778 / NImag=0

M06GD3 – SMD solvent:



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.574915	-1.677330	-1.130697
2	6	0	-2.806102	-1.251552	-0.770610
3	6	0	-1.576986	-1.406340	1.066957
4	7	0	-0.829283	-1.787232	0.025431
5	1	0	-1.156458	-1.924054	-2.093834
6	1	0	-3.694198	-1.051981	-1.351579
7	7	0	-2.794657	-1.102647	0.599999
8	6	0	-3.909601	-0.641967	1.416261
9	1	0	-4.079413	-1.339498	2.238254
10	6	0	0.587106	-2.159433	0.059688
11	6	0	1.498972	-0.963555	-0.107260
12	1	0	0.738597	-2.881858	-0.747966
13	1	0	0.779146	-2.680771	1.001607
14	6	0	2.955227	-1.385810	-0.120437
15	1	0	1.245831	-0.445895	-1.043628
16	1	0	1.320221	-0.247653	0.707192
17	6	0	3.903495	-0.213510	-0.288163
18	1	0	3.190173	-1.917412	0.814176
19	1	0	3.119262	-2.109813	-0.932899
20	1	0	3.660922	0.320350	-1.219815
21	1	0	3.739066	0.508244	0.526505
22	6	0	5.362579	-0.628668	-0.309610
23	6	0	6.316190	0.537856	-0.487386
24	1	0	5.521971	-1.356514	-1.120430

25	1	0	5.604622	-1.159073	0.624524
26	6	0	7.776320	0.122248	-0.511035
27	1	0	6.074084	1.068740	-1.421434
28	1	0	6.158447	1.266643	0.323082
29	6	0	8.715416	1.298706	-0.693404
30	1	0	8.015518	-0.406216	0.423014
31	1	0	7.929679	-0.607487	-1.319091
32	1	0	9.765082	0.988530	-0.708927
33	1	0	8.510192	1.822690	-1.634618
34	1	0	8.596298	2.026095	0.118566
35	7	0	-1.025173	1.888215	1.162426
36	8	0	-0.853700	1.458454	0.003516
37	8	0	-0.116200	1.806278	1.996535
38	8	0	-2.123671	2.392124	1.483471
39	1	0	-3.697694	0.352629	1.816358
40	8	0	-3.014282	2.273990	-1.586574
41	1	0	-2.172995	1.874378	-1.277548
42	8	0	-3.934087	1.873267	-0.570425
43	1	0	-3.474927	2.149131	0.254216
44	1	0	-4.799473	-0.603146	0.788282
45	6	0	-1.174309	-1.349598	2.480860
46	1	0	-0.088083	-1.344972	2.578998
47	1	0	-1.569535	-0.443909	2.950880
48	1	0	-1.573523	-2.212106	3.026011
49	6	0	-5.942282	-0.147525	-2.419109
50	6	0	-6.710065	-0.197064	-1.340490
51	1	0	-6.045206	-0.867153	-3.227587
52	1	0	-7.475462	-0.959164	-1.217112
53	1	0	-6.611524	0.524904	-0.533020
54	1	0	-5.177588	0.616338	-2.542738

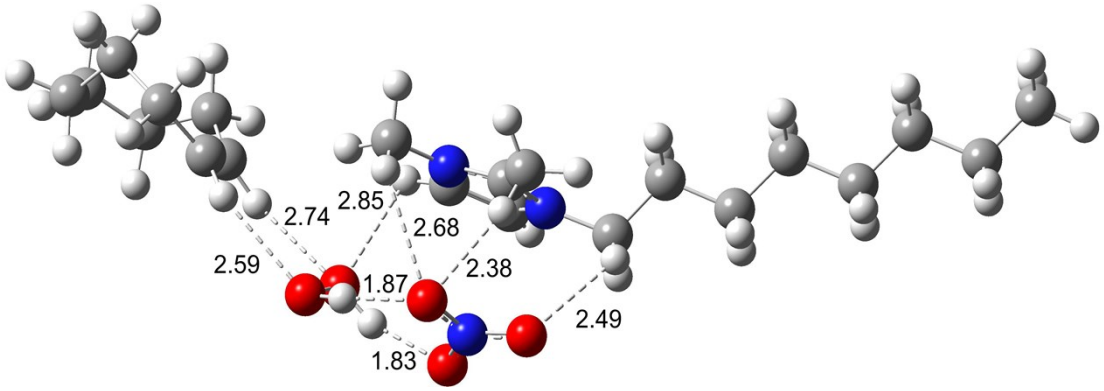
Sum of electronic and thermal Enthalpies= -1129.538174

Sum of electronic and thermal Free Energies= -1129.636296

HF= -1130.0301122 / NImag=0

Complex B4 cyclooctene / H_2O_2 / NO_3^- / OMMIM$^+$ - Complex charge=0, Multiplicity=1

B3LYP – gas-phase only:



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.527204	-0.052103	0.586594
2	6	0	0.604949	-0.560727	-0.694584
3	6	0	-0.621953	-0.415742	-1.252834
4	7	0	-1.433954	0.188968	-0.307813
5	6	0	-0.718659	0.401382	0.811541
6	6	0	-1.175565	1.060787	2.060594
7	6	0	-2.832161	0.593818	-0.541363
8	6	0	-3.842286	-0.464993	-0.094267
9	6	0	-5.285173	-0.033883	-0.382423
10	6	0	-6.323063	-1.073361	0.056339
11	6	0	-7.767824	-0.650032	-0.231939
12	6	0	-8.807879	-1.686664	0.207185
13	6	0	-10.253576	-1.266300	-0.081501
14	6	0	-11.285971	-2.307243	0.360811
15	6	0	1.656071	0.073463	1.514050
16	8	0	2.689756	1.677980	-1.127787
17	8	0	3.280953	2.617546	-0.183969
18	8	0	0.707086	3.248496	0.644858
19	7	0	-0.084385	3.283042	-0.352236
20	8	0	0.376869	3.173245	-1.515227
21	8	0	-1.308886	3.396524	-0.158219
22	6	0	5.181511	-0.843686	-0.562943

23	6	0	5.502519	-0.114758	0.511835
24	1	0	-0.977894	-0.647773	-2.240830
25	1	0	1.531381	-0.925148	-1.099937
26	1	0	2.573731	-0.100338	0.957562
27	1	0	1.679225	1.087938	1.906960
28	1	0	-2.916032	0.789073	-1.611468
29	1	0	-2.978150	1.552963	-0.045516
30	1	0	-3.627792	-1.410473	-0.605586
31	1	0	-3.721816	-0.657681	0.978054
32	1	0	-5.488016	0.918649	0.122219
33	1	0	-5.398147	0.160900	-1.456166
34	1	0	-6.117135	-2.026148	-0.447982
35	1	0	-6.209973	-1.266709	1.130783
36	1	0	-7.880473	-0.456980	-1.306456
37	1	0	-7.972451	0.303736	0.270930
38	1	0	-8.603068	-2.641319	-0.294868
39	1	0	-8.696467	-1.879369	1.282262
40	1	0	-10.458625	-0.312716	0.419973
41	1	0	-10.365508	-1.074551	-1.155555
42	1	0	-12.304914	-1.977181	0.140980
43	1	0	-11.129202	-3.262449	-0.150284
44	1	0	-11.223068	-2.494642	1.437435
45	1	0	1.559905	-0.652985	2.323403
46	1	0	-2.261939	1.094427	2.109620
47	1	0	-0.803989	0.520910	2.934140
48	1	0	-0.792594	2.086446	2.079542
49	1	0	1.993472	2.233510	-1.541723
50	1	0	2.470794	2.979109	0.243114
51	1	0	4.540656	-0.339324	-1.283988
52	1	0	5.065137	0.881876	0.546096
53	6	0	6.395506	-0.422540	1.687718
54	1	0	6.956334	0.496156	1.906979
55	1	0	5.764087	-0.574992	2.575576
56	6	0	5.613030	-2.236978	-0.967399
57	1	0	4.869620	-2.616118	-1.676066
58	1	0	5.593061	-2.928203	-0.119906
59	6	0	7.002257	-2.300047	-1.652794

60	1	0	7.147295	-1.384609	-2.237542
61	1	0	7.001123	-3.125972	-2.373348
62	6	0	7.399870	-1.580810	1.591502
63	1	0	7.957608	-1.593294	2.533940
64	1	0	6.874230	-2.539278	1.556449
65	6	0	8.404142	-1.485115	0.414307
66	1	0	8.389692	-0.471458	-0.002546
67	1	0	9.415475	-1.632347	0.806888
68	6	0	8.200809	-2.508631	-0.715913
69	1	0	8.131406	-3.509483	-0.268414
70	1	0	9.105423	-2.521472	-1.335316

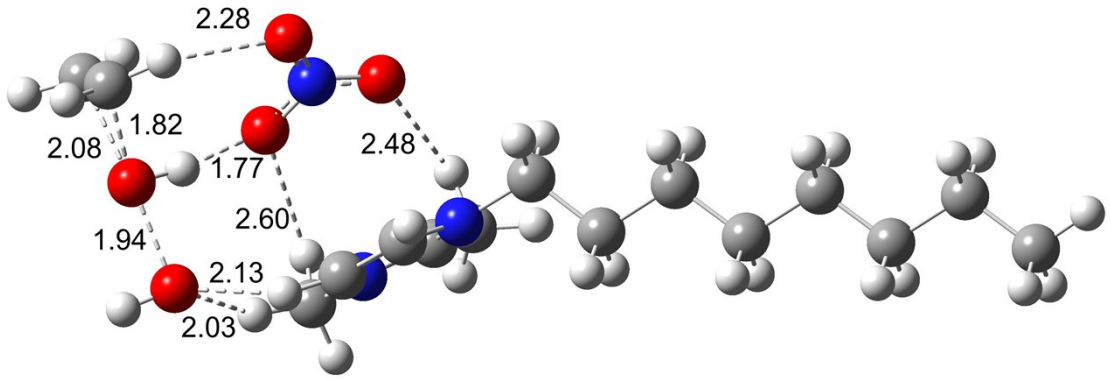
Sum of electronic and thermal Enthalpies= -1364.834427

Sum of electronic and thermal Free Energies= -1364.954518

HF= -1365.4867385 / NImag=0

Transition state C4a – Oxidation of ethene – Charge=0, Multiplicity = 1

B3LYP (gas-phase):



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-1.894665	1.683792	0.206705
2	6	0	-1.966829	1.299949	-1.120571
3	6	0	-0.873077	0.534388	-1.361905
4	7	0	-0.152674	0.453310	-0.179728
5	6	0	-0.798671	1.153790	0.768924
6	6	0	-0.433542	1.253702	2.204037
7	6	0	1.043794	-0.375052	0.017173
8	6	0	2.349981	0.389820	-0.212284
9	6	0	3.580521	-0.507686	-0.039046
10	6	0	4.903940	0.233675	-0.260965
11	6	0	6.138389	-0.658980	-0.090901
12	6	0	7.462856	0.080504	-0.310288
13	6	0	8.699020	-0.810315	-0.141743
14	6	0	10.017591	-0.063276	-0.361803
15	6	0	-2.931999	2.449374	0.910079
16	8	0	-4.843325	1.715907	-1.422551
17	8	0	-5.756717	0.069384	-0.936574
18	6	0	-6.867523	-1.430619	-0.022828
19	6	0	-6.167063	-1.681156	-1.187383
20	8	0	-3.860271	-0.499377	0.983492
21	7	0	-3.035515	-1.466545	0.854235
22	8	0	-3.305053	-2.415314	0.095512
23	8	0	-1.961568	-1.431473	1.495378
24	1	0	-0.561849	0.013418	-2.250029

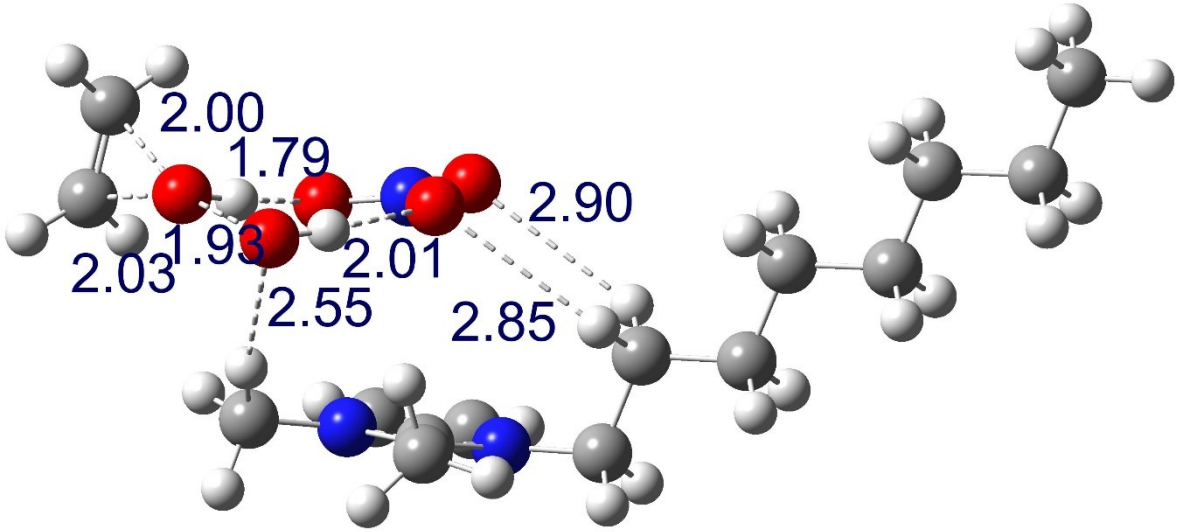
25	1	0	-2.842928	1.545007	-1.710063
26	1	0	-3.782227	2.535910	0.230723
27	1	0	-3.244996	1.889881	1.789606
28	1	0	0.956447	-1.213579	-0.675724
29	1	0	0.991995	-0.799462	1.020313
30	1	0	2.341679	0.820068	-1.220012
31	1	0	2.406022	1.234374	0.484216
32	1	0	3.574187	-0.945255	0.967176
33	1	0	3.515933	-1.351234	-0.737663
34	1	0	4.908986	0.671452	-1.267267
35	1	0	4.967877	1.077231	0.438246
36	1	0	6.074298	-1.501942	-0.790835
37	1	0	6.131469	-1.098306	0.914892
38	1	0	7.470219	0.520683	-1.315998
39	1	0	7.527902	0.923473	0.390075
40	1	0	8.691995	-1.250327	0.862893
41	1	0	8.634965	-1.651925	-0.842102
42	1	0	10.877944	-0.726012	-0.234716
43	1	0	10.070010	0.358627	-1.370479
44	1	0	10.127676	0.762973	0.347697
45	1	0	-2.546178	3.433896	1.183629
46	1	0	0.638966	1.130048	2.350661
47	1	0	-0.725080	2.223504	2.608759
48	1	0	-0.961659	0.465242	2.749697
49	1	0	-5.626837	2.031548	-1.885232
50	1	0	-5.015741	-0.059975	-0.282528
51	1	0	-7.877820	-1.044052	-0.044283
52	1	0	-6.399456	-1.590569	0.939674
53	1	0	-6.664685	-1.637685	-2.147546
54	1	0	-5.207991	-2.182628	-1.137290

Sum of electronic and thermal Enthalpies= -1130.220818

Sum of electronic and thermal Free Energies= -1130.319821

HF= -1130.7130049 / NImag=1 (-420.1699 cm^{-1})

M06GD3 – SMD solvent:



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.177101	-2.523845	-1.390426
2	7	0	-0.573669	-2.389555	-0.155347
3	6	0	-1.472163	-1.925708	0.722632
4	7	0	-2.639383	-1.804958	0.078426
5	6	0	-2.470713	-2.163224	-1.242252
6	6	0	0.864854	-2.543508	0.073717
7	6	0	1.594245	-1.229217	-0.098172
8	6	0	3.089047	-1.388814	0.097111
9	6	0	3.836949	-0.077709	-0.056420
10	6	0	5.335380	-0.217712	0.135289
11	6	0	6.081105	1.095638	-0.009264
12	6	0	7.581085	0.961966	0.184295
13	6	0	8.307675	2.285046	0.040112
14	6	0	-1.254563	-1.581795	2.134630
15	6	0	-3.879733	-1.336829	0.680613
16	8	0	-2.717370	1.091644	-1.163017
17	7	0	-1.468745	1.081379	-1.063449
18	8	0	-0.777176	0.843012	-2.061141
19	8	0	-0.935065	1.296655	0.039645
20	8	0	-4.279276	2.118502	0.885481
21	8	0	-2.904544	1.813928	2.208235
22	6	0	-5.840220	1.752021	-0.370385

23	6	0	-5.356529	3.016692	-0.541956
24	1	0	-0.623401	-2.865872	-2.250594
25	1	0	-3.289501	-2.128339	-1.943291
26	1	0	-4.266447	-2.086163	1.374740
27	1	0	1.217185	-3.289393	-0.644776
28	1	0	1.012381	-2.957420	1.075524
29	1	0	1.382468	-0.832200	-1.101509
30	1	0	1.196580	-0.498460	0.620496
31	1	0	3.285173	-1.809211	1.095100
32	1	0	3.477477	-2.122056	-0.625651
33	1	0	3.632841	0.343207	-1.052889
34	1	0	3.442279	0.652125	0.666981
35	1	0	5.730432	-0.944341	-0.591612
36	1	0	5.537448	-0.644473	1.130074
37	1	0	5.879454	1.523162	-1.003991
38	1	0	5.684481	1.822454	0.716889
39	1	0	7.779131	0.532704	1.177007
40	1	0	7.975227	0.237366	-0.542691
41	1	0	9.387822	2.179050	0.182568
42	1	0	8.144838	2.716255	-0.954940
43	1	0	7.945860	3.013683	0.775472
44	1	0	-3.702398	-0.399160	1.212697
45	1	0	-3.651599	1.729409	0.225760
46	1	0	-2.183118	1.631891	1.584579
47	1	0	-4.604157	-1.174376	-0.117041
48	1	0	-1.335171	-0.495929	2.269297
49	1	0	-2.017215	-2.053276	2.761296
50	1	0	-0.269946	-1.903818	2.473395
51	1	0	-6.639272	1.545668	0.332253
52	1	0	-5.492354	0.931037	-0.989663
53	1	0	-5.769008	3.854720	0.007623
54	1	0	-4.623372	3.235758	-1.311279

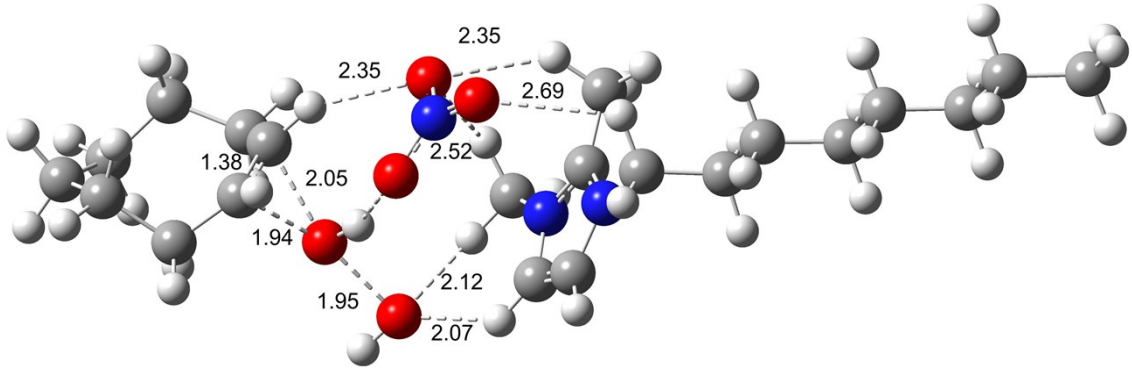
Sum of electronic and thermal Enthalpies= -1129.495654

Sum of electronic and thermal Free Energies= -1129.592450

HF= -1129.9844853 / NImag=1 (-551.2942 cm^{-1})

Transition state C4 – Oxidation of cyclooctene – Charge=0, Multiplicity = 1

B3LYP (gas-phase) only:



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.059011	1.753252	0.505104
2	6	0	-0.046361	2.118746	-0.829199
3	6	0	1.046785	1.534609	-1.379463
4	7	0	1.683325	0.815243	-0.379909
5	6	0	0.991523	0.956508	0.764650
6	6	0	1.262081	0.300159	2.068770
7	6	0	2.830109	-0.078869	-0.593806
8	6	0	4.170034	0.545089	-0.196565
9	6	0	5.342802	-0.405079	-0.465039
10	6	0	6.699195	0.171493	-0.043666
11	6	0	7.872988	-0.776263	-0.315162
12	6	0	9.229129	-0.216209	0.127614
13	6	0	10.402852	-1.164179	-0.144197
14	6	0	11.752922	-0.602035	0.310056
15	6	0	-1.111543	2.119633	1.463189
16	8	0	-2.931162	2.567483	-0.985449
17	8	0	-3.909200	0.927543	-0.593268
18	6	0	-4.715160	-0.629981	0.475441
19	6	0	-4.937859	-0.687825	-0.888997
20	8	0	-1.485514	-1.184919	1.202958
21	7	0	-1.041294	-1.301911	0.027047
22	8	0	-1.720366	-0.857390	-0.942134

23	8	0	0.070394	-1.831238	-0.176991
24	1	0	1.399571	1.522207	-2.395305
25	1	0	-0.883011	2.660148	-1.251367
26	1	0	-1.939461	2.536389	0.885389
27	1	0	-1.447396	1.217937	1.973815
28	1	0	2.821748	-0.335211	-1.654191
29	1	0	2.626645	-1.004469	-0.053843
30	1	0	4.311937	1.479808	-0.750729
31	1	0	4.149638	0.814574	0.865464
32	1	0	5.171927	-1.351144	0.063753
33	1	0	5.370297	-0.654927	-1.533104
34	1	0	6.869861	1.120316	-0.568149
35	1	0	6.671262	0.415607	1.026024
36	1	0	7.909459	-1.008777	-1.387205
37	1	0	7.691949	-1.730428	0.196217
38	1	0	9.411926	0.739131	-0.381598
39	1	0	9.193301	0.014103	1.200475
40	1	0	10.217570	-2.120372	0.360097
41	1	0	10.443255	-1.389627	-1.216794
42	1	0	12.567108	-1.301802	0.102517
43	1	0	11.983928	0.337028	-0.202835
44	1	0	11.755493	-0.399720	1.385828
45	1	0	-0.725109	2.849852	2.177754
46	1	0	2.249163	-0.157344	2.080644
47	1	0	1.205977	1.025693	2.883798
48	1	0	0.509317	-0.479032	2.233446
49	1	0	-3.726365	2.993892	-1.321184
50	1	0	-3.039261	0.479060	-0.718880
51	1	0	-3.807659	-1.099150	0.842131
52	1	0	-4.226265	-1.267956	-1.467317
53	6	0	-6.217313	-0.315082	-1.576946
54	6	0	-7.273443	-1.444358	-1.387842
55	1	0	-6.013442	-0.158202	-2.637879
56	1	0	-6.593734	0.634320	-1.188909
57	6	0	-8.455609	-1.098767	-0.460311
58	1	0	-7.679714	-1.732494	-2.361843
59	1	0	-6.768134	-2.337960	-1.008097

60	1	0	-8.951740	-2.038149	-0.189711
61	1	0	-9.196764	-0.525291	-1.029756
62	6	0	-5.637148	-0.030951	1.497183
63	6	0	-6.991258	-0.764742	1.725435
64	1	0	-5.844621	1.009907	1.227303
65	1	0	-5.095983	0.002172	2.445603
66	6	0	-8.158117	-0.301287	0.824204
67	1	0	-6.852041	-1.849195	1.655988
68	1	0	-7.275711	-0.569573	2.763757
69	1	0	-9.078731	-0.316146	1.417667
70	1	0	-8.000229	0.753237	0.572310

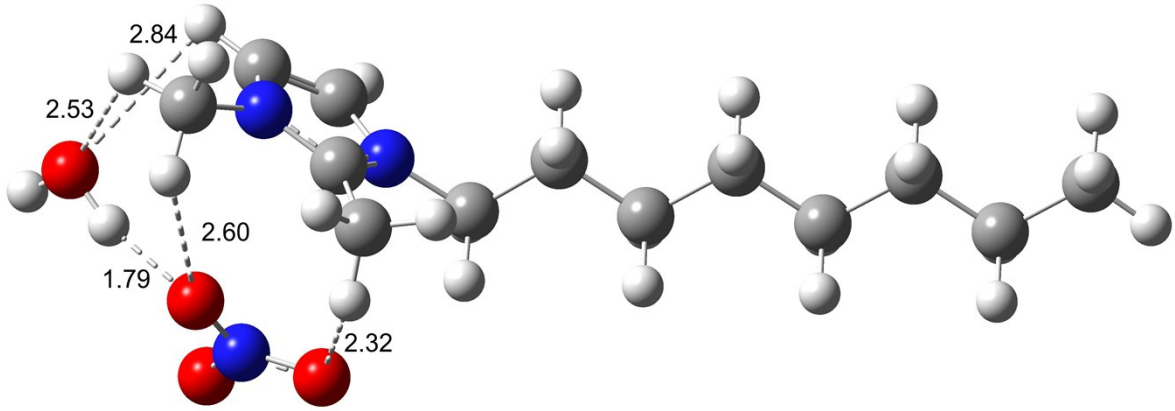
Sum of electronic and thermal Enthalpies= -1364.796058

Sum of electronic and thermal Free Energies= -1364.906854

HF= -1365.4455043 / NImag=1 (-370.7303 cm^{-1})

Complex D4 - H_2O / NO_3^- / OMMIM$^+$ - Complex charge=0, Multiplicity=1

B3LYP (gas-phase):



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.880844	-1.048846	-1.575067
2	6	0	2.998999	-1.701571	-1.174913
3	6	0	1.977224	-0.929721	0.642021
4	7	0	1.255377	-0.573684	-0.434296
5	1	0	1.494544	-0.850797	-2.559108
6	1	0	3.799373	-2.145553	-1.738094
7	7	0	3.037173	-1.631387	0.204328
8	6	0	4.159374	-2.081102	1.033421
9	1	0	4.993735	-2.300922	0.372570
10	1	0	4.459750	-1.266459	1.689591
11	6	0	0.042205	0.261656	-0.421330
12	6	0	-1.245608	-0.552179	-0.274771
13	1	0	0.045610	0.821310	-1.358145
14	1	0	0.168320	0.997894	0.372227
15	6	0	-2.487909	0.346350	-0.286543
16	1	0	-1.308247	-1.284919	-1.087590
17	1	0	-1.214897	-1.125738	0.658745
18	6	0	-3.799481	-0.432716	-0.135388
19	1	0	-2.408643	1.085169	0.520216
20	1	0	-2.512087	0.919637	-1.221637
21	1	0	-3.878260	-1.171594	-0.943144
22	1	0	-3.774617	-1.005799	0.800364

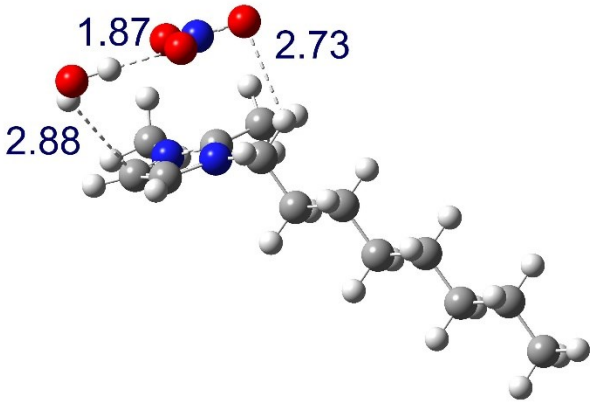
23	6	0	-5.042459	0.464325	-0.146137
24	6	0	-6.356996	-0.307474	0.013207
25	1	0	-5.068672	1.034547	-1.083508
26	1	0	-4.958980	1.206502	0.658005
27	6	0	-7.599678	0.590229	0.003547
28	1	0	-6.442290	-1.050054	-0.790982
29	1	0	-6.331522	-0.877711	0.951041
30	6	0	-8.909127	-0.186606	0.167375
31	1	0	-7.513247	1.333295	0.805564
32	1	0	-7.626690	1.158007	-0.934415
33	1	0	-9.774040	0.482290	0.156788
34	1	0	-9.042289	-0.913635	-0.640087
35	1	0	-8.927205	-0.737080	1.113358
36	7	0	3.392662	2.083148	0.223911
37	8	0	2.251119	2.291733	0.707606
38	8	0	3.864721	2.800674	-0.664572
39	8	0	4.064392	1.085506	0.665417
40	1	0	3.878394	-2.965088	1.608597
41	6	0	1.682461	-0.551994	2.045363
42	1	0	0.636798	-0.745063	2.293096
43	1	0	2.310485	-1.112336	2.735383
44	1	0	1.893260	0.517473	2.154442
45	1	0	6.397796	0.236182	-1.478404
46	8	0	5.799796	-0.297924	-0.948801
47	1	0	5.267819	0.351873	-0.434388

Sum of electronic and thermal Enthalpies= -976.556369

Sum of electronic and thermal Free Energies= -976.644962

HF= -976.9892614 / NImag=0

M06GD3 – SMD solvent:



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	3.004284	1.857317	0.214140
2	6	0	3.066599	1.374749	1.504040
3	6	0	2.068289	0.473846	1.636426
4	7	0	1.420162	0.405111	0.419678
5	6	0	2.006588	1.249264	-0.438053
6	1	0	1.755071	-0.130764	2.473276
7	6	0	1.647914	1.497698	-1.842064
8	6	0	0.228711	-0.408953	0.164355
9	6	0	-1.043353	0.388948	0.352788
10	6	0	-2.272652	-0.456581	0.082700
11	6	0	-3.564951	0.316565	0.266284
12	6	0	-4.802681	-0.514779	-0.014094
13	6	0	-6.095588	0.258451	0.165864
14	6	0	-7.336852	-0.568950	-0.116740
15	6	0	-8.618238	0.220857	0.066311
16	6	0	3.971692	2.749915	-0.404134
17	8	0	4.118345	-0.802054	-0.980548
18	7	0	3.227586	-1.667369	-1.025188
19	8	0	3.012672	-2.392918	-0.028299
20	8	0	2.538680	-1.808954	-2.047232
21	8	0	4.758310	-1.765413	2.124338
22	1	0	3.814016	1.721874	2.199748
23	1	0	3.455480	3.533717	-0.960308
24	1	0	0.275195	-1.253773	0.858504
25	1	0	0.300728	-0.816605	-0.849305

26	1	0	-1.071462	0.782154	1.378923
27	1	0	-1.029522	1.258267	-0.320351
28	1	0	-2.224006	-0.853181	-0.942641
29	1	0	-2.268996	-1.331895	0.749554
30	1	0	-3.612246	0.708784	1.293779
31	1	0	-3.558874	1.197019	-0.394611
32	1	0	-4.808425	-1.395376	0.646930
33	1	0	-4.752563	-0.907973	-1.041375
34	1	0	-6.146759	0.651404	1.193443
35	1	0	-6.088781	1.140273	-0.493961
36	1	0	-7.282359	-0.960974	-1.142534
37	1	0	-7.341574	-1.448305	0.543292
38	1	0	-9.507243	-0.383633	-0.139815
39	1	0	-8.703948	0.598180	1.092413
40	1	0	-8.643894	1.088185	-0.604308
41	1	0	4.572015	3.202670	0.383591
42	1	0	4.871969	-0.812026	2.053435
43	1	0	4.171755	-1.984344	1.376373
44	1	0	4.619678	2.185524	-1.079472
45	1	0	0.855940	0.826598	-2.174235
46	1	0	1.303991	2.530231	-1.964800
47	1	0	2.523669	1.357084	-2.484126

Sum of electronic and thermal Enthalpies= -975.944351

Sum of electronic and thermal Free Energies= -976.031774

HF=-976.3740649 / NImag=0

5.8. Structures along a hypothetic [OMIM]Pernitrate pathway

B3LYP (gas-phase)

Zero-point: H_2O_2 + cyclooctene + [OMIM][NO_3]

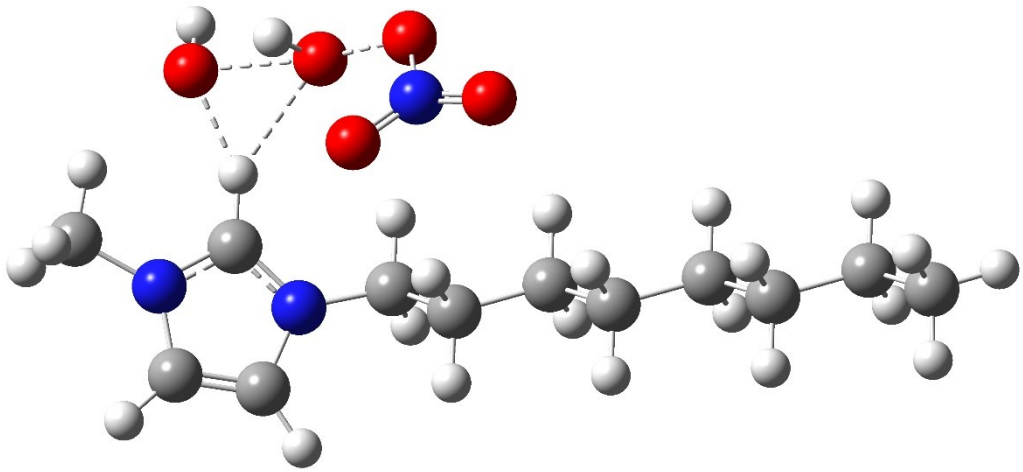
Table S 8: Calculated energies for a [OMIM]Pernitrate formation

	ΔG in kcal/mol
TS pernitrate formation	+36,6
[OMIM] Pernitrate + Olefin	+6,4
TS epoxidation COE	+40,6

For comparison: Transition state energy via outer-sphere mechanism:

ΔG=+29,8 kcal/mol

Transition state of the pernitrate formation:



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.220619	2.243661	0.778843
2	8	0	-2.128537	2.255166	-0.874173
3	8	0	-1.027387	1.630079	1.456512
4	8	0	0.964040	2.396073	1.019750
5	8	0	-0.631419	2.844541	-0.367727
6	8	0	-4.179435	1.838963	-1.061640
7	1	0	-4.319321	2.320077	-1.884284

8	1	0	-2.730035	2.693114	-0.247511
9	1	0	-3.345618	0.341600	-0.842960
10	6	0	-3.246938	-0.649310	-0.355669
11	7	0	-4.227037	-1.175117	0.387645
12	6	0	-2.572210	-2.629695	0.376667
13	6	0	-3.826134	-2.413291	0.856826
14	1	0	-1.906208	-3.463955	0.509426
15	1	0	-4.453411	-3.023466	1.483418
16	7	0	-2.229967	-1.517959	-0.376238
17	6	0	-5.497079	-0.487521	0.655220
18	1	0	-5.460972	0.471461	0.131556
19	1	0	-6.325330	-1.094654	0.287331
20	1	0	-5.602360	-0.326966	1.728813
21	6	0	-0.947264	-1.281203	-1.066704
22	6	0	0.248053	-1.290451	-0.112220
23	1	0	-1.044627	-0.310074	-1.553009
24	1	0	-0.838702	-2.042486	-1.844480
25	6	0	1.550703	-0.934525	-0.839689
26	1	0	0.061601	-0.577456	0.695739
27	1	0	0.346818	-2.279341	0.351399
28	6	0	2.765965	-0.900574	0.094012
29	1	0	1.729917	-1.655965	-1.647933
30	1	0	1.439542	0.045597	-1.317798
31	1	0	2.582526	-0.169350	0.889390
32	1	0	2.876087	-1.876459	0.585320
33	6	0	4.070606	-0.546285	-0.628260
34	6	0	5.288989	-0.500287	0.300337
35	1	0	3.954636	0.427549	-1.119831
36	1	0	4.253308	-1.274608	-1.429632
37	6	0	6.594769	-0.142188	-0.418592
38	1	0	5.105683	0.228752	1.099735
39	1	0	5.405693	-1.473147	0.796260
40	6	0	7.807212	-0.097220	0.515927
41	1	0	6.777400	-0.869765	-1.219106
42	1	0	6.478173	0.830056	-0.912339
43	1	0	8.720891	0.162767	-0.025965
44	1	0	7.668120	0.645642	1.307706

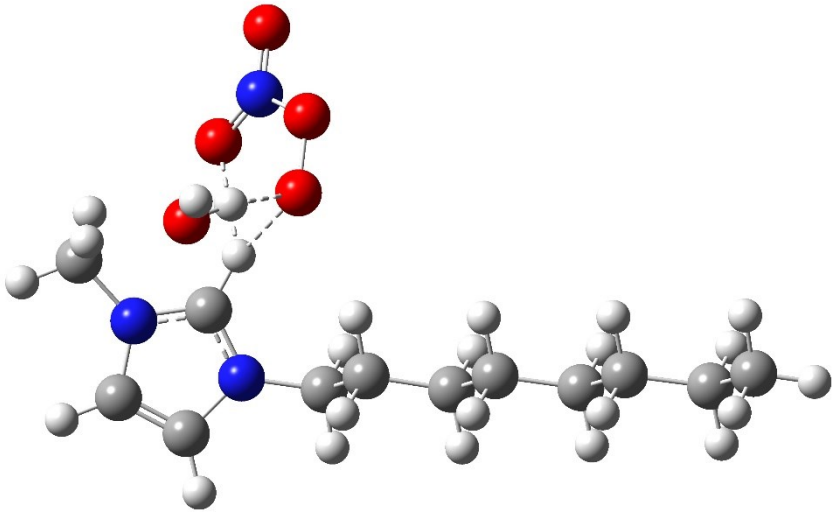
45	1	0	7.971420	-1.066290	0.998107

Sum of electronic and thermal Enthalpies= -1012.342041

Sum of electronic and thermal Free Energies= -1012.427655

HF=-1012.7462788 / NImag=1 (-402.7212 cm^{-1})

[OMIM]Pernitrate + H_2O:



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	2.827197	-2.892266	-0.711095
2	8	0	1.255788	-1.502427	0.337748
3	8	0	3.139889	-4.025672	-0.996133
4	8	0	3.408627	-1.854615	-0.967639
5	8	0	1.605888	-2.815249	0.017513
6	8	0	2.321417	-0.602627	2.618488
7	1	0	1.984934	-1.037979	3.405949
8	1	0	1.886788	-1.059683	1.846474
9	1	0	2.217011	-0.085161	-0.268666
10	6	0	2.461683	0.986648	-0.225127
11	7	0	1.660488	1.983121	-0.621577
12	6	0	3.456693	2.900998	0.266057
13	6	0	2.263595	3.190957	-0.321412
14	1	0	4.228870	3.547038	0.645621
15	1	0	1.805220	4.135741	-0.555939
16	7	0	3.560478	1.523823	0.312272
17	6	0	4.640229	0.743864	0.936490
18	1	0	4.268336	0.324489	1.872418
19	1	0	4.924369	-0.064155	0.264351
20	1	0	5.488122	1.405843	1.104512
21	6	0	0.327299	1.785280	-1.225964

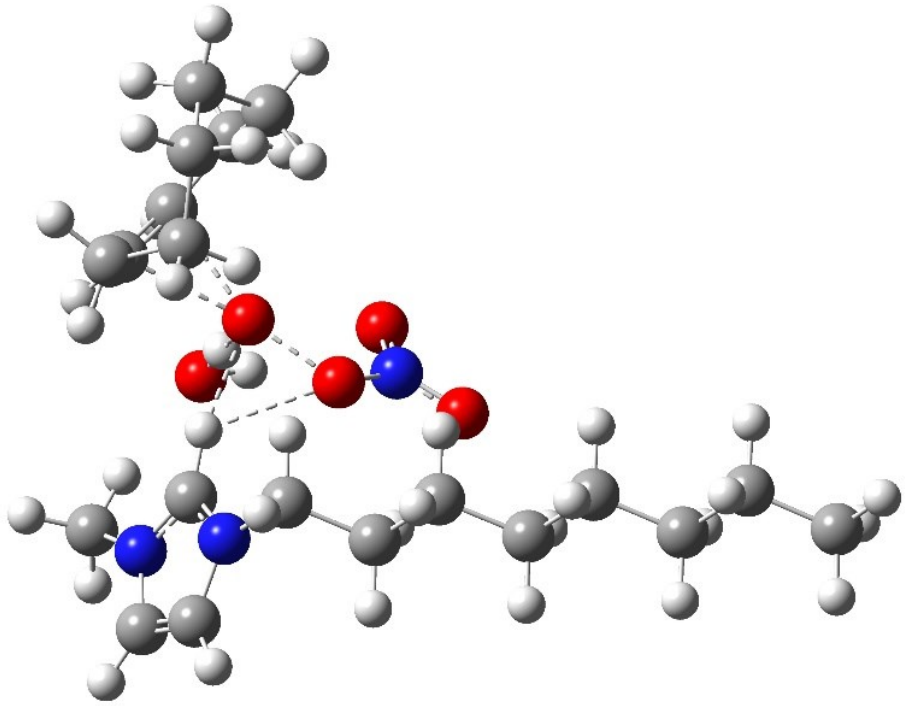
22	6	0	-0.702959	1.267289	-0.220428
23	1	0	0.444602	1.082626	-2.053170
24	1	0	0.030134	2.748857	-1.645205
25	6	0	-2.080022	1.087250	-0.869253
26	1	0	-0.354061	0.308075	0.174979
27	1	0	-0.770622	1.968507	0.619234
28	6	0	-3.134337	0.560479	0.111321
29	1	0	-2.422344	2.041595	-1.291840
30	1	0	-1.992580	0.389277	-1.711098
31	1	0	-2.784316	-0.387414	0.536347
32	1	0	-3.226665	1.258975	0.952914
33	6	0	-4.511146	0.355210	-0.530169
34	6	0	-5.571245	-0.161586	0.448737
35	1	0	-4.417460	-0.349544	-1.366243
36	1	0	-4.854076	1.302520	-0.966980
37	6	0	-6.947201	-0.375988	-0.192213
38	1	0	-5.227178	-1.106251	0.888905
39	1	0	-5.668964	0.544514	1.283834
40	6	0	-8.001106	-0.888043	0.793990
41	1	0	-7.289994	0.567136	-0.635452
42	1	0	-6.850579	-1.084882	-1.023438
43	1	0	-8.969237	-1.031337	0.306015
44	1	0	-7.702982	-1.847530	1.228146
45	1	0	-8.146244	-0.183452	1.619138

Sum of electronic and thermal Enthalpies= -1012.388342

Sum of electronic and thermal Free Energies= -1012.475901

HF=-1012.7952799 / NImag=0

Transition state of the cyclooctene epoxidation:



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.374535	-4.426009	-1.068675
2	7	0	2.109385	-3.494998	-0.356634
3	6	0	1.509514	-2.301175	-0.455927
4	7	0	0.413479	-2.447305	-1.210593
5	6	0	0.309482	-3.769573	-1.600775
6	6	0	3.352322	-3.760401	0.381696
7	6	0	-0.560174	-1.374146	-1.507378
8	6	0	-1.885834	-1.574724	-0.772503
9	6	0	-2.860349	-0.425384	-1.052024
10	6	0	-4.205937	-0.603921	-0.339718
11	6	0	-5.179877	0.553828	-0.584571
12	6	0	-6.536196	0.367241	0.104650
13	6	0	-7.508520	1.529345	-0.127298
14	6	0	-8.864693	1.330001	0.555978
15	6	0	3.857209	0.865060	-0.466682
16	6	0	3.425079	1.178556	-1.881824
17	6	0	2.173069	2.040064	-2.130307

18	6	0	2.431510	3.547407	-2.255018
19	6	0	3.175994	4.164643	-1.064282
20	6	0	2.542348	3.819087	0.301200
21	6	0	3.385176	2.896258	1.183475
22	6	0	3.815537	1.530039	0.719199
23	8	0	3.230306	-1.353549	2.399207
24	1	0	2.873212	-1.227617	3.284273
25	1	0	2.782767	-0.642752	1.869056
26	1	0	1.839399	-1.350737	-0.011160
27	1	0	1.666938	-5.459907	-1.129484
28	1	0	-0.503088	-4.126802	-2.208832
29	1	0	3.472720	-2.991211	1.148807
30	1	0	3.269604	-4.737937	0.856324
31	1	0	4.198047	-3.759003	-0.308020
32	1	0	-0.699186	-1.354546	-2.591792
33	1	0	-0.092318	-0.442041	-1.195317
34	1	0	-2.339559	-2.527133	-1.073883
35	1	0	-1.683604	-1.623471	0.300493
36	1	0	-2.400789	0.513750	-0.724611
37	1	0	-3.029950	-0.333357	-2.133497
38	1	0	-4.669823	-1.543275	-0.668976
39	1	0	-4.026322	-0.706855	0.736535
40	1	0	-5.337771	0.675772	-1.664552
41	1	0	-4.722193	1.487826	-0.235475
42	1	0	-6.997391	-0.564581	-0.248701
43	1	0	-6.378594	0.238270	1.183073
44	1	0	-7.051141	2.458443	0.233550
45	1	0	-7.659885	1.664012	-1.205516
46	1	0	-9.533245	2.175856	0.372623
47	1	0	-9.363342	0.427035	0.189221
48	1	0	-8.749963	1.226365	1.639590
49	1	0	4.316420	0.997952	1.524125
50	1	0	4.313420	3.424979	1.452694
51	1	0	2.859772	2.738694	2.131392
52	1	0	4.388763	-0.083154	-0.407233
53	1	0	1.554683	3.372226	0.161501
54	1	0	2.375463	4.738086	0.872135

55	1	0	4.283904	1.616754	-2.414225
56	1	0	3.270882	0.208348	-2.368201
57	1	0	3.210781	5.250133	-1.202421
58	1	0	4.220993	3.833349	-1.076093
59	1	0	1.455176	1.833724	-1.333471
60	1	0	1.708322	1.704516	-3.064732
61	1	0	1.466230	4.054717	-2.375970
62	1	0	2.997422	3.743788	-3.174675
63	8	0	1.987529	0.388174	0.714773
64	8	0	0.364786	-0.075269	1.134415
65	7	0	0.027287	0.039234	2.420446
66	8	0	-1.156376	-0.196301	2.659014
67	8	0	0.868879	0.348706	3.249293

Sum of electronic and thermal Enthalpies= -1325.492851

Sum of electronic and thermal Free Energies= -1325.601010

HF= -1326.1125753 / NImag=1 (-469.5678 cm^{-1})

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