

SUPPORTING INFORMATION

**Fragmentations of deprotonated alkyl hydroperoxides (ROO^-) upon
collisional activation:
A combined experimental and computational study.**

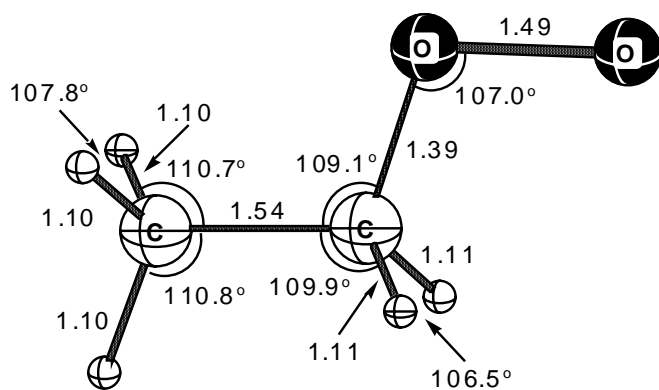
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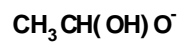
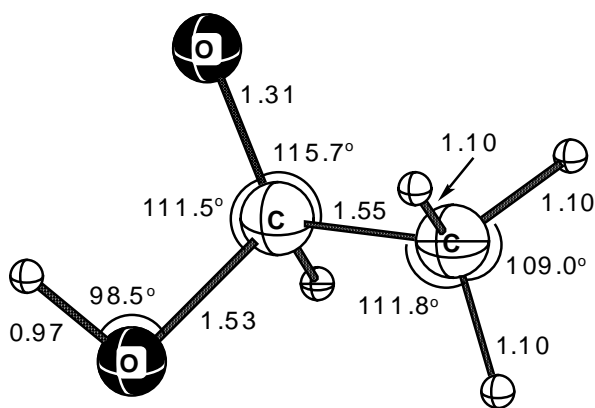
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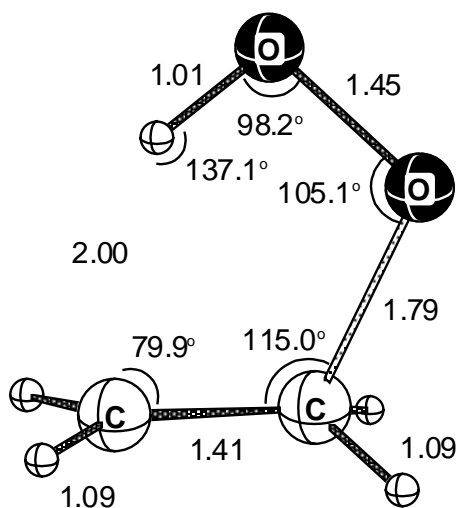
Figure S1.



- dih(C₁C₂O₃O₄) = 180.0°
- dih(H₅C₁C₂O₃) = 180.0°
- dih(H₆C₁C₂O₃) = 59.7°
- dih(H₇C₁C₂O₃) = -59.7°
- dih(C₁C₂O₃H₈) = 121.1°
- dih(C₁C₂O₃H₉) = -121.1°



- O₁C₂H₆ = 133.1°
- C₂C₄H₈ = 109.0°
- C₂C₄H₉ = 109.3°
- dih(H₅O₁C₂C₄) = 127.1°
- dih(H₅O₁C₂O₃) = 1.5°
- dih(H₅O₁C₂H₆) = -121.5°
- dih(O₁C₂C₄H₇) = 52.1°
- dih(O₁C₂C₄H₈) = -68.5°
- dih(O₁C₂C₄H₉) = 172.9°



TS1

$$H_7C_1 = 1.09 \text{ \AA}$$

$$H_9C_2 = 1.09 \text{ \AA}$$

$$H_6C_1C_2 = 121.4^\circ$$

$$H_7C_1C_2 = 121.3^\circ$$

$$H_6C_1H_7 = 116.9^\circ$$

$$H_8C_2C_1 = 118.7^\circ$$

$$H_9C_2C_1 = 116.6^\circ$$

$$H_8C_2H_9 = 112.8^\circ$$

$$\text{dih}(C_1C_2O_3O_4) = -22.9^\circ$$

$$\text{dih}(C_2O_3O_4H_6) = 19.0^\circ$$

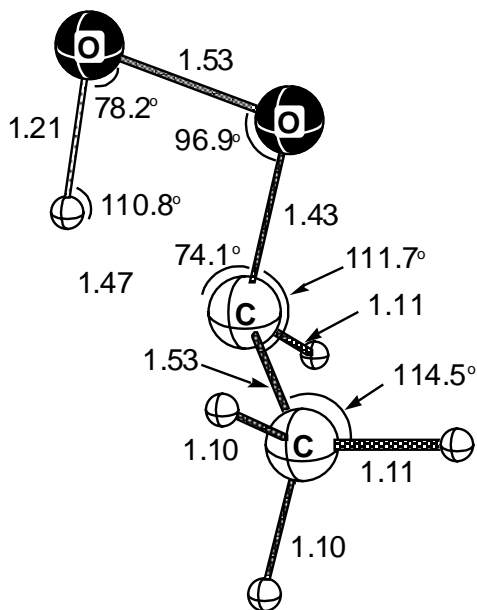
$$\text{dih}(O_3O_4H_6C_1) = -16.3^\circ$$

$$\text{dih}(H_6C_1C_2O_3) = -87.8^\circ$$

$$\text{dih}(H_7C_1C_2O_3) = 99.6^\circ$$

$$\text{dih}(H_6C_2O_3O_4) = -146.1^\circ$$

$$\text{dih}(H_9C_2O_3O_4) = 100.6^\circ$$



TS2

$$H_6C_1C_2 = 110.7^\circ$$

$$H_7C_1C_2 = 109.9^\circ$$

$$H_8C_1C_2 = 114.5^\circ$$

$$H_9C_2C_1 = 111.0^\circ$$

$$\text{dih}(C_1C_2O_3O_4) = -118.0^\circ$$

$$\text{dih}(C_2O_3O_4H_6) = -1.2^\circ$$

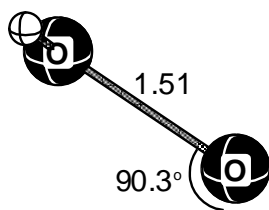
$$\text{dih}(O_3O_4H_6C_1) = 1.3^\circ$$

$$\text{dih}(H_6C_1C_2O_3) = 61.2^\circ$$

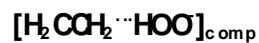
$$\text{dih}(H_7C_1C_2O_3) = 179.9^\circ$$

$$\text{dih}(H_6C_1O_2O_4) = -59.7^\circ$$

$$\text{dih}(H_9C_2O_3O_4) = 118.8^\circ$$



1.95



O₃H₆ = 0.97

O₄O₅H₆ = 99.5°

dih(C₁C₂H₃O₄) = 121.8°

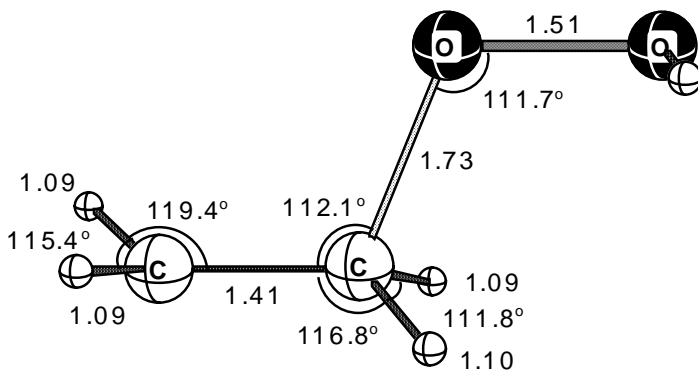
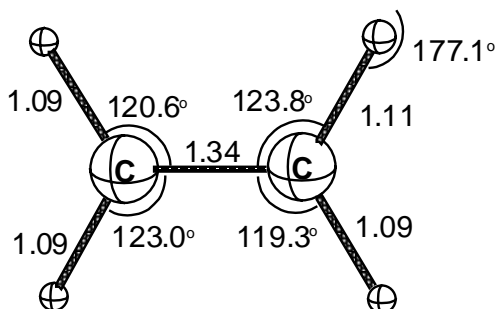
dih(C₂H₃O₄O₅) = -116.9°

dih(H₃O₄O₅H₆) = 106.2°

dih(C₁C₂H₃H₇) = 179.7°

dih(C₁C₂H₃H₈) = -0.2°

dih(C₁C₂H₃H₉) = 0.2°



TS3

O₄H₅ = 1.09

O₃O₄H₅ = 99.8°

dih(C₁C₂O₃O₄) = 178.3°

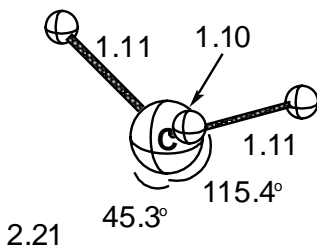
dih(C₂O₃O₄H₅) = -89.0°

dih(C₁C₂O₃H₆) = 123.1°

dih(C₁C₂O₃H₇) = -123.6°

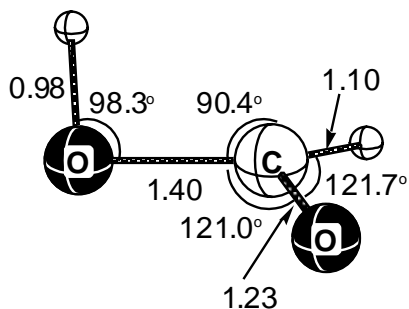
dih(C₁C₂O₃H₈) = 26.0°

dih(C₁C₂O₃H₉) = -26.1°



2.21

2.48



TS4

C₂C₄H₇ = 133.1°

C₂C₄H₈ = 93.1°

C₂C₄H₉ = 104.0°

dih(H₅O₁C₂O₃) = 137.3°

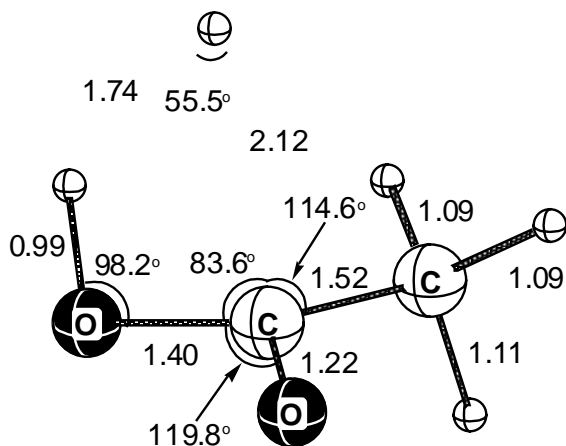
dih(H₅O₁C₂C₄) = 16.0°

dih(H₅O₁C₂H₆) = -65.6°

dih(O₁C₂C₄H₇) = 5.6°

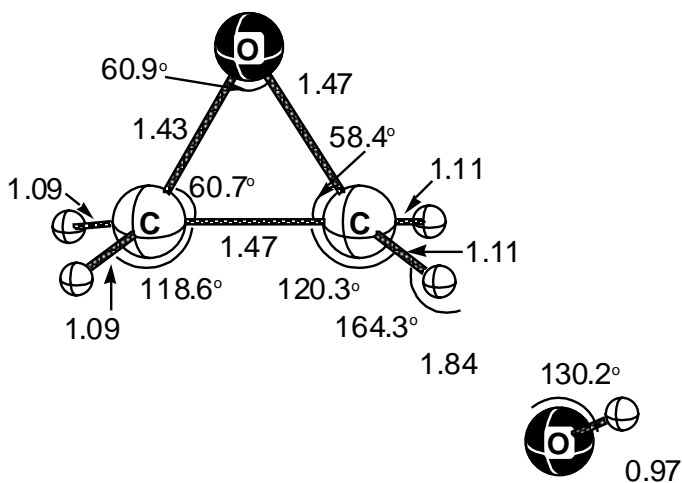
dih(O₁C₂C₄H₈) = 112.8°

dih(O₁C₂C₄H₉) = -137.3°



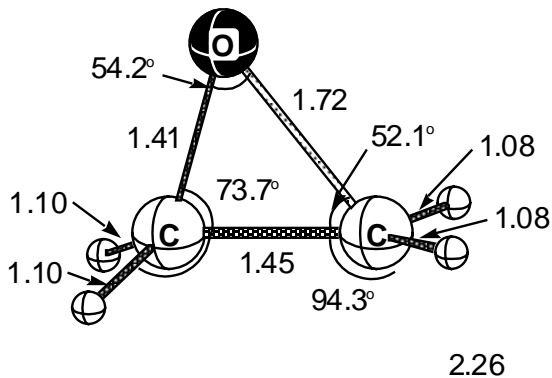
TS5

$C_2C_4H_7 = 111.9^\circ$
 $C_2C_4H_8 = 109.4^\circ$
 $C_2C_4H_9 = 107.6^\circ$
 $dih(H_5O_1C_2O_4) = 128.2^\circ$
 $dih(H_6O_1C_2C_4) = -76.6^\circ$
 $dih(H_5O_1C_2H_6) = 9.9^\circ$
 $dih(O_1C_2C_4H_7) = 34.9^\circ$
 $dih(O_1C_2C_4H_8) = 156.2^\circ$
 $dih(O_1C_2C_4H_9) = -85.6^\circ$



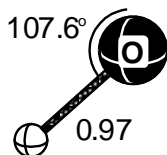
[cyc-H₂OCH₂O...HO]_{comp}

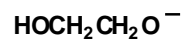
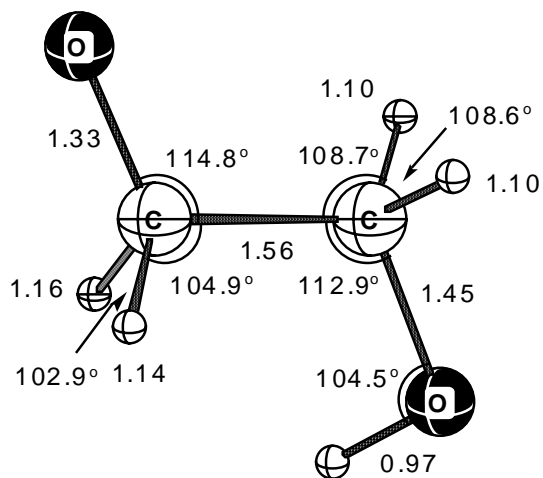
$H_5C_1H_6 = 115.1^\circ$
 $H_7C_2H_8 = 117.5^\circ$
 $dih(C_1C_2O_3O_4) = 104.6^\circ$
 $dih(H_5C_1C_2O_3) = -104.3^\circ$
 $dih(H_6C_1C_2O_3) = 102.9^\circ$
 $dih(H_7C_2C_1O_3) = 105.6^\circ$
 $dih(H_8C_2C_1O_3) = -100.5^\circ$
 $dih(C_1C_2O_4H_5) = -99.7^\circ$



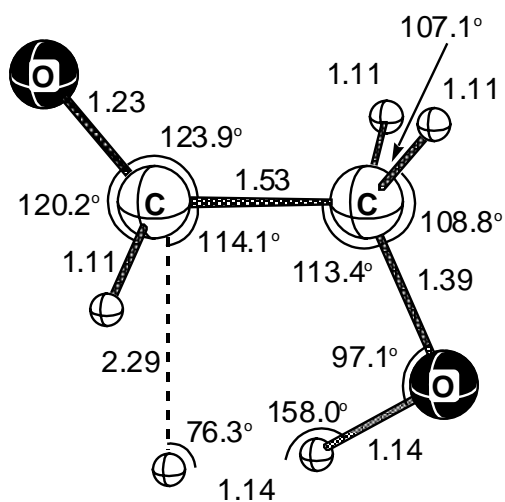
TS6

$H_5C_1H_6 = 111.1^\circ$
 $H_7C_2H_8 = 119.7^\circ$
 $dih(C_1C_2O_3O_4) = 0.0^\circ$
 $dih(H_5C_1C_2O_3) = -111.1^\circ$
 $dih(H_6C_1C_2O_3) = 111.1^\circ$
 $dih(H_7C_2C_1O_3) = 87.5^\circ$
 $dih(H_8C_2C_1O_3) = -87.5^\circ$
 $dih(C_1C_2O_4H_5) = 0.0^\circ$





- dih(C₁C₂O₃O₄) = -10.0°
- dih(H₅C₁C₂O₃) = -127.5°
- dih(H₆C₁C₂O₃) = 125.3°
- dih(H₇C₂C₁O₃) = 67.6°
- dih(H₈C₂C₁O₃) = -51.5°
- dih(C₁C₂O₄H₉) = 29.4°



- dih(C₁C₂O₃O₄) = -33.9°
- dih(H₅C₁C₂O₃) = -164.7°
- dih(H₆C₁C₂O₃) = 120.7°
- dih(H₇C₂C₁O₃) = 86.8°
- dih(H₈C₂C₁O₃) = -26.9°
- dih(C₁C₂O₄H₉) = 36.5°