SUPPORTING INFORMATION:

Direct evidence for base-mediated decomposition of alkyl hydroperoxides (ROOH) in the gas phase

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Table S1. Electronic energies calculated at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory, zero-point energies, relative energies and imaginary frequencies for the F^- + CH_3OOH potential energy surface. All calculations utilized the GAUSSIAN98 suite of programs.[1]

Structure[a]	Electronic Energy[b] (Hartrees)	Zero-point Energy[c] (Hartrees)	Relative Energy (kcal mol^{-1})[d]	Imaginary Frequency (cm^{-1})
F^- + CH_3OOH	-290.10549	0.05469	0.0	-
$(F^-\ldots CH_3OOH)_{complex}$	-290.13003	0.05380	-15.9	-
TS1	-290.12257	0.04836	-14.6	647i
HF + CH_2O + HO^-	-290.15223	0.04405	-35.8	-
$(HF\ldots CH_2O\ldots HO^-)_{complex}$	-290.20982	0.04893	-69.0	-
F^- + CH_2O + H_2O	-290.18734	0.04786	-55.5	-
TS2	-290.12447	0.05452	-12.0	189i
$(CH_3OOH\ldots F^-)_{complex}$	-290.16269	0.05424	-36.1	-
HF + CH_3OO^-	-290.09815	0.05243	1.9	-

[a] Structures calculated at B3LYP/6-31+G(d) level of theory. Important structures are presented in Table S3.
[b] Electronic energy is calculated as a single point energy at the CCSD(T)/aug-cc-pVDZ level of theory.
[c] Zero-point energy is calculated from the harmonic frequencies which are determined at the B3LYP/6-31+G(d) level of theory.
[d] Relative energy calculations include zero-point energies which have been corrected using the empirical scaling factor of 0.9804.[2]

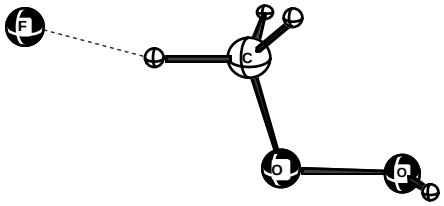
Table S2. Electronic energies calculated at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory, zero-point energies, relative energies and imaginary frequencies for the NC^- + CH_3OOH potential energy surface. All calculations utilized the GAUSSIAN98 suite of programs.[1]

Structure[a]	Electronic Energy[b] (Hartrees)	Zero-point Energy[c] (Hartrees)	Relative Energy (kcal mol^{-1})[d]	Imaginary Frequency (cm^{-1})
NC^- + CH_3OOH	-283.01842	0.05953	0.0	-
$(NC^-\ldots CH_3OOH)_{complex}$	-283.02993	0.06005	-7.2	-
TS1	-283.00812	0.05269	+6.5	647i
HCN + CH_2O + HO^-	-283.05357	0.05142	-22.0	-

[a] Structures calculated at B3LYP/6-31+G(d) level of theory. Important structures are presented in Table S4.
[b] Electronic energy is calculated as a single point energy at the CCSD(T)/aug-cc-pVDZ level of theory.
[c] Zero-point energy is calculated from the harmonic frequencies which are determined at the B3LYP/6-31+G(d) level of theory.
[d] Relative energy calculations include zero-point energies which have been corrected using the empirical scaling factor of 0.9804.[2]

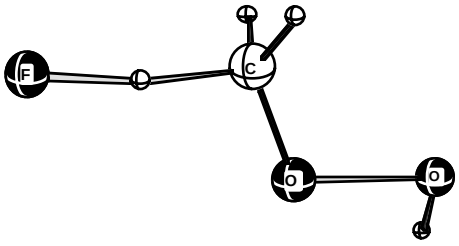
[1] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J., J.A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN98 A.7*; Gaussian Inc.: Pittsburgh PA, 1998.
[2] Scott, A. P.; Radom, L. *J Phys. Chem.* **1996**, *100*, 16502

Table S3. Calculated geometries for significant structures on the (F^- + CH_3OOH) potential surface. All structures have been calculated at the B3LYP/6-31+G(d) level of theory.



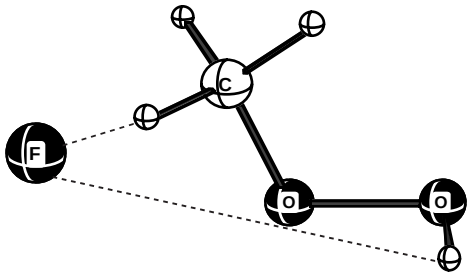
$(F^-...CH_3OOH)_{complex}$

FH_1 = 1.647 Å
H_1C = 1.142 Å
CH_2 = 1.102 Å
CH_3 = 1.100 Å
CO_1 = 1.417 Å
O_1O_2 = 1.495 Å
O_2H_4 = 0.974 Å
FH_1C = 167.0° dih(FH_1CO_1) = 167.4°
H_1CO_1 = 107.4° dih($H_1CO_1O_2$) = -178.1°
H_2CO_1 = 110.4° dih($CO_1O_2H_4$) = 98.8°
H_3CO_1 = 110.4° dih(FH_1CH_2) = 48.0°
H_2CH_3 = 109.7° dih(FH_1CH_3) = -72.2°
CO_1O_2 = 109.0°
$O_1O_2H_4$ = 99.5°



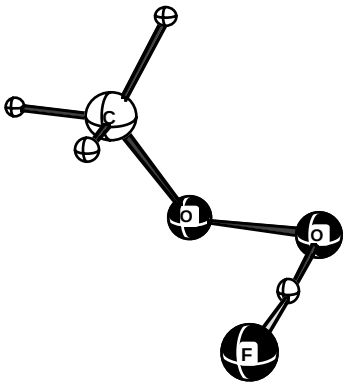
TS1

FH_1 = 1.272 Å
H_1C = 1.303 Å
CH_2 = 1.105 Å
CH_3 = 1.105 Å
CO_1 = 1.341 Å
O_1O_2 = 1.686 Å
O_2H_4 = 0.973 Å
FH_1C = 170.2° dih(FH_1CO_1) = -175.1°
H_1CO_1 = 105.2° dih($H_1CO_1O_2$) = 178.7°
H_2CO_1 = 114.4° dih($CO_1O_2H_4$) = -131.8°
H_3CO_1 = 114.4° dih(FH_1CH_2) = 63.6°
H_2CH_3 = 111.3° dih(FH_1CH_3) = -54.1°
CO_1O_2 = 110.8°
$O_1O_2H_4$ = 94.7°



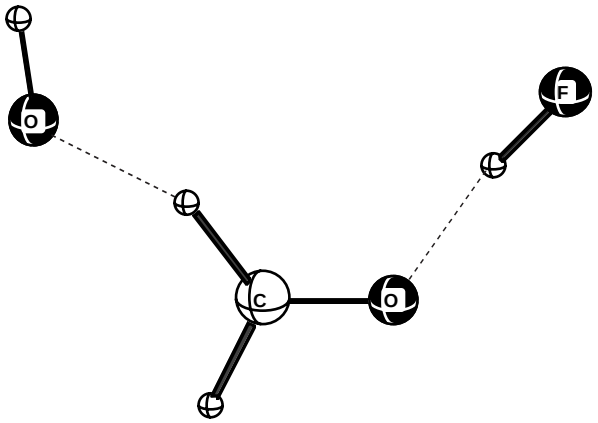
TS2

FH_1 = 1.748 Å
H_1C = 1.122 Å
CH_2 = 1.095 Å
CH_3 = 1.101 Å
CO_1 = 1.455 Å
O_1O_2 = 1.464 Å
O_2H_4 = 0.945 Å
FH_1C = 168.2° dih(FH_1CO_1) = 127.9°
H_1CO_1 = 110.4° dih($H_1CO_1O_2$) = -120.7°
H_2CO_1 = 108.5° dih($CO_1O_2H_4$) = 89.7°
H_3CO_1 = 107.1° dih(FH_1CH_2) = 8.5°
H_2CH_3 = 108.5° dih(FH_1CH_3) = -112.0°
CO_1O_2 = 109.6°
$O_1O_2H_4$ = 99.8°



$(F^-...HOOCH_3)_{complex}$

FH_4 = 1.313 Å
H_4O_2 = 1.104 Å
O_2O_1 = 1.461 Å
O_1C = 1.410 Å
CH_1 = 1.099 Å
CH_2 = 1.104 Å
CH_3 = 1.101 Å
FH_4O_2 = 175.4° dih($FH_4O_2O_1$) = -92.2°
$H_4O_2O_1$ = 102.6° dih($H_4O_2O_1C$) = 71.9°
O_2O_1C = 106.8° dih($O_2O_1CH_1$) = -60.2°
O_1CH_1 = 111.0° dih($O_2O_1CH_2$) = 61.8°
O_1CH_2 = 111.2° dih($O_2O_1CH_3$) = -179.5°
O_1CH_3 = 105.8°
H_2CH_3 = 109.4°

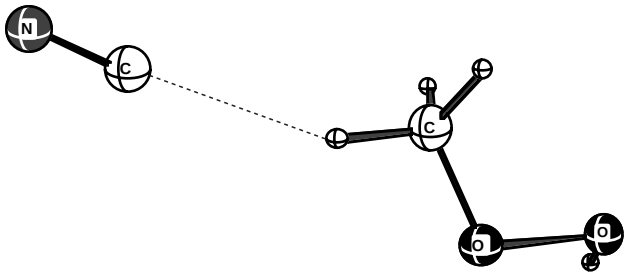


$(HF\ldots CH_2O..HO^-)_{complex}$

FH_1 = 0.984 Å
H_1O_1 = 1.567 Å
O_1C = 1.239 Å
CH_2 = 1.143 Å
CH_3 = 1.115 Å
H_2O_2 = 1.643 Å
O_2H_4 = 0.971 Å

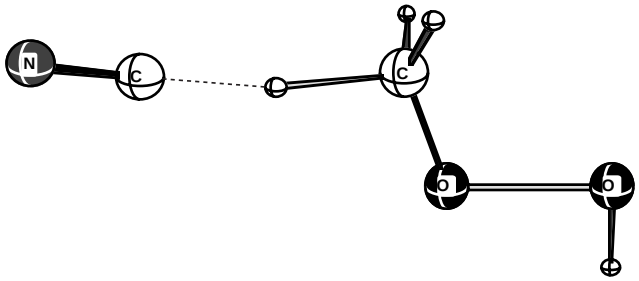
FH_1O_1 = 172.0°	dih(FH_1O_1C) = -180.0°
H_1O_1C = 126.2°	dih($H_1O_1CH_2$) = 0.0°
O_1CH_2 = 127.9°	dih($H_1O_1CH_3$) = 180.0°
O_1CH_3 = 116.0°	dih($O_1CH_2O_2$) = -180.0°
CH_2O_2 = 155.5°	dih($CH_2O_2H_4$) = 179.9°
H_2CH_3 = 116.0°	
$H_2O_2H_4$ = 126.4°	

Table S4. Calculated geometries for significant structures on the (NC^- + CH_3OOH) potential surface. All structures have been calculated at the B3LYP/6-31+G(d) level of theory.



$(NC^-...CH_3OOH)_{complex}$

NC_1 = 1.182 Å
C_1H_1 = 2.438 Å
H_1C_2 = 1.101 Å
C_2H_2 = 1.097 Å
C_2H_3 = 1.099 Å
C_2O_1 = 1.425 Å
O_1O_2 = 1.469 Å
O_2H_4 = 0.974 Å
NC_1H_1 = 173.0° dih($NC_1H_1C_2$) = 20.0°
$C_1H_1C_2$ = 154.1° dih($C_1H_1C_2O_1$) = -163.1°
$H_1C_2O_1$ = 106.4° dih($H_1C_2O_1O_2$) = 178.3°
$H_2C_2O_1$ = 110.5° dih($C_2O_1O_2H_4$) = -105.3°
$H_3C_2O_1$ = 110.8° dih($C_1H_1C_2H_2$) = 77.1°
$H_2C_2H_3$ = 110.2° dih($C_1H_1C_2H_3$) -43.8°
$C_2O_1O_2$ = 107.7°
$O_1O_2H_4$ = 100.0°



TS1

NC_1 = 1.172 Å
C_1H_1 = 1.444 Å
H_1C_2 = 1.373 Å
C_2H_2 = 1.107 Å
C_2H_3 = 1.107 Å
C_2O_1 = 1.309 Å
O_1O_2 = 1.786 Å
O_2H_4 = 0.973 Å
NC_1H_1 = 177.5° dih($NC_1H_1C_2$) = 6.2°
$C_1H_1C_2$ = 169.6° dih($C_1H_1C_2O_1$) = -178.0°
$H_1C_2O_1$ = 104.7° dih($H_1C_2O_1O_2$) = 179.3°
$H_2C_2O_1$ = 116.6° dih($C_2O_1O_2H_4$) = -157.9°
$H_3C_2O_1$ = 116.6° dih($C_1H_1C_2H_2$) = 60.2°
$H_2C_2H_3$ = 112.5° dih($C_1H_1C_2H_3$) -56.1°
$C_2O_1O_2$ = 110.9°
$O_1O_2H_4$ = 93.7°