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**Electronic Supplementary Information**

# The reactions of *N*-methylformamide and *N*,*N*-dimethylformamide with OH and their photo-oxidation under atmospheric conditions: Experimental and theoretical studies

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**Table S1**. Conditions and results for OH + MF (OH precursor: *t*-BuOOH)

| *T* /K | *P* /mbar | [MF]/$10^{14}$ cm$^3$ | $k_{bim}$/$10^{-12}$ cm$^{-3}$ | $\sigma$/$10^{-12}$ cm$^{-3}$ |
|---|---|---|---|---|
| 262 | 600 | 4-54 | 7.08 | 0.30 |
| 275 | 600 | 9-51 | 5.86 | 0.34 |
| 277 | 600 | 4-51 | 6.84 | 0.21 |
| 294 | 30 | 61-243 | 4.88 | 0.59 |
| 294 | 50 | 35-319 | 4.78 | 0.11 |
| 294 | 50 | 37-370 | 4.89 | 0.20 |
| 294 | 50 | 15-119 | 5.18 | 0.24 |
| 294 | 100 | 26-254 | 4.89 | 0.13 |
| 294 | 100 | 17-174 | 4.92 | 0.19 |
| 294 | 100 | 19-164 | 4.42 | 0.22 |
| 294 | 200 | 12-118 | 5.36 | 0.27 |
| 295 | 300 | 9-102 | 5.16 | 0.15 |
| 294 | 400 | 6-61 | 5.92 | 0.18 |
| 294 | 400 | 6-34 | 5.46 | 0.26 |
| 294 | 500 | 5-50 | 5.76 | 0.24 |
| 294 | 600 | 4-43 | 5.94 | 0.20 |
| 294 | 600 | 4-43 | 5.66 | 0.09 |

**Table S2**. Conditions and results for OH + DMF (OH precursor: 2,4-pentanedione)

| *T* /K | *P* /mbar | [DMF]/$10^{14}$ cm$^3$ | $k_{bim}$/$10^{-12}$ cm$^{-3}$ | $\sigma$/$10^{-12}$ cm$^{-3}$ |
|---|---|---|---|---|
| 258 | 50 | 22-130 | 13.00 | 0.52 |
| 258 | 100 | 53-85 | 11.00 | 0.43 |
| 260 | 200 | 16-61 | 10.70 | 0.50 |
| 261 | 100 | 11-66 | 9.82 | 0.46 |
| 264 | 100 | 31-82 | 10.00 | 0.41 |
| 270 | 100 | 11-64 | 8.96 | 0.41 |
| 270 | 200 | 15-61 | 10.60 | 0.46 |
| 271 | 100 | 21-107 | 10.30 | 0.41 |
| 272 | 200 | 10-35 | 10.40 | 0.48 |
| 273 | 50 | 126-28 | 11.60 | 0.42 |
| 274 | 600 | 14-51 | 9.02 | 0.26 |
| 275 | 100 | 20-98 | 10.30 | 0.41 |
| 278 | 100 | 21-95 | 8.83 | 0.40 |
| 278 | 100 | 20-61 | 10.10 | 0.70 |
| 280 | 200 | 19-43 | 6.40 | 0.18 |
| 285 | 100 | 19-86 | 7.33 | 0.26 |
| 287 | 100 | 19-56 | 8.69 | 0.42 |
| 293 | 300 | 14-46 | 8.35 | 0.27 |
| 293 | 300 | 15-49 | 9.55 | 0.25 |
| 293 | 500 | 7-28 | 6.88 | 0.31 |
| 293 | 600 | 5-20 | 7.24 | 0.27 |
| 294 | 30 | 15-126 | 8.96 | 0.63 |
| 294 | 30 | 127 | 9.22 | 0.26 |

| | | | | |
|---|---|---|---|---|
| 294 | 100 | 20-90 | 9.08 | 0.42 |
| 294 | 100 | 10-49 | 7.40 | 0.32 |
| 294 | 100 | 20-79 | 7.53 | 0.37 |
| 294 | 200 | 10-49 | 6.71 | 0.23 |
| 294 | 400 | 5-39 | 6.00 | 0.35 |
| 295 | 50 | 17-89 | 7.49 | 0.41 |
| 295 | 100 | 14-52 | 6.86 | 0.28 |

**Table S3**. Energies, enthalpies and Gibbs free energies (/Hartree) from G3 calculations.

| Species | $E_{ZPE}$ | $E_{v=0}$ | $H_{298}$ | $G_{298}$ |
|---|---|---|---|---|
| H | 0.000000 | -0.501003 | -0.498642 | -0.511657 |
| OH | 0.008131 | -75.694904 | -75.691600 | -75.711799 |
| $HO_2$ | 0.014012 | -150.826905 | -150.823099 | -150.849032 |
| $H_2O$ | 0.020511 | -76.382044 | -76.378265 | -76.399642 |
| $O_2$ ( $X^3\Sigma_g^-$) | 0.004065 | -150.248213 | -150.244907 | -150.268117 |
| NO | 0.004519 | -129.833908 | -129.830603 | -129.853861 |
| $NO_2$ | 0.008797 | -204.979605 | -204.975723 | -205.002867 |
| CO | 0.004960 | -113.267368 | -113.264064 | -113.286466 |
| $CO_2$ | 0.011381 | -188.500298 | -188.49673 | -188.520964 |
| HONO | 0.020599 | -205.603061 | -205.598924 | -205.626946 |
| HNCO | 0.020352 | -168.595311 | -168.591081 | -168.618188 |
| $\dot{C}H_3$ | 0.027651 | -39.793295 | -39.789051 | -39.811580 |
| $CH_2O$ | 0.026073 | -114.431062 | -114.427247 | -114.452676 |
| $CH_2$=NH | 0.038646 | -94.554861 | -94.550988 | -94.576736 |
| $CH_3NHCHO$ | 0.071433 | -209.045726 | -209.039653 | -209.073426 |
| $CH_3NH\dot{C}O$ | 0.059316 | -208.397083 | -208.391098 | -208.425039 |
| $\dot{C}H_2NHCHO$ | 0.056616 | -208.398342 | -208.392566 | -208.425679 |
| $CH_3\dot{N}CHO$ | 0.057178 | -208.374321 | -208.368407 | -208.403024 |
| $\dot{O}OCH_2NHCHO$ | 0.069264 | -358.692554 | -358.685284 | -358.723787 |
| $CHONHCH_2\dot{O}$ | 0.064335 | -283.566819 | -283.560475 | -283.596429 |
| $CH_3NCO$ | 0.048719 | -207.854145 | -207.84837 | -207.882025 |
| CHONHCHO | 0.054743 | -283.056534 | -283.050563 | -283.084501 |
| $CHO\dot{N}H\_e$ | 0.030111 | -169.103249 | -169.099004 | -169.127958 |
| $CH_3\dot{N}H$ | 0.047221 | -95.102758 | -95.098350 | -95.126170 |
| $CH_3NHNO_2$ | 0.065852 | -300.161384 | -300.155275 | -300.189535 |
| $CH_3NHC(O)\dot{O}$ | 0.063815 | -283.570802 | -283.564060 | -283.601477 |
| $CH_3NHC(O)O\dot{O}$ | 0.068068 | 358.703579 | -358.695776 | -358.735593 |
| $CH_3NHC(O)OONO_2$ | 0.083390 | -563.726510 | -563.716352 | -563.762363 |
| $CH_3C(O)OONO_2$ | 0.066134 | -508.403622 | -508.394814 | -508.437179 |
| $(CH_3)_2NCHO$ | 0.098596 | -248.312865 | -248.30557 | -248.342520 |
| $(CH_3)_2N\dot{C}O$ | 0.086572 | -247.663357 | -247.656134 | -247.693501 |
| *cis* $\dot{C}H_2(CH_3)NCHO$ | 0.085001 | -247.664327 | -247.65706 | -247.694345 |
| *trans* $\dot{C}H_2(CH_3)NCHO$ | 0.084963 | -247.664176 | -247.656985 | -247.693813 |
| $\dot{O}OCH_2(CH_3)NCHO$ | 0.096177 | -397.960004 | -397.95119 | -397.993723 |
| $\dot{O}CH_2(CH_3)NCHO$ | 0.091260 | -322.832296 | -322.824515 | -322.864029 |

| | | | | |
|---|---|---|---|---|
| $CHO(CH_3)NCHO$ | 0.081667 | -322.323443 | -322.315984 | -322.353721 |
| $(CH_3)_2NC(O)O\dot{O}$ | 0.095160 | -397.961721 | -397.952665 | -397.995157 |
| $(CH_3)_2NC(O)\dot{O}$ | 0.091101 | -322.849782 | -322.841672 | -322.881885 |
| $(CH_3)_2NC(O)OONO_2$ | 0.110311 | -602.989667 | -602.978005 | -603.027889 |
| $(CH_3)_2\dot{N}$ | 0.074639 | -134.372623 | -134.366887 | -134.399549 |
| $(CH_3)_2NNO$ | 0.086549 | -264.277809 | -264.270658 | -264.307320 |
| $(CH_3)_2NNO_2$ | 0.092535 | -339.427398 | -339.419770 | -339.457842 |
| $CH_3N{=}CH_2$ | 0.065786 | -133.820774 | -133.815890 | -133.845559 |

**Table S4**. Electronic energies of reactants, intermediates and products (/Hartree), and relative energies including Zero Point Energies, Δ (/kJ mol$^{-1}$), of stationary points on the potential energy surface of the MF + OH reaction.

| Species | MP2/TZ[a] | MP2/aTZ | CCSD(T*)-F12a/aTZ //MP2/aTZ | BHandHLYP/TZ | BHandHLYP/aTZ | CCSD(T*)-F12a/aTZ //BHandHLYP/aTZ |
|---|---|---|---|---|---|---|
| cis-MF | -208.8190606 | -208.8369023 | -208.9678261 | -209.1596369 | -209.1635719 | -208.9670304 |
| | (0.0749516)[b] | (0.0746535) | | (0.076748) | (0.0766176) | |
| ts | -208.7878794 | -208.8052284 | -208.9373198 | -209.1270907 | -209.1307785 | -208.9362773 |
| | (0.0739589) | (0.0737423) | | (0.0757135) | (0.0756557) | |
| | Δ = 74.0 [c] | Δ = 74.7 | Δ = 72.0 | Δ = 78.6 | Δ = 78.9 | Δ = 72.6 |
| trans-MF | -208.7878794 | -208.8052284 | -208.9373198 | -209.1270907 | -209.1307785 | -208.9362773 |
| | (0.0739589) | (0.0737423) | | (0.0757135) | (0.0756557) | |
| | Δ = 5.2 | Δ = 6.1 | Δ = 5.7 | Δ = 4.1 | Δ = 4.7 | Δ = 5.6 |
| OH | -75.618907 | -75.626337 | -75.670689 | -75.732475 | -75.735902 | -75.670629 |
| | (0.008704) | (0.008646) | | (0.008821) | (0.008809) | |
| PRE | -284.4515519 | -284.476373 | -284.6515885 | -284.9061841 | -284.9119441 | -284.6507221 |
| | (0.0869127) | (0.0863779) | | (0.0889272) | (0.0885533) | |
| | Δ = -27.1 | Δ = -26.4 | Δ = -26.2 | Δ = -28.1 | Δ = -24.5 | Δ = -26.1 |
| TS_carbonyl/ts3 | -284.4346397 | -284.4602466 | -284.6404865 | -284.9046348 | -284.9119441 | -284.6495188 |
| | (0.0826315) | (0.0823408) | | (0.0889792) | (0.08855) | |
| | Δ =6.0 | Δ =5.3 | Δ = -7.7 | Δ =10.2 | Δ =12.3 | Δ =-10.9 |
| POST-C | -284.4919154 | -284.5174724 | -284.6878091 | -284.9318686 | -284.9384919 | -284.6865978 |
| | (0.0867352) | (0.086252) | | (0.0882788) | (0.0881831) | |
| | Δ =-133.6 | Δ =-134.6 | Δ = -121.7 | Δ = -97.3 | Δ = -95.2 | Δ =-121.3 |
| CH3NHCO | -208.1622161 | -208.1791191 | -208.307492 | -208.5047357 | -208.5083329 | -208.3066598 |
| | (0.0625556) | (0.062363) | | (0.0640262) | (0.0638993) | |
| H2O | -76.4170246 | -76.4220492 | -76.37084003 | -76.4170246 | -76.4220492 | -76.37084003 |
| | (0.0221444) | (0.022099) | | (0.0221444) | (0.022099) | |
| PROD-C | Δ = -111.3 | Δ = -116.6 | Δ = -103.7 | Δ = -76.3 | Δ = -79.6 | Δ = -103.1 |
| TS_methyl | -284.4328213 | -284.4578626 | -284.6404865 | -284.9335047 | -284.9409038 | -284.6878084 |
| | (0.0821738) | (0.0816072) | | (0.0880454) | (0.087682) | |

| | | | | | | |
|---|---|---|---|---|---|---|
| | Δ = 9.6 | Δ = 9.7 | Δ = -9.6 | Δ = 1.5 | Δ =3.3 | Δ =-11.7 |
| | -284.4900841 | -284.5168115 | -284.6886859 | -284.9335047 | -284.9409038 | -284.6878084 |
| POST-methyl | (0.0859657) | (0.0850403) | | (0.0880454) | (0.087682) | |
| | Δ = -130.8 | Δ =-136.1 | Δ =-127.2 | Δ = -102.2 | Δ =-102.9 | Δ = -125.7 |
| | -208.1587264 | -208.1763695 | -208.3063733 | -208.504204 | -208.5084608 | -208.3055519 |
| CH2NHCHO | (0.0606224) | (0.06062) | | (0.0621348) | (0.0622477) | |
| PROD | Δ = -107.2 | Δ =-114.0 | Δ =-105.4 | Δ =-79.8 | Δ = -84.3 | Δ = -104.5 |
| | -284.4242908 | -284.4489244 | -284.6314834 | -284.8760771 | -284.8820765 | -284.6314514 |
| TSNH | (0.0813304) | (0.0810683) | | (0.0826467) | (0.0825098) | |
| | Δ =29.8 | Δ =31.7 | Δ =12.6 | Δ =34.4 | Δ =38.0 | Δ =8.6 |
| | -284.4558361 | -284.4829995 | -284.6588985 | -284.907818 | -284.914827 | -284.6602455 |
| POST | (0.0847174) | (0.0841528) | | (0.0863398) | (0.0859752) | |
| | Δ = -44.1 | Δ =-49.6 | Δ =-51.3 | Δ =-39.2 | Δ = -38.9 | Δ =-57.9 |
| | -208.1292204 | -208.1457128 | -208.2800134 | -208.482683 | -208.4859079 | -208.2812658 |
| CH3NCHO | (0.0605549) | (0.0603591) | | (0.0614653) | (0.0614025) | |
| PROD-trans | Δ = -29.9 | Δ =-34.2 | Δ =-36.8 | Δ =-25.1 | Δ =-27.3 | Δ =-43.0 |

[a] TZ,cc-pVTZ; aTZ, aug-cc-pVTZ; T* denotes scaled tripples as recomended in the Molpro manual. [b] Zero point energy (ZPE) in parentheses. [c] Energy difference incl. ZPE in kJ $mol^{-1}$.

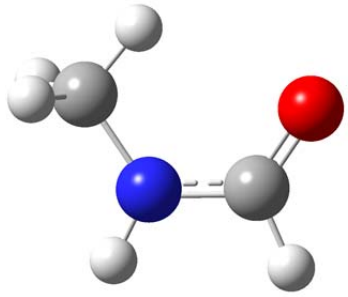
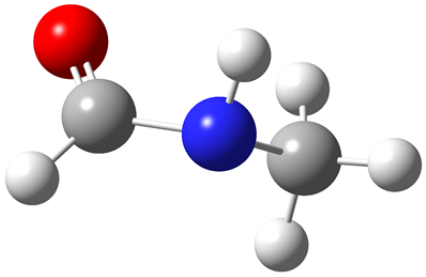
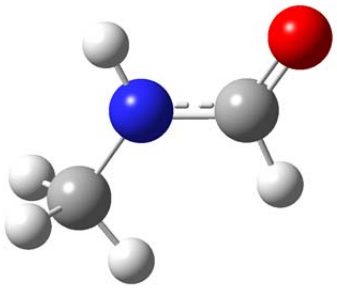
**Table S5**. Electronic energies of reactants, intermediates and products (/Hartree), and relative energies including Zero Point Energies, Δ (/kJ mol$^{-1}$), of stationary points on the potential energy surface of the DMF + OH reaction.

| Species | MP2/TZ | MP2/aTZ | CCSD(T*)-F12a/aTZ //MP2/aTZ | BHandHLYP/TZ | BHandHLYP/aTZ | CCSD(T*)-F12a/aTZ //BHandHLYP/aTZ |
|---|---|---|---|---|---|---|
| DMF | -248.035171 | -248.055326 | -248.218091 | -248.454204 | -248.457732 | -248.217186 |
| | 0.103383 | 0.103162 | | 0.105704 | 0.105634 | |
| OH | -75.618907 | -75.626337 | -75.670689 | -75.732475 | -75.735902 | -75.670629 |
| | 0.008704 | 0.008646 | | 0.008821 | 0.008809 | |
| PRE | -323.668274 | -323.695257 | -323.902423 | -324.201048 | -324.206826 | -323.901381 |
| | 0.115472 | 0.115053 | | 0.117883 | 0.117663 | |
| | Δ = -28.4 [c] | Δ = -27.2 | Δ = -27.3 | Δ = -28.9 | Δ = -27.0 | Δ = -27.2 |
| TS3/CHO | -323.649086 | -323.676900 | -323.892376 | -324.184058 | -324.190337 | -323.892512 |
| | 0.110048 | 0.109511 | | 0.112377 | 0.112280 | |
| | Δ = 7.8 | Δ = 6.5 | Δ = -15.5 | Δ =1.2 | Δ = 3.0 | Δ = -18.8 |
| POST-C | -323.704635 | -323.733454 | -323.935617 | -324.223263 | -324.230058 | -323.934449 |
| | 0.114997 | 0.114373 | | 0.117351 | 0.116891 | |
| | Δ = -125.1 | Δ = -129.2 | Δ = -116.2 | Δ = -88.6 | Δ = -89.2 | Δ = -116.0 |
| (CH3)2CO | -247.377755 | -247.397183 | -247.557589 | -247.799265 | -247.802624 | -247.556629 |
| | 0.090987 | 0.090810 | | 0.092922 | 0.092853 | |
| H2O | -76.417025 | -76.422049 | -76.370840 | -76.417025 | -76.422049 | -76.370840 |
| | 0.022144 | 0.022099 | | 0.022144 | 0.022099 | |
| PROD-C | Δ = -109.8 | Δ = -115.3 | Δ = -103.5 | Δ = -76.3 | Δ = -80.2 | Δ = -102.8 |
| TS2/cis | -323.647004 | -323.674650 | -323.887785 | -324.179882 | -324.186324 | -323.887844 |
| | 0.110060 | 0.109553 | | 0.112144 | 0.111943 | |
| | Δ = 13.3 | Δ = 12.5 | Δ = -3.3 | Δ = 11.6 | Δ = 12.6 | Δ = -6.6 |
| POST-cis | -323.700950 | -323.729847 | -323.933615 | -324.221278 | -324.228282 | -323.932398 |
| | 0.113358 | 0.112797 | | 0.115794 | 0.115453 | |
| | Δ = -119.7 | Δ = -123.9 | Δ = -115.1 | Δ = -87.5 | Δ = -88.3 | Δ = -114.4 |
| cis-CH2NCH3CHO | -247.375211 | -247.394946 | -247.556894 | -247.799078 | -247.802772 | -247.555952 |
| | 0.089175 | 0.088743 | | 0.090626 | 0.090322 | |

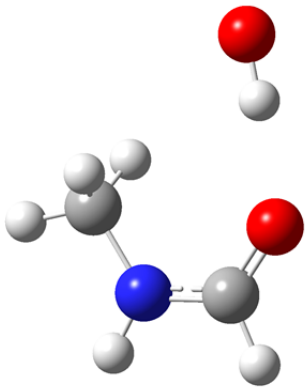
| | | | | | | |
|---|---|---|---|---|---|---|
| PROD-cis | Δ = -107.9 | Δ = -115.4 | Δ = -107.9 | Δ = -81.9 | Δ = -87.2 | Δ = -2.9 |
| TS1/trans | -323.650350 | -323.678314 | -323.890682 | -324.180835 | -324.187101 | -323.890246 |
| | 0.111117 | 0.110776 | | 0.112925 | 0.112658 | |
| | Δ = 7.2 | Δ = 6.1 | Δ = -7.7 | Δ = 11.1 | Δ = 12.5 | Δ = -11.1 |
| POST-trans | -323.703008 | -323.735433 | -323.939481 | -324.227819 | -324.234991 | -323.938384 |
| | 0.113525 | 0.113700 | | 0.116775 | 0.116420 | |
| | Δ = -124.7 | Δ = -120.9 | Δ = -128.1 | Δ = -102.1 | Δ = -103.4 | Δ = -127.6 |
| trans-CH2NCH3CHO | -247.374870 | -247.394930 | -247.557127 | -247.798756 | -247.802688 | -247.556196 |
| | 0.089202 | 0.089119 | | 0.091085 | 0.091138 | |
| PROD-trans | Δ = -106.9 | Δ = -114.3 | Δ = -106.7 | Δ = -79.8 | Δ = -84.8 | Δ = -106.1 |

[a] TZ,cc-pVTZ; aTZ, aug-cc-pVTZ; T* denotes scaled tripples as recomended in the Molpro manual. [b] Zero point energy (ZPE) in parentheses. [c] Energy difference incl. ZPE in kJ $mol^{-1}$.

**Table S6**. Cartesian coordinates of reactants, intermediates and products in the reactions between the OH radical and N-methyl formamide from MP2/cc-pVTZ calculations.

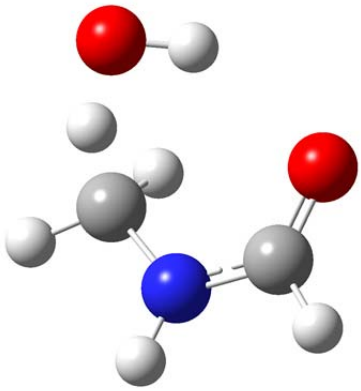
| | | X | Y | Z |
|---|---|---|---|---|
| cis-MF | C | 0.861861 | 0.433607 | -0.000001 |
|  | H | 1.429919 | 1.375546 | -0.000011 |
| | N | -0.478567 | 0.645075 | 0.000010 |
| | H | -0.797046 | 1.598607 | -0.000026 |
| | O | 1.401750 | -0.661942 | 0.000000 |
| | C | -1.441128 | -0.437707 | -0.000002 |
| | H | -2.070099 | -0.400508 | 0.887790 |
| | H | -2.069975 | -0.400610 | -0.887887 |
| | H | -0.881229 | -1.368423 | 0.000088 |
| ts_rot | C | -0.82044 | 0.386504 | 0.230457 |
|  | H | -1.244942 | 1.099425 | 0.949409 |
| | N | 0.521579 | 0.704216 | -0.171378 |
| | H | 0.497958 | 0.841034 | -1.179047 |
| | O | -1.450546 | -0.572353 | -0.152965 |
| | C | 1.432549 | -0.421819 | 0.112496 |
| | H | 1.100371 | -1.363932 | -0.327296 |
| | H | 2.418619 | -0.170022 | -0.268657 |
| | H | 1.508653 | -0.5453 | 1.191241 |
| trans-MF | C | -0.724692 | 0.34524 | 0.000004 |
|  | H | -0.497465 | 1.423411 | 0.000011 |
| | N | 0.398578 | -0.414985 | 0.000011 |
| | H | 0.253903 | -1.412984 | -0.000006 |
| | O | -1.865064 | -0.089232 | -0.000006 |
| | C | 1.742191 | 0.118928 | -0.000006 |
| | H | 2.293529 | -0.190983 | 0.886743 |
| | H | 2.293492 | -0.190932 | -0.886795 |
| | H | 1.682015 | 1.205229 | 0.000028 |
| OH | O | 0.000000 | 0.000000 | 0.107715 |
| | H | 0.000000 | 0.000000 | -0.861717 |
| $H_2O$ | O | 0.000000 | 0.000000 | 0.118231 |
| | H | 0.000000 | 0.758132 | -0.472925 |
| | H | 0.000000 | -0.758132 | -0.472925 |

Pre



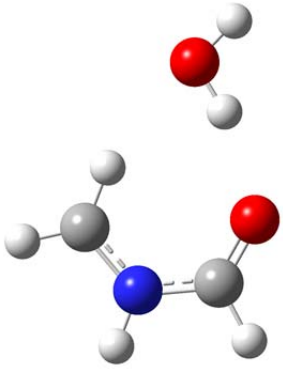
| | | | |
|---|---|---|---|
| C | 0.943621 | -0.996329 | 0.018930 |
| O | -0.256614 | -1.247903 | -0.054329 |
| N | 1.460083 | 0.244697 | 0.041390 |
| H | 1.702217 | -1.787349 | 0.073288 |
| C | 0.616508 | 1.425510 | -0.031317 |
| H | -0.106841 | 1.428069 | 0.780568 |
| H | 1.245972 | 2.307013 | 0.040618 |
| H | 0.069632 | 1.448147 | -0.972172 |
| O | -2.631996 | 0.280517 | 0.015683 |
| H | -1.834320 | -0.288540 | -0.021055 |
| H | 2.459363 | 0.339223 | 0.091702 |

ts1/methyl



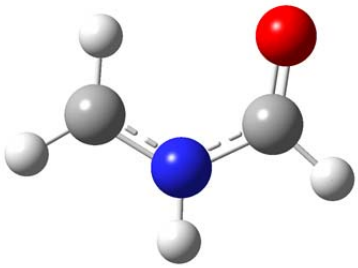
| | | | |
|---|---|---|---|
| C | 1.274599 | -0.343541 | -0.226509 |
| O | 0.794712 | -1.259732 | 0.429357 |
| N | 0.744697 | 0.903006 | -0.269624 |
| H | 2.183203 | -0.452846 | -0.832193 |
| C | -0.472922 | 1.200117 | 0.419446 |
| H | -1.344060 | 0.501203 | 0.008377 |
| H | -0.403558 | 0.969065 | 1.478367 |
| H | -0.782945 | 2.223945 | 0.240887 |
| O | -1.983250 | -0.619281 | -0.330377 |
| H | -1.283755 | -1.222696 | -0.016191 |
| H | 1.116476 | 1.552941 | -0.941349 |

post1/methyl



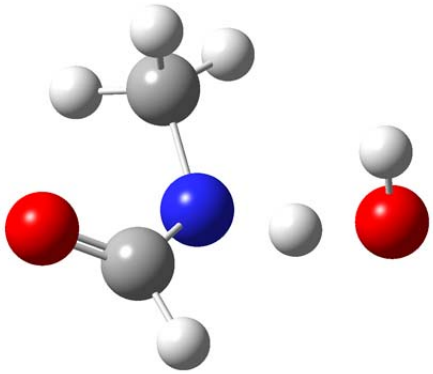
| | | | |
|---|---|---|---|
| C | 1.043500 | -0.941872 | 0.001035 |
| O | -0.133492 | -1.276102 | -0.002816 |
| N | 1.485847 | 0.347828 | 0.001450 |
| H | 1.865967 | -1.667143 | 0.004507 |
| C | 0.672757 | 1.460068 | -0.002727 |
| H | -3.289203 | -0.155775 | -0.018055 |
| H | -0.392415 | 1.323684 | -0.007011 |
| H | 1.150229 | 2.420801 | -0.001226 |
| O | -2.460080 | 0.327929 | 0.004737 |
| H | -1.769546 | -0.355460 | 0.001277 |
| H | 2.485073 | 0.475302 | 0.005145 |

CH2NHCHO



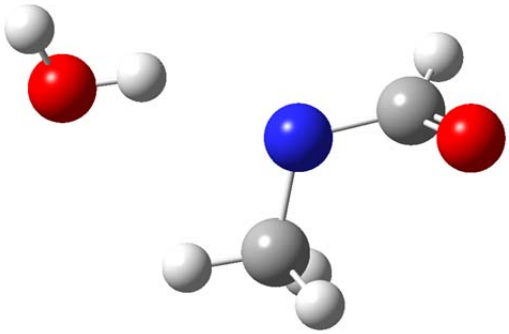
| | | | |
|---|---|---|---|
| C | -0.790645 | 0.452760 | 0.000000 |
| H | -1.297694 | 1.427104 | 0.000000 |
| N | 0.576063 | 0.578442 | 0.000000 |
| H | 0.952516 | 1.512103 | 0.000000 |
| O | -1.375301 | -0.614307 | 0.000000 |
| C | 1.430517 | -0.499869 | 0.000000 |
| H | 2.486673 | -0.313588 | 0.000001 |
| H | 0.989236 | -1.477603 | 0.000001 |

tsn



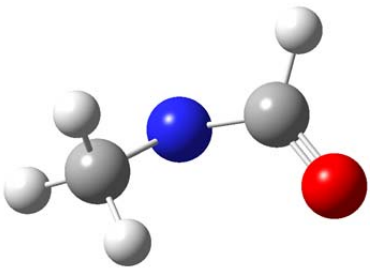
| | | | |
|---|---|---|---|
| C | 0.753885 | -0.788560 | 0.176937 |
| H | 0.358625 | -1.778910 | 0.431253 |
| N | -0.119891 | 0.234767 | 0.492142 |
| H | -1.194003 | -0.095806 | 0.528903 |
| O | 1.867031 | -0.594647 | -0.276975 |
| C | 0.128258 | 1.546300 | -0.085522 |
| H | 0.331078 | 1.492735 | -1.155191 |
| H | -0.731204 | 2.179857 | 0.110823 |
| H | 1.003659 | 1.970679 | 0.403197 |
| O | -2.143776 | -0.605078 | -0.130006 |
| H | -2.007818 | -0.360568 | -1.056620 |

post_tsn



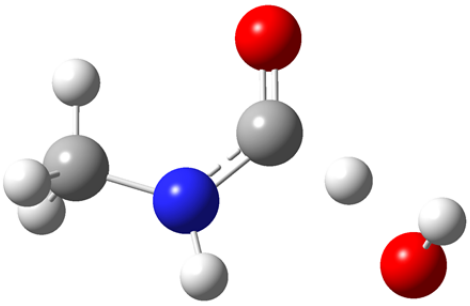
| | | | |
|---|---|---|---|
| C | -1.389805 | -0.454027 | -0.400821 |
| H | -1.580438 | -0.772891 | -1.438755 |
| N | -0.073752 | -0.033610 | -0.199418 |
| H | 1.852854 | -0.671384 | -0.008747 |
| O | -2.218122 | -0.528788 | 0.479095 |
| C | 0.079147 | 1.382427 | 0.032486 |
| H | -0.578133 | 1.671532 | 0.858453 |
| H | 1.113817 | 1.607680 | 0.267646 |
| H | -0.235456 | 1.948649 | -0.849477 |
| O | 2.792364 | -0.452005 | 0.074947 |
| H | 3.213627 | -1.272371 | 0.344487 |

CH3NCHO



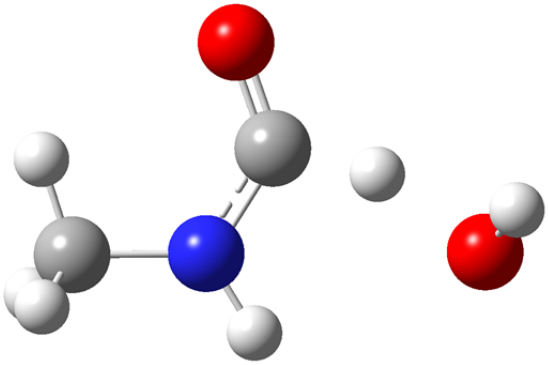
| | | | |
|---|---|---|---|
| C | -0.772382 | 0.408759 | -0.176055 |
| H | -1.091526 | 1.242545 | -0.823106 |
| N | 0.496336 | 0.602469 | 0.361781 |
| O | -1.489907 | -0.531151 | 0.091338 |
| C | 1.493166 | -0.324570 | -0.110376 |
| H | 1.112865 | -1.343203 | 0.014701 |
| H | 1.681309 | -0.176236 | -1.178402 |
| H | 2.417552 | -0.196317 | 0.442227 |

ts3/carbonyl



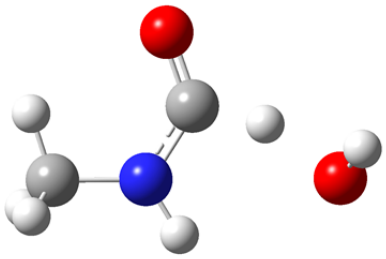
| | | | |
|---|---|---|---|
| C | 0.168239 | 0.512247 | -0.061547 |
| O | -0.228602 | 1.655512 | 0.008095 |
| N | -0.552370 | -0.624027 | -0.040057 |
| H | 1.298653 | 0.232666 | -0.172373 |
| O | -2.000891 | -0.636711 | 0.048021 |
| H | -2.332391 | 0.393272 | 0.143476 |
| H | -2.440429 | -1.071133 | -0.847839 |
| H | -2.327255 | -1.199680 | 0.920061 |
| O | 2.464405 | -0.606219 | -0.048008 |
| H | 2.806569 | -0.152657 | 0.738530 |
| H | -0.029062 | -1.481841 | -0.100993 |

ts3/post



| | | | |
|---|---|---|---|
| C | -0.374896 | 0.850429 | 0.032128 |
| O | -1.372892 | 1.521745 | -0.019290 |
| N | -0.220282 | -0.475591 | 0.073543 |
| H | 2.285800 | 0.805883 | -0.091759 |
| C | -1.345386 | -1.397282 | -0.027037 |
| H | -2.233772 | -0.896376 | 0.348121 |
| H | -1.519752 | -1.701887 | -1.058290 |
| H | -1.146847 | -2.276957 | 0.579796 |
| O | 2.663907 | -0.082151 | -0.092015 |
| H | 3.419122 | -0.024419 | 0.500656 |
| H | 0.730998 | -0.812744 | 0.066563 |

CH3NHCO

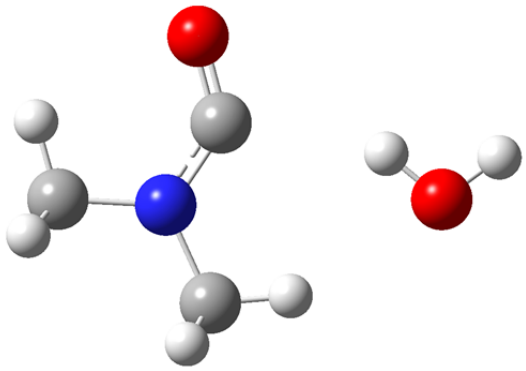


| | | | |
|---|---|---|---|
| C | -0.861226 | 0.505005 | -0.012496 |
| N | 0.471146 | 0.654118 | 0.021254 |
| H | 0.828114 | 1.589054 | -0.056234 |
| O | -1.517506 | -0.502009 | 0.002336 |
| C | 1.389539 | -0.479157 | -0.005347 |
| H | 1.670486 | -0.742898 | -1.024109 |
| H | 2.281735 | -0.235589 | 0.565503 |
| H | 0.891813 | -1.328413 | 0.454433 |

**Table S7**. Cartesian coordinates of reactants, intermediates and products in the reactions between the OH radical and N,N-methyl formamide from MP2/cc-pVTZ calculations.

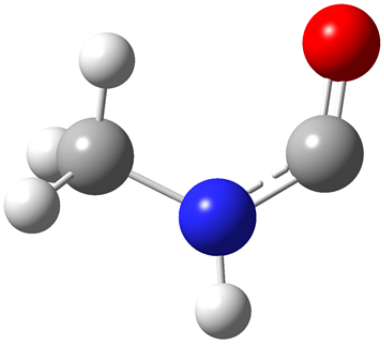
| | | X | Y | Z |
|---|---|---|---|---|
| DMF | C | 0.857401 | -0.648112 | -0.000004 |
| | O | 1.949073 | -0.096030 | 0.000002 |
| | N | -0.345691 | -0.019596 | 0.000000 |
| | H | 0.747863 | -1.743752 | 0.000005 |
| | C | -1.587501 | -0.754999 | 0.000001 |
| | H | -2.178718 | -0.514994 | 0.885888 |
| | H | -2.178717 | -0.514999 | -0.885888 |
| | H | -1.377343 | -1.822673 | 0.000004 |
| | C | -0.417946 | 1.424882 | 0.000000 |
| | H | -0.946642 | 1.777897 | 0.886988 |
| | H | 0.595741 | 1.815414 | -0.000007 |
| | H | -0.946654 | 1.777896 | -0.886982 |
| DMF*OH | C | 0.261754 | -0.172101 | 0.000034 |
| | O | 1.027516 | 0.793572 | 0.000034 |
| | N | -1.082065 | -0.094691 | 0.000004 |
| | H | 0.631802 | -1.206290 | 0.000059 |
| | C | -1.749120 | 1.191199 | -0.000024 |
| | H | -0.992507 | 1.970027 | -0.000010 |
| | H | -2.375969 | 1.287245 | -0.887233 |
| | H | -2.376018 | 1.287259 | 0.887148 |
| | C | -1.909378 | -1.280724 | -0.000007 |
| | H | -1.276961 | -2.165604 | 0.000008 |
| | H | -2.545145 | -1.301800 | 0.886232 |
| | H | -2.545111 | -1.301810 | -0.886271 |
| | O | 3.561045 | -0.356184 | -0.000031 |
| | H | 2.726335 | 0.164462 | -0.000006 |
| Carbonyl_ts3 | C | -0.305741 | 0.632598 | -0.000265 |
| | O | -0.265505 | 1.847226 | -0.000156 |
| | N | 0.724391 | -0.234633 | -0.000070 |
| | H | -1.320734 | 0.045819 | -0.000516 |
| | C | 2.090306 | 0.254747 | 0.000320 |
| | H | 2.066348 | 1.340581 | 0.000446 |
| | H | 2.614420 | -0.101647 | 0.887854 |
| | H | 2.614857 | -0.101428 | -0.887043 |
| | C | 0.516728 | -1.667735 | -0.000196 |
| | H | -0.549302 | -1.878571 | -0.000564 |
| | H | 0.969915 | -2.114055 | -0.886569 |
| | H | 0.969296 | -2.114133 | 0.886454 |
| | O | -2.634405 | -0.489978 | 0.000251 |
| | H | -3.044014 | 0.390219 | 0.000511 |

post3



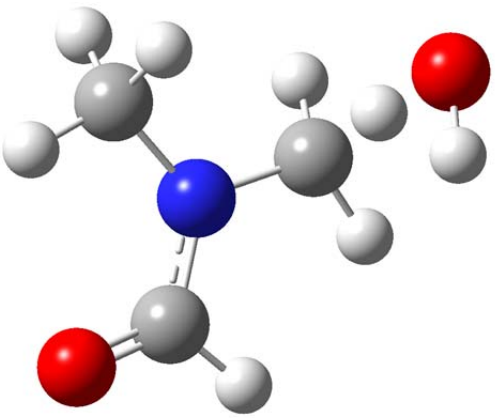
| | | | |
|---|---|---|---|
| C | -0.008134 | 0.807688 | 0.000005 |
| O | -0.317354 | 1.973393 | 0.000003 |
| N | -0.753447 | -0.298092 | 0.000001 |
| H | 2.222798 | 0.391508 | 0.000000 |
| C | -2.208499 | -0.219798 | -0.000007 |
| H | -2.501961 | 0.825994 | -0.000009 |
| H | -2.607024 | -0.711983 | -0.887689 |
| H | -2.607035 | -0.711983 | 0.887669 |
| C | -0.150981 | -1.618660 | 0.000006 |
| H | 0.930959 | -1.524791 | 0.000013 |
| H | -0.465636 | -2.170900 | 0.886483 |
| H | -0.465624 | -2.170900 | -0.886476 |
| O | 2.970513 | -0.223162 | -0.000004 |
| H | 3.748061 | 0.342477 | -0.000010 |

(CH3)2CO



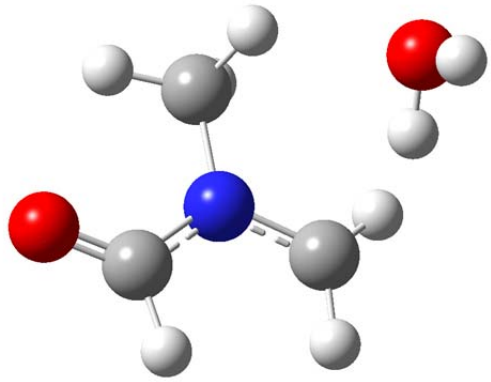
| | | | |
|---|---|---|---|
| C | 0.866771 | -0.660986 | 0.000001 |
| O | 1.981185 | -0.204286 | -0.000001 |
| N | -0.322226 | -0.046053 | 0.000003 |
| C | -1.555003 | -0.804569 | -0.000001 |
| H | -1.315949 | -1.863800 | -0.000001 |
| H | -2.146256 | -0.569005 | 0.886415 |
| H | -2.146252 | -0.569005 | -0.886419 |
| C | -0.420976 | 1.406414 | 0.000000 |
| H | 0.582714 | 1.821802 | 0.000001 |
| H | -0.956447 | 1.745758 | -0.887623 |
| H | -0.956452 | 1.745760 | 0.887618 |

ts_cis/2



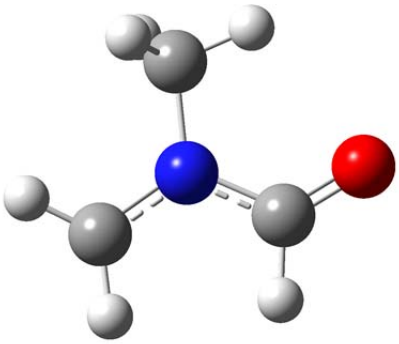
| | | | |
|---|---|---|---|
| C | 1.304838 | -0.733909 | 0.045773 |
| O | 2.306255 | -0.469822 | -0.600227 |
| N | 0.322528 | 0.152081 | 0.378366 |
| H | 1.101214 | -1.739677 | 0.445218 |
| C | 0.377502 | 1.521733 | -0.095900 |
| H | -0.442403 | 1.708810 | -0.790045 |
| H | 0.294514 | 2.208984 | 0.746182 |
| H | 1.329189 | 1.667209 | -0.598307 |
| C | -0.864481 | -0.275915 | 1.035623 |
| H | -1.770071 | -0.246833 | 0.301917 |
| H | -0.770002 | -1.295439 | 1.400581 |
| H | -1.153212 | 0.400468 | 1.840344 |
| O | -2.735028 | -0.263142 | -0.732329 |
| H | -2.323894 | -0.975836 | -1.246979 |

Post2



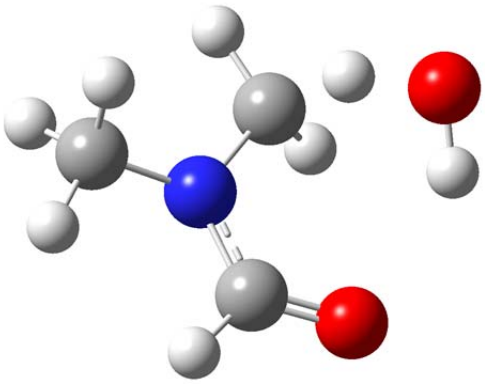
| | | | |
|---|---|---|---|
| C | -1.431407 | 0.246103 | -0.576968 |
| O | -2.180147 | -0.709678 | -0.639130 |
| N | -0.382335 | 0.371427 | 0.306340 |
| H | -1.520171 | 1.128007 | -1.228279 |
| C | -0.097969 | -0.707186 | 1.244078 |
| H | 0.854141 | -1.171018 | 0.993521 |
| H | -0.060306 | -0.303874 | 2.254531 |
| H | -0.898872 | -1.435403 | 1.164802 |
| C | 0.442872 | 1.473465 | 0.260026 |
| H | 2.180420 | 0.218825 | -0.640454 |
| H | 0.147283 | 2.289958 | -0.378054 |
| H | 1.099419 | 1.634333 | 1.098475 |
| O | 2.703934 | -0.589854 | -0.559798 |
| H | 3.203156 | -0.638848 | -1.380308 |

cis-CH2NCH3CHO



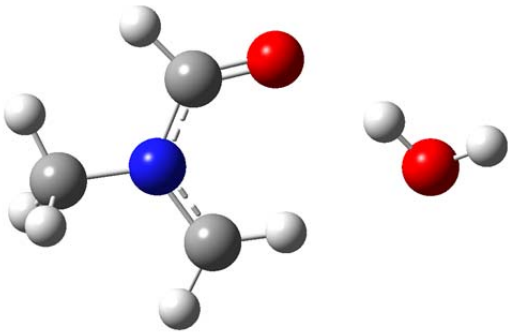
| | | | |
|---|---|---|---|
| C | 0.850265 | -0.622724 | 0.004658 |
| O | 1.890402 | 0.010963 | -0.000903 |
| N | -0.408197 | -0.072168 | 0.008120 |
| H | 0.812263 | -1.721512 | 0.010174 |
| C | -0.555862 | 1.373690 | -0.002813 |
| H | 0.434240 | 1.812433 | 0.070938 |
| H | -1.032259 | 1.692253 | -0.928848 |
| H | -1.165137 | 1.685886 | 0.843819 |
| C | -1.531750 | -0.869931 | -0.029230 |
| H | -1.401967 | -1.936484 | 0.014327 |
| H | -2.488895 | -0.401308 | 0.104282 |

ts1/trans



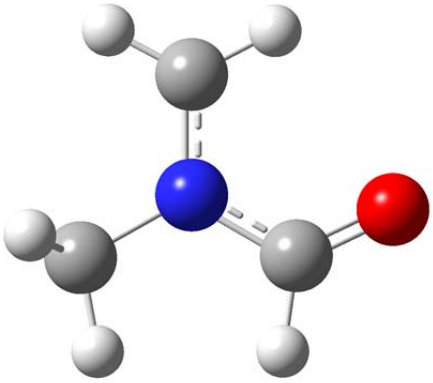
| | | | |
|---|---|---|---|
| C | -0.292701 | 1.214094 | -0.090336 |
| O | 0.825697 | 1.598469 | 0.238326 |
| N | -0.778481 | -0.020409 | 0.187945 |
| H | -1.004882 | 1.847294 | -0.636615 |
| C | -1.986512 | -0.516022 | -0.442043 |
| H | -1.748762 | -1.268053 | -1.195794 |
| H | -2.648604 | -0.954250 | 0.303366 |
| H | -2.501341 | 0.311852 | -0.924556 |
| C | 0.090097 | -0.939904 | 0.856012 |
| H | 1.006858 | -1.199855 | 0.146247 |
| H | 0.535366 | -0.498550 | 1.742806 |
| H | -0.421046 | -1.874487 | 1.067304 |
| O | 2.069220 | -0.943926 | -0.640144 |
| H | 2.092618 | 0.013199 | -0.450142 |

Post1



| | | | |
|---|---|---|---|
| C | 0.420123 | 1.084375 | -0.002868 |
| O | -0.790921 | 1.264909 | -0.038754 |
| N | 1.031016 | -0.139311 | -0.010105 |
| H | 1.139515 | 1.911393 | 0.038272 |
| C | 2.481854 | -0.224961 | 0.041612 |
| H | 2.791923 | -0.773291 | 0.929834 |
| H | 2.857669 | -0.733832 | -0.844708 |
| H | 2.899987 | 0.777387 | 0.079609 |
| C | 0.303438 | -1.303421 | -0.065479 |
| H | -3.7373 | -0.216063 | -0.396221 |
| H | -0.769475 | -1.249299 | -0.10186 |
| H | 0.852565 | -2.226847 | -0.057774 |
| O | -2.977783 | -0.521746 | 0.105883 |
| H | -2.334854 | 0.204463 | 0.04696 |

trans-CH2NCH3CHO



| | | | |
|---|---|---|---|
| C | -0.828025 | -0.633315 | 0.000002 |
| O | -1.926711 | -0.107627 | -0.000001 |
| N | 0.363165 | 0.057607 | 0.000005 |
| H | -0.673529 | -1.721422 | 0.000001 |
| C | 1.627369 | -0.655138 | -0.000002 |
| H | 1.433418 | -1.724838 | -0.000004 |
| H | 2.204728 | -0.400412 | -0.888019 |
| H | 2.204737 | -0.400417 | 0.888011 |
| C | 0.363758 | 1.429021 | -0.000005 |
| H | -0.587617 | 1.926616 | -0.000007 |
| H | 1.311186 | 1.934835 | 0.000024 |

**Table S8**. Dipole moments from MP2/aug-cc-pVTZ calculations and rate coefficients from long range transition state theory for the formation of the pre-reaction complexes

| | $\mu_{Amide}$/D | $\mu_{OH}$/D | C[a]/$10^{-10}$cm$^3$s$^{-1}$ |
|---|---|---|---|
| MF+OH | 4.30 | 1.76 | 7.59 |
| DMF+OH | 4.41 | 1.76 | 7.55 |

[a] Constant C of the rate coefficient expressed in the form $k(T) = C \times (T/298\ \mathrm{K})^{-1/6}$

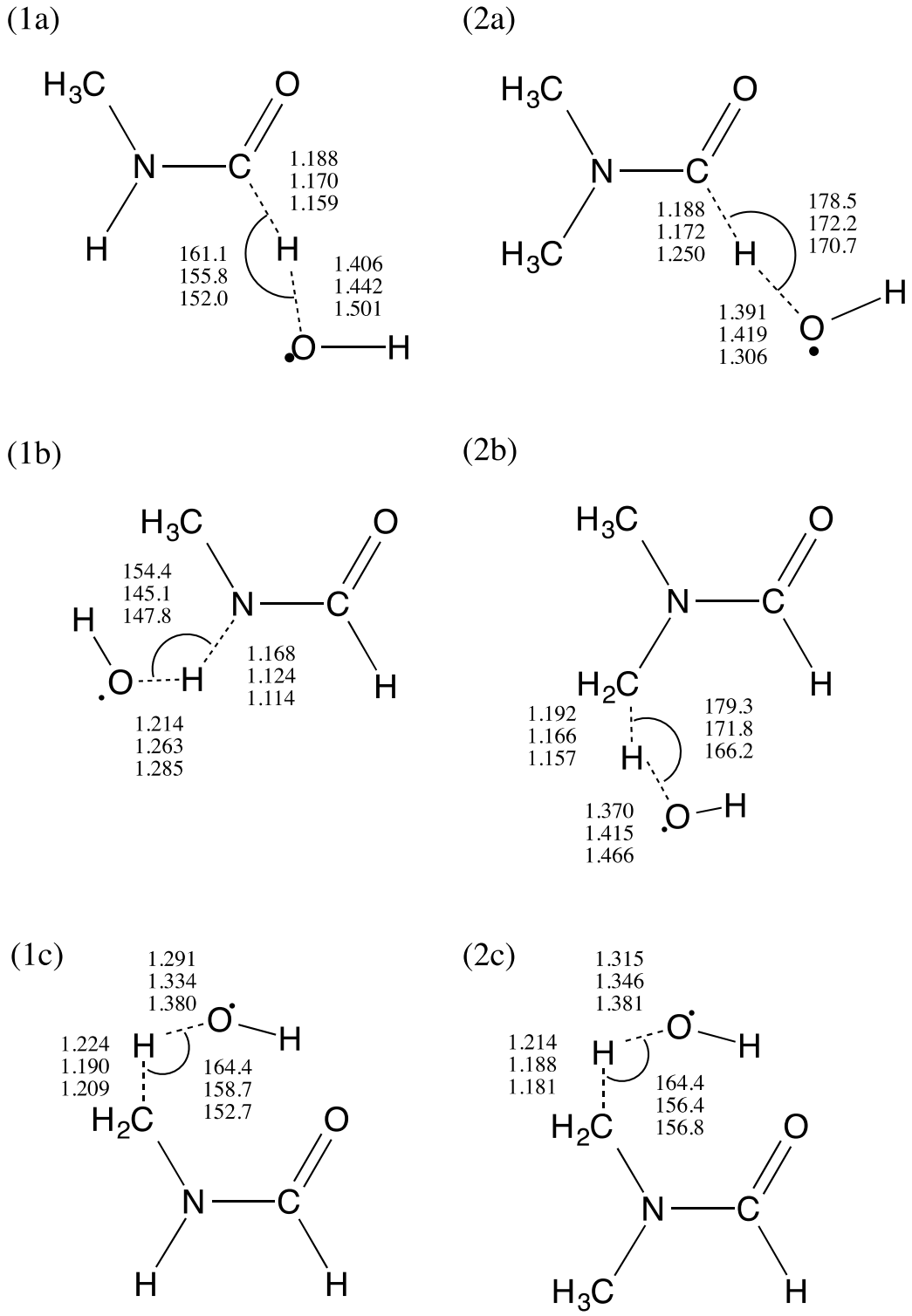



**Figure S1**. Comparison of selected geometry parameters for the transition states of the OH radicals with MF and DMF (top BHandHLYP/aug-cc-pVTZ, middle MP2/aug-cc-pVTZ, bottom CASPT2(3,3)/cc-pVTZ). Bond lenghts in Angstrom, angles in degrees.

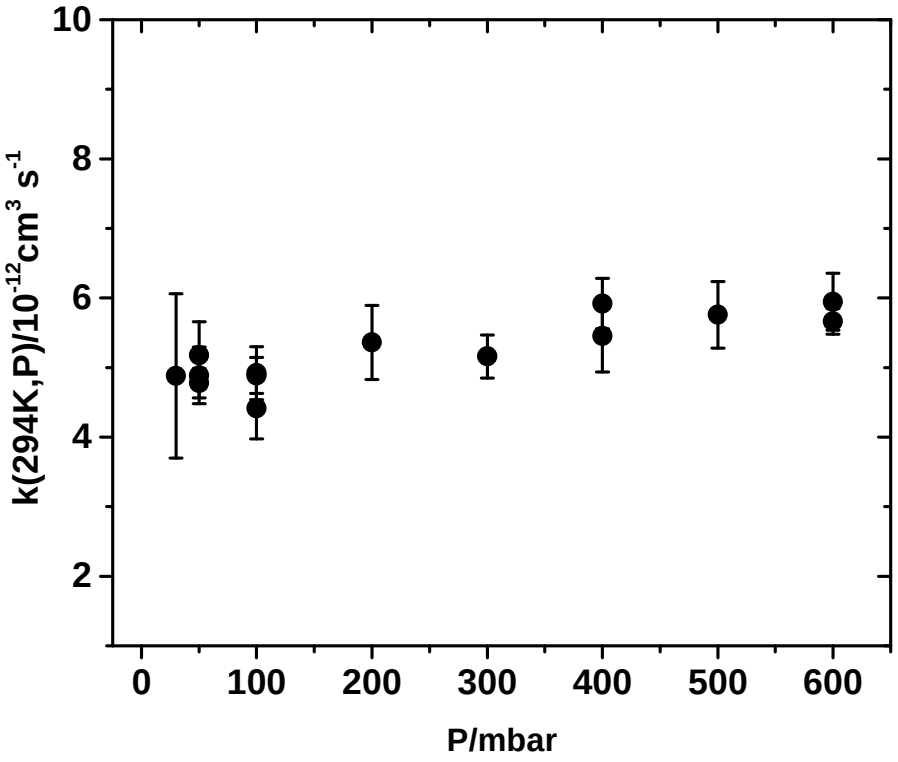



**Figure S2**. Experimentally determined rate coefficients for MF + OH at $T = 294$ K and various pressures. Error bars on the individual data points denote two standard deviations and do not include possible systematic errors.

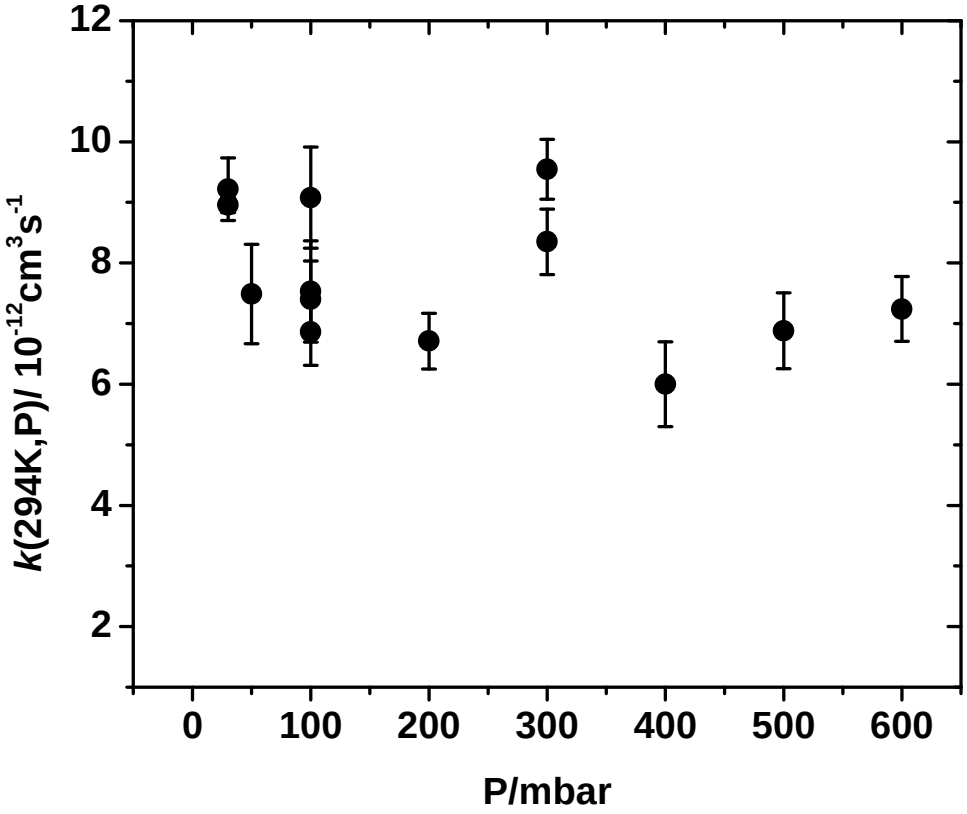



**Figure S3**. Experimentally determined rate coefficients for DMF + OH at $T = 294$ K and various pressures. Error bars on the individual data points denote two standard deviations and do not include possible systematic errors.

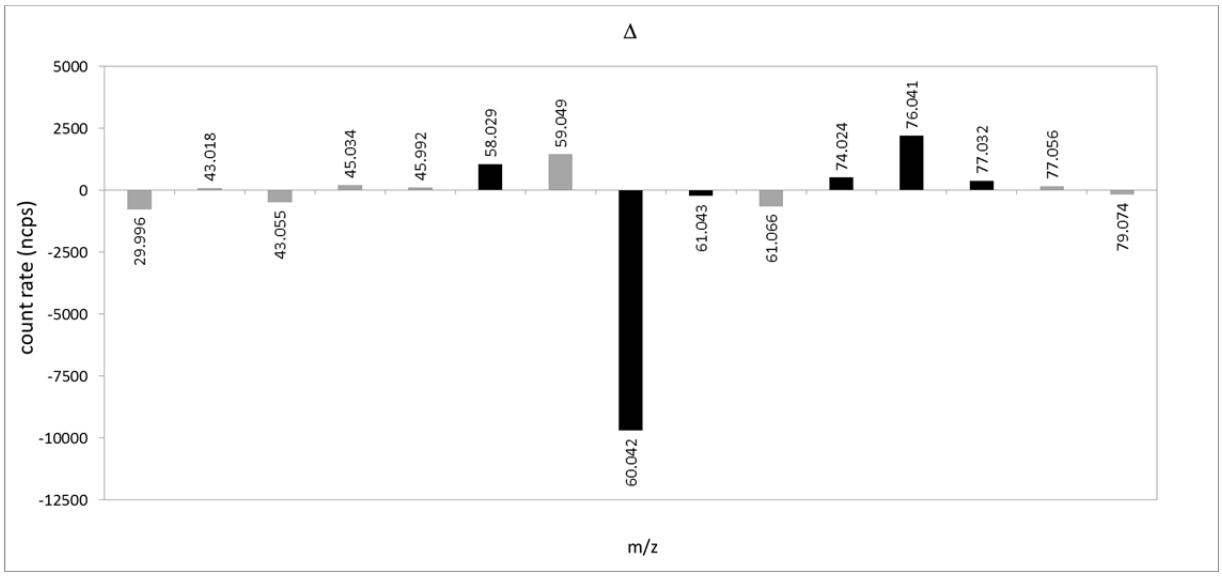



**Figure S4**. PTR-ToF-MS signal change as observed during 15 minutes of photo-oxidation of *N*-methylformamide. The bars shaded in grey indicate signals associated with isopropyl nitrite, isopropyl nitrite photo-oxidation products and compounds commonly produced in smog chambers as artefacts. The black bars indicate signals associated with the reagent amides and their photo-oxidation products.

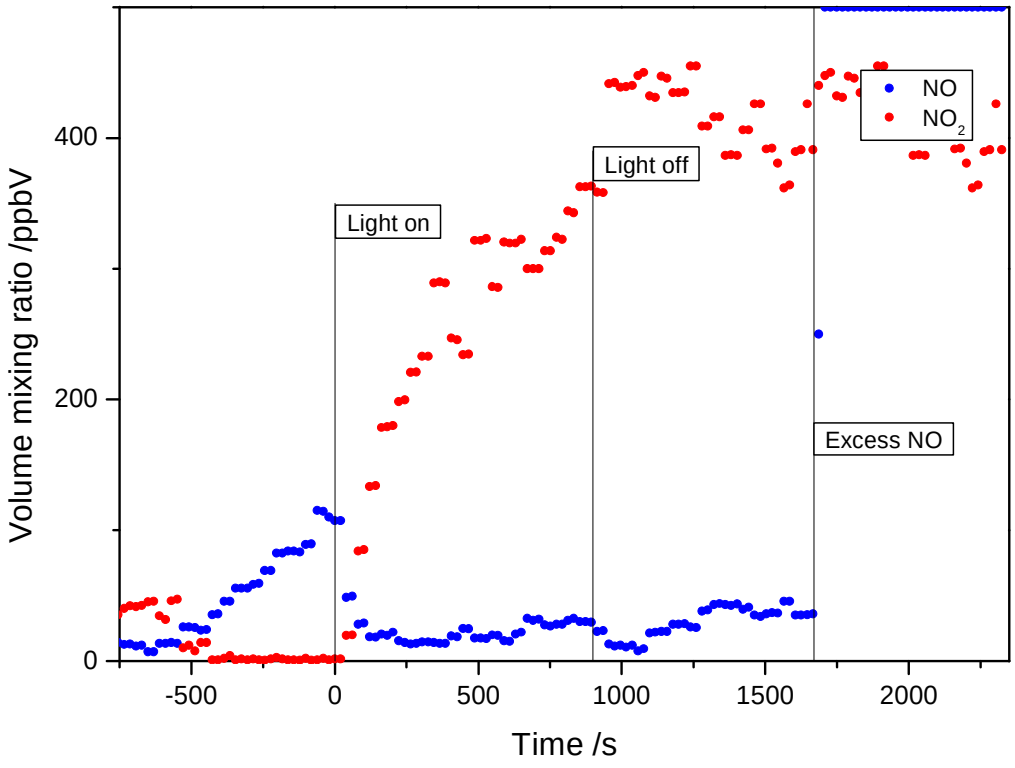



**Figure S5**. NO and $NO_2$ volume mixing ratios during the *N*-methylformamide photo-oxidation experiment documented in Figure 7 in the main text and in Figure S4.

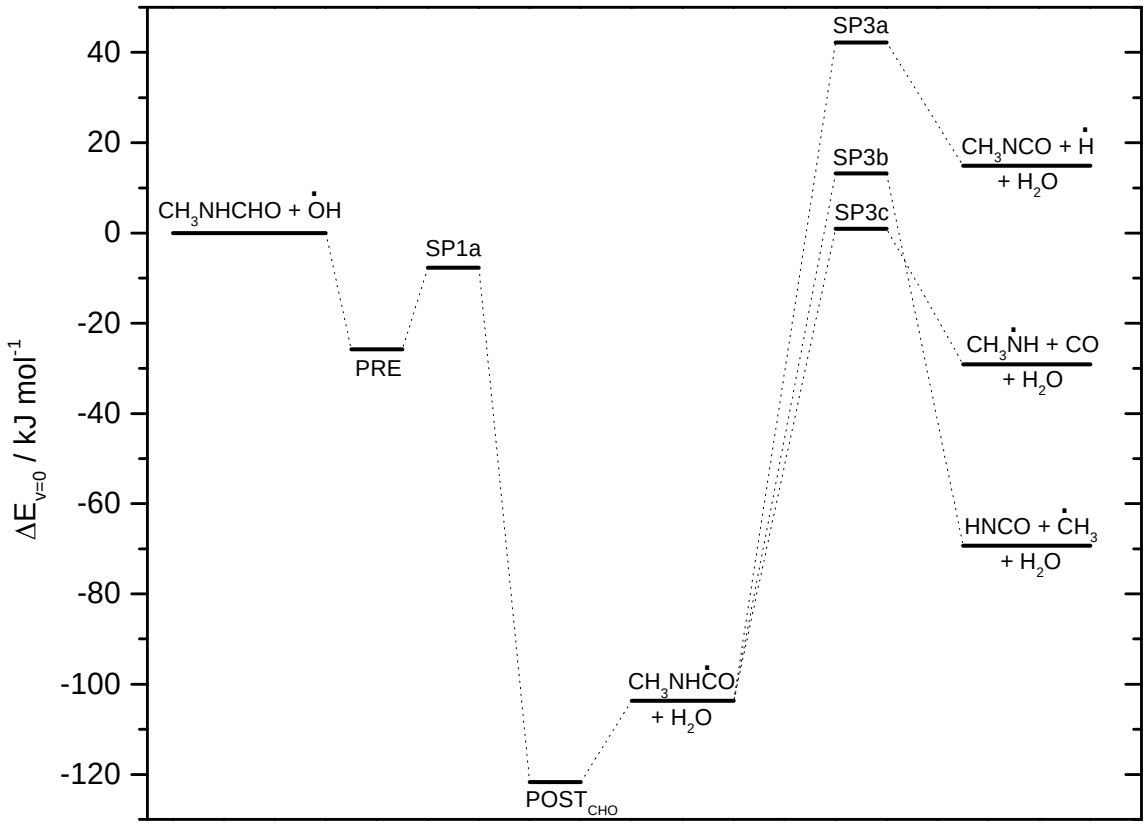


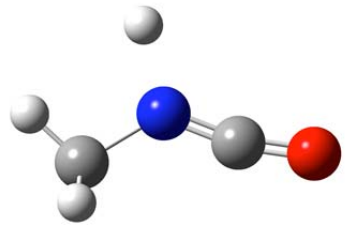
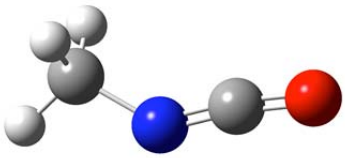
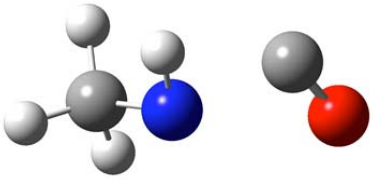
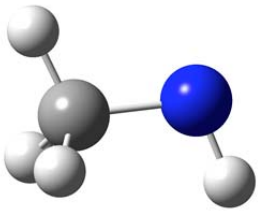
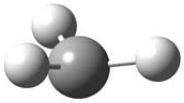
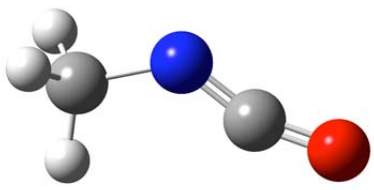

**Figure S6**. Relative energies of stationary points on the potential energy surface related to $CH_3NH\dot{C}O$ radical formation and dissociation.

**Table S9**. Electronic energies of reactants, intermediates and products (/Hartree), and relative energies including Zero Point Energies, Δ (/kJ $mol^{-1}$), of stationary points on the potential energy surface of the $CH_3NH\dot{C}O$ radical dissociation reactions.

| | MP2/aTZ[a] | | CCSD(T*)-F12a/aTZ //MP2/aTZ | |
|---|---|---|---|---|
| Species | $E_{Elec}$ | $E_{ZPE}$ | $E_{Elec}$ | $\Delta E_{v=0}$ |
| cis-MF | -208.836902 | 0.074654 | -208.967826 | |
| OH | -75.626337 | 0.008646 | -75.670689 | |
| Sum Reactants | -284.463240 | 0.083299 | -284.638515 | 0 |
| SP3a | -208.115307 | 0.054048 | -208.243583 | 42.2 |
| $CH_3NCO$ | -207.633560 | 0.051118 | -207.751257 | |
| H | -0.499821 | 0 | -0.499821 | |
| $H_2O$ | -76.328992 | 0.021395 | -76.370991 | |
| Sum Products | -284.462373 | 0.072513 | -284.622069 | 14.9 |
| SP3b | -208.121257 | 0.056574 | -208.257157 | 13.2 |
| $CH_3NH$ | -94.994213 | 0.049747 | -95.070097 | |
| CO | -113.142411 | 0.004806 | -113.201152 | |
| $H_2O$ | -76.328992 | 0.021395 | -76.370991 | |
| Sum Products | -284.465616 | 0.075948 | -284.642240 | -29.1 |
| SP3c | -208.125550 | 0.057882 | -208.263141 | 0.9 |
| HNCO | -168.420274 | 0.021216 | -168.506202 | |
| $CH_3$ | -39.738318 | 0.030227 | -39.777259 | |
| $H_2O$ | -76.328992 | 0.021395 | -76.370991 | |
| Sum Products | -284.487584 | 0.072838 | -284.654452 | -69.3 |

[a] aTZ, aug-cc-pVTZ; T* denotes scaled triples as recommended in the Molpro manual.

**Table S10**. Cartesian coordinates of stationary points on the potential energy surface of the $CH_3NH\dot{C}O$ radical dissociation reactions. Results from MP2/aug-cc-pVTZ calculations.[a]

| | Atom | X | Y | Z |
|---|---|---|---|---|
| SP3a | C | -1.663740 | -0.314323 | -0.000017 |
|  | N | -0.411599 | 0.437248 | -0.000074 |
| | C | 0.731286 | -0.013118 | 0.000028 |
| | O | 1.892327 | -0.180744 | 0.000091 |
| | H | -2.462067 | 0.425211 | -0.000138 |
| | H | -1.741196 | -0.932859 | 0.890133 |
| | H | -1.741138 | -0.933089 | -0.890012 |
| | H | -0.718297 | 1.790597 | -0.000266 |
| $CH_3NCO$ | C | -1.728735 | 0.181809 | 0.000000 |
|  | H | -2.475215 | -0.605961 | -0.000367 |
| | H | -1.866227 | 0.796658 | -0.887301 |
| | H | -1.866481 | 0.796063 | 0.887674 |
| | N | -0.420722 | -0.425283 | -0.000004 |
| | C | 0.730535 | -0.057894 | 0.000006 |
| | O | 1.892772 | 0.155841 | -0.000002 |
| SP3b | C | -1.039040 | 0.305508 | 0.416461 |
|  | N | 0.720637 | 0.675755 | -0.308444 |
| | O | -1.768398 | -0.345793 | -0.186820 |
| | C | 1.520825 | -0.482777 | 0.068376 |
| | H | 0.965911 | 1.442695 | 0.318169 |
| | H | 2.545491 | -0.299899 | -0.265763 |
| | H | 1.551326 | -0.678748 | 1.141499 |
| | H | 1.149283 | -1.364378 | -0.449255 |
| | C | -0.630447 | -0.013434 | 0.000013 |
|  | H | -1.122547 | 0.955140 | 0.000451 |
| | H | -0.959734 | -0.578551 | 0.878125 |
| | H | -0.959790 | -0.579446 | 0.877540 |
| | N | 0.802546 | 0.152663 | 0.000009 |
| $CH_3NH$ | H | 1.206931 | -0.785184 | 0.000009 |
| CO | C | 0.000000 | 0.000000 | -0.650833 |
| | O | 0.000000 | 0.000000 | 0.488125 |
| SP3c | C | -1.239658 | 1.421573 | 0.000011 |
|  | C | -1.112655 | -1.295454 | 0.000021 |
| | N | -0.185944 | -0.174053 | -0.000069 |
| | C | 1.044651 | -0.196203 | -0.000016 |
| | O | 2.165102 | 0.185232 | 0.000025 |
|  | H | -0.479311 | 2.189669 | 0.000684 |
| | H | -1.810269 | 1.335739 | 0.914741 |
| | H | -1.809340 | 1.336414 | -0.915359 |
| | H | -0.585490 | -2.244684 | -0.000620 |
| | H | -1.744864 | -1.229712 | -0.883769 |
| | H | -1.743960 | -1.230402 | 0.884511 |

| | | | | |
|---|---|---|---|---|
| HNCO | N | 0.535763 | -1.044610 | 0.000000 |
| | H | 1.532032 | -1.180258 | 0.000000 |
| | C | 0.000000 | 0.052452 | 0.000000 |
| | O | -0.660296 | 1.022227 | 0.000000 |
| $CH_3$ | C | 0.000000 | 0.000000 | 0.000000 |
| | H | 0.000000 | 1.075068 | 0.000000 |
| | H | 0.931036 | -0.537534 | 0.000000 |
| | H | -0.931036 | -0.537534 | 0.000000 |

[a] Structures for cis-MF, OH and $H_2O$ are included in Table S6.

**Table S11**. Electronic energies of reactants, intermediates and products (/Hartree), and relative energies including Zero Point Energies, Δ (/kJ $mol^{-1}$), of stationary points on the potential energy surface of the $CH_3NH\dot{C}O + O_2$ reaction.

| | MP2/aTZ[a] | | CCSD(T*)-F12a/aTZ //MP2/aTZ | |
|---|---|---|---|---|
| Species | $E_{Elec}$ | $E_{ZPE}$ | $E_{Elec}$ | $\Delta E_{v=0}$ |
| $CH_3NH\dot{C}O$ | -208.179119 | 0.062363 | -208.307492 | |
| $O_2$ | -150.120938 | 0.003314 | -150.191209 | |
| Sum Reactants | -358.300057 | 0.065677 | -358.498701 | 0 |
| $CH_3NHC(O)O\dot{O}$ | -358.353696 | 0.070993 | -358.563100 | -155.1 |
| SP4 | -358.326026 | 0.066262 | -358.526304 | -70.9 |
| $CH_3NCO*HO_2$ | -358.336953 | 0.067775 | -358.540485 | -104.2 |
| $CH_3NCO$ | -207.633560 | 0.051118 | -207.751257 | |
| $HO_2$ | -150.692618 | 0.014430 | -150.779057 | |
| Sum Products | -358.326178 | 0.065548 | -358.530314 | -83.3 |

[a] aTZ, aug-cc-pVTZ; T* denotes scaled triples as recommended in the Molpro manual.

**Table S12**. Cartesian coordinates of stationary points on the potential energy surface of the $CH_3NH\dot{C}O + O_2$ reaction. Results from MP2/aug-cc-pVTZ calculations.[a]

| | Atom | X | Y | Z |
|---|---|---|---|---|
| $O_2$ ( $X^3\Sigma_g^-$) | O | 0.000000 | 0.000000 | 0.612212 |
| | O | 0.000000 | 0.000000 | -0.612212 |
| $CH_3NHC(O)O\dot{O}$ | C | 2.106940 | -0.579384 | -0.000017 |
| | N | 0.656986 | -0.606622 | 0.000038 |
| | C | -0.055015 | 0.518287 | 0.000004 |
| | O | 0.277311 | 1.670721 | -0.000006 |
| | H | 2.497277 | -1.072370 | 0.887627 |
| | H | 2.422913 | 0.459565 | 0.000951 |
| | H | 2.497263 | -1.070690 | -0.888605 |
| | H | 0.137356 | -1.469855 | -0.000027 |
| | O | -1.500508 | 0.278115 | 0.000004 |
| | O | -1.834960 | -0.978051 | -0.000016 |
| SP4 | C | -2.063835 | -0.803488 | -0.000055 |
| | N | -0.648369 | -0.442134 | 0.000134 |
| | C | -0.253903 | 0.747103 | 0.000022 |
| | O | -0.213707 | 1.921234 | -0.000017 |
| | H | -2.282122 | -1.395500 | -0.885527 |
| | H | -2.693937 | 0.083916 | 0.000645 |
| | H | -2.281969 | -1.396772 | 0.884597 |
| | H | 0.520551 | -1.193049 | 0.000037 |
| | O | 1.724502 | 0.136183 | -0.000027 |
| | O | 1.637016 | -1.140585 | -0.000018 |
| $CH_3NCO*HO_2$ | C | -1.907009 | -1.300584 | -0.000005 |
| | N | -0.782223 | -0.369292 | 0.000009 |
| | C | -0.802623 | 0.855029 | 0.000002 |
| | O | -0.719944 | 2.023458 | 0.000000 |
| | H | -1.509826 | -2.310233 | 0.000134 |
| | H | -2.518222 | -1.162134 | -0.888919 |
| | H | -2.518398 | -1.161958 | 0.888760 |
| | H | 0.937429 | -0.972594 | 0.000008 |
| | O | 2.210732 | 0.306433 | -0.000006 |
| | O | 1.927008 | -0.971730 | 0.000004 |
| $CH_3NCO$ | C | -1.728735 | 0.181809 | 0.000000 |
| | H | -2.475215 | -0.605961 | -0.000367 |
| | H | -1.866227 | 0.796658 | -0.887301 |
| | H | -1.866481 | 0.796063 | 0.887674 |
| | N | -0.420722 | -0.425283 | -0.000004 |
| | C | 0.730535 | -0.057894 | 0.000006 |
| | O | 1.892772 | 0.155841 | -0.000002 |
| $HO_2$ | O | 0.055406 | 0.709672 | 0.000000 |
| | O | 0.055406 | -0.603317 | 0.000000 |
| | H | -0.886498 | -0.850838 | 0.000000 |

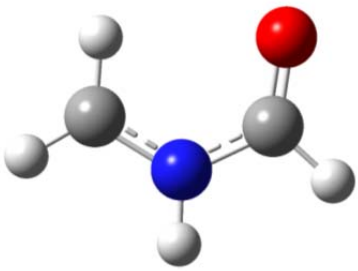
[a] Structure of $CH_3NH\dot{C}O$ is included in Table S6.

**Table S13**. Electronic energies of reactants, intermediates and products (/Hartree), and relative energies including Zero Point Energies, Δ (/kJ mol$^{-1}$), of stationary points on the potential energy surface of the $\dot{C}H_2NHCHO + O_2$ reaction. See Figure 9 in the main text.

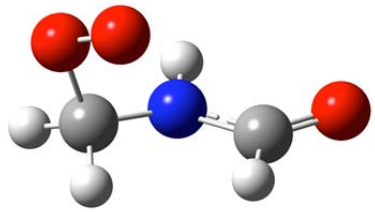
| | MP2/aTZ[a] | | CCSD(T*)-F12a/aTZ //MP2/aTZ | |
|---|---|---|---|---|
| Species | $E_{Elec}$ | $E_{ZPE}$ | $E_{Elec}$ | $\Delta E_{v=0}$ |
| $\dot{C}H_2NHCHO$ | -208.176370 | 0.060620 | -208.306373 | |
| $O_2$ | -150.120938 | 0.003314 | -150.191209 | |
| Sum Reactants | -358.297308 | 0.063934 | -358.497582 | 0 |
| $\dot{O}OCH_2NHCHO$ | -358.340350 | 0.071706 | -358.549313 | -115.1 |
| SP13a | -358.294848 | 0.066005 | -358.499879 | -0.6 |
| $CH_2$=NCHO*$HO_2$ | -358.304574 | 0.067444 | -358.514230 | -34.5 |
| $CH_2$=NCHO | -207.595846 | 0.049914 | -207.719980 | |
| $HO_2$ | -150.692618 | 0.014430 | -150.779057 | |
| Sum Products | -358.288464 | 0.064344 | -358.499038 | -2.7 |
| SP13b | -358.294243 | 0.066902 | -358.507547 | -18.4 |
| $HOOCH_2NH\dot{C}O$ | -358.338735 | 0.070622 | -358.538798 | -90.6 |
| SP15 | -358.278810 | 0.065473 | -358.486938 | 32.0 |
| HNCO*$HOO\dot{C}H_2$ | -358.323809 | 0.064584 | -358.521643 | -61.5 |

[a] aTZ, aug-cc-pVTZ; T* denotes scaled triples as recommended in the Molpro manual.

**Table S14**. Cartesian coordinates of stationary points on the potential energy surface of the $\dot{C}H_2NHCHO + O_2$ reaction. Results from MP2/aug-cc-pVTZ calculations.

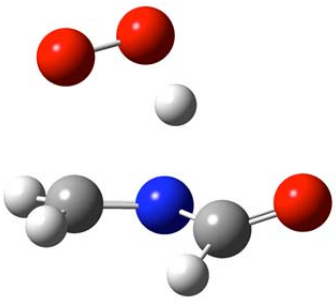
| | Atom | X | Y | Z |
|---|---|---|---|---|
| $\dot{C}H_2NHCHO$ | C | -0.790645 | 0.452760 | 0.000000 |
|  | H | -1.297694 | 1.427104 | 0.000000 |
| | N | 0.576063 | 0.578442 | 0.000000 |
| | H | 0.952516 | 1.512103 | 0.000000 |
| | O | -1.375301 | -0.614307 | 0.000000 |
| | C | 1.430517 | -0.499869 | 0.000000 |
| | H | 2.486673 | -0.313588 | 0.000001 |
| | H | 0.989236 | -1.477603 | 0.000001 |
| $O_2$ ($X^3\Sigma_g^-$) | O | 0.000000 | 0.000000 | 0.612212 |
| | O | 0.000000 | 0.000000 | -0.612212 |

ȮOCH$_2$NHCHO



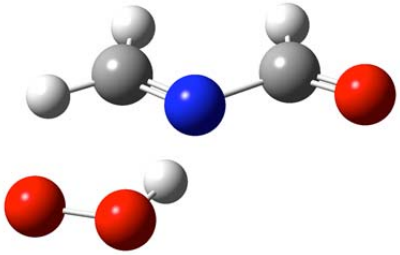
| | | | |
|---|---|---|---|
| C | 0.804211 | 0.928782 | 0.301416 |
| N | -0.493338 | 0.760595 | -0.210298 |
| C | -1.386341 | -0.141828 | 0.324143 |
| O | 1.783722 | 0.005160 | -0.300977 |
| O | 1.486797 | -1.216859 | 0.019078 |
| O | -2.436428 | -0.444119 | -0.202023 |
| H | 1.213390 | 1.906534 | 0.064281 |
| H | 0.821604 | 0.736470 | 1.370765 |
| H | -0.707554 | 1.091637 | -1.139946 |
| H | -1.054026 | -0.533980 | 1.295004 |

SP13a



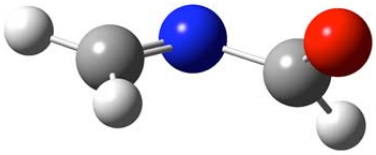
| | | | |
|---|---|---|---|
| C | 0.497921 | 1.338349 | -0.056984 |
| N | -0.384417 | 0.548769 | -0.614131 |
| C | -1.484494 | 0.221807 | 0.217499 |
| O | 1.829276 | -0.204088 | 0.477864 |
| O | 1.319049 | -1.132579 | -0.226303 |
| O | -2.115205 | -0.799667 | 0.096040 |
| H | 1.289082 | 1.754042 | -0.665288 |
| H | 0.339094 | 1.775183 | 0.927853 |
| H | 0.448511 | -0.633515 | -0.677015 |
| H | -1.731288 | 0.992643 | 0.969468 |

$CH_2$=NCHO*$HO_2$



| | | | |
|---|---|---|---|
| C | -0.247814 | 1.603742 | 0.000002 |
| N | -0.474031 | 0.343324 | 0.000003 |
| C | -1.862528 | -0.005402 | -0.000002 |
| O | 2.560851 | 0.114292 | -0.000003 |
| O | 1.909316 | -1.018309 | 0.000002 |
| O | -2.238190 | -1.146500 | 0.000000 |
| H | 0.779292 | 1.945195 | 0.000005 |
| H | -1.059067 | 2.336129 | -0.000002 |
| H | 0.954620 | -0.731521 | 0.000006 |
| H | -2.550390 | 0.861028 | -0.000008 |

$CH_2$=NCHO

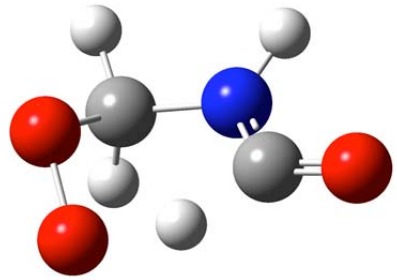


| | | | |
|---|---|---|---|
| C | 1.440342 | -0.358129 | 0.092563 |
| N | 0.630663 | 0.571233 | -0.236098 |
| C | -0.711397 | 0.421098 | 0.165073 |
| O | -1.414432 | -0.519102 | -0.135183 |
| H | 2.471208 | -0.296416 | -0.236691 |
| H | 1.136382 | -1.214413 | 0.695530 |
| H | -1.080445 | 1.287198 | 0.729496 |

$HO_2$

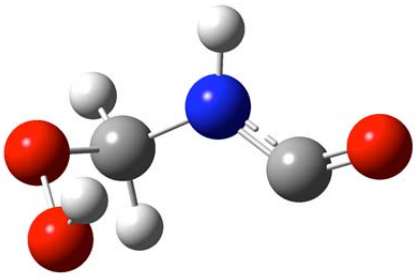
| | | | |
|---|---|---|---|
| O | 0.055406 | 0.709672 | 0.000000 |
| O | 0.055406 | -0.603317 | 0.000000 |
| H | -0.886498 | -0.850838 | 0.000000 |

SP13b



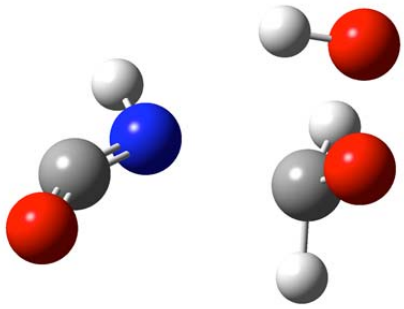
| | | | |
|---|---|---|---|
| C | 1.030964 | 0.931044 | 0.191512 |
| N | -0.415448 | 0.978619 | 0.076126 |
| C | -1.126894 | -0.176012 | 0.052411 |
| O | 1.499384 | -0.212030 | -0.492341 |
| O | 1.032105 | -1.283030 | 0.242269 |
| O | -2.305352 | -0.353606 | -0.102476 |
| H | 1.461508 | 1.796790 | -0.305038 |
| H | 1.342831 | 0.869005 | 1.233259 |
| H | -0.864333 | 1.809064 | -0.281395 |
| H | -0.265380 | -1.066052 | 0.177136 |

$HOOCH_2NH\dot{C}O$



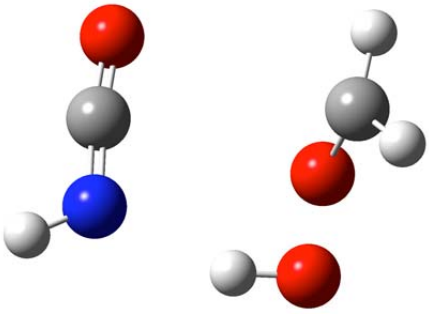
| | | | |
|---|---|---|---|
| C | -0.717929 | -0.929871 | 0.325088 |
| N | 0.570058 | -0.686658 | -0.251379 |
| C | 1.480008 | 0.127323 | 0.326456 |
| O | -1.759735 | -0.198609 | -0.290833 |
| O | -1.593032 | 1.176430 | 0.138057 |
| O | 2.546858 | 0.490042 | -0.079333 |
| H | -1.017400 | -1.964634 | 0.165161 |
| H | -0.666864 | -0.693772 | 1.385725 |
| H | 0.762306 | -1.024500 | -1.187398 |
| H | -1.193656 | 1.561904 | -0.656225 |

SP15



| | | | |
|---|---|---|---|
| C | -1.710262 | 0.038477 | 0.254212 |
| O | -2.369741 | -0.645736 | -0.444860 |
| N | -0.698767 | 0.693423 | 0.602702 |
| C | 0.967364 | 1.000023 | -0.376172 |
| O | 1.416556 | -0.243600 | -0.700958 |
| O | 1.818973 | -0.885805 | 0.534084 |
| H | -0.733667 | 1.221733 | 1.460344 |
| H | 1.562026 | 1.542734 | 0.351469 |
| H | 0.646221 | 1.510596 | -1.274512 |
| H | 0.947881 | -1.158902 | 0.869413 |

$HNCO*HOOCH_2$



| | | | |
|---|---|---|---|
| C | -1.658852 | -0.002904 | 0.037148 |
| O | -1.870163 | 1.111851 | -0.237769 |
| N | -1.303749 | -1.152834 | 0.287896 |
| C | 1.551402 | 1.040006 | 0.557343 |
| O | 1.246180 | 0.277525 | -0.529728 |
| O | 1.543420 | -1.101130 | -0.203635 |
| H | -1.967231 | -1.829474 | 0.632976 |
| H | 2.338303 | 0.677920 | 1.199726 |
| H | 1.407466 | 2.086610 | 0.339488 |
| H | 0.636913 | -1.393802 | 0.014648 |

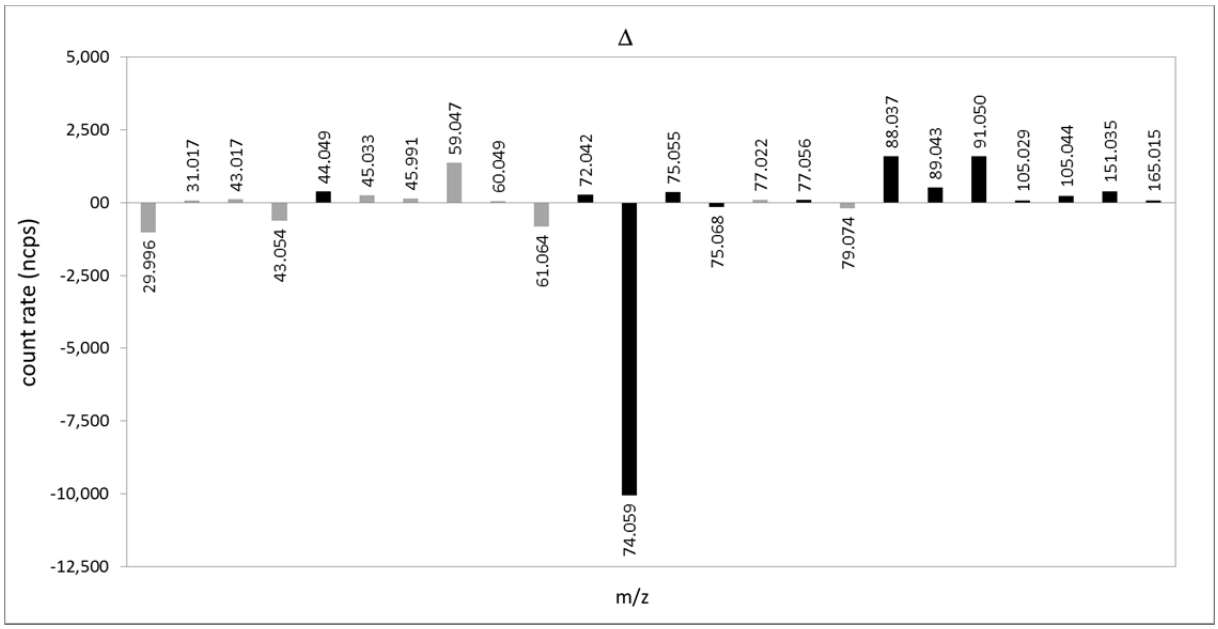



**Figure S7**. PTR-ToF-MS signal change as observed during 15 minutes of photo-oxidation of *N*,*N*-dimethylformamide. The bars shaded in grey indicate signals associated with isopropyl nitrite, isopropyl nitrite photo-oxidation products and compounds commonly produced in smog chambers as artefacts. The black bars indicate signals associated with the reagent amides and their photo-oxidation products.

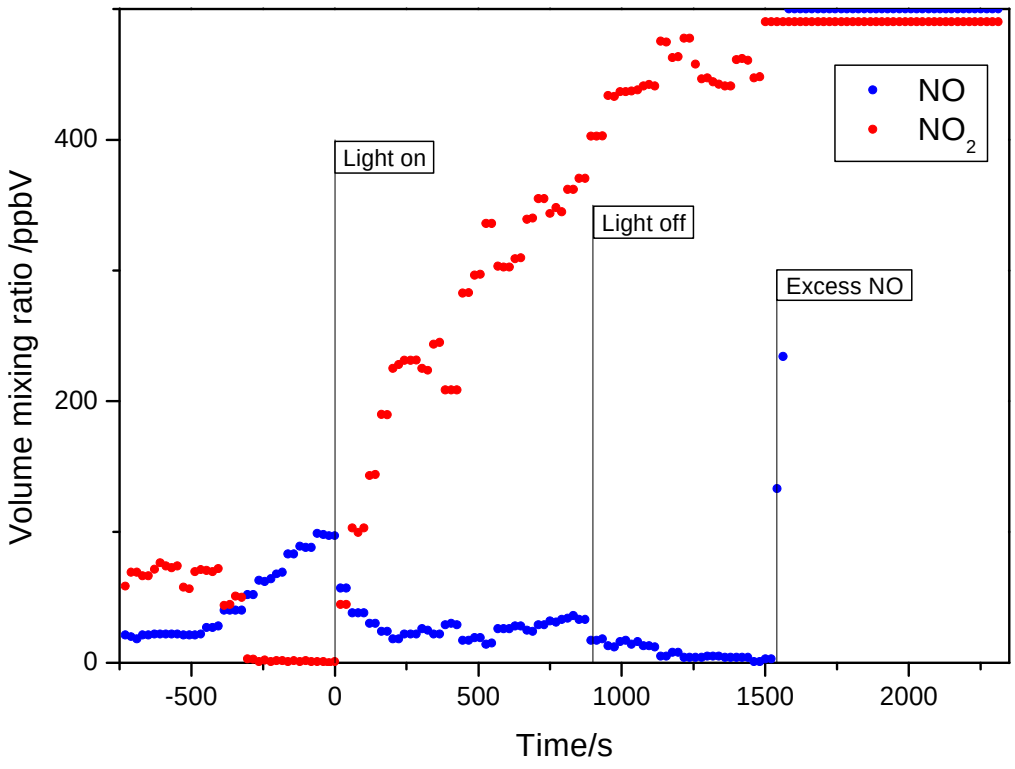



**Figure S8**. NO and $NO_2$ volume mixing ratios during the *N*,*N*-dimethylformamide photo-oxidation experiment documented in Figure 9 in the main text and in Figure S7.

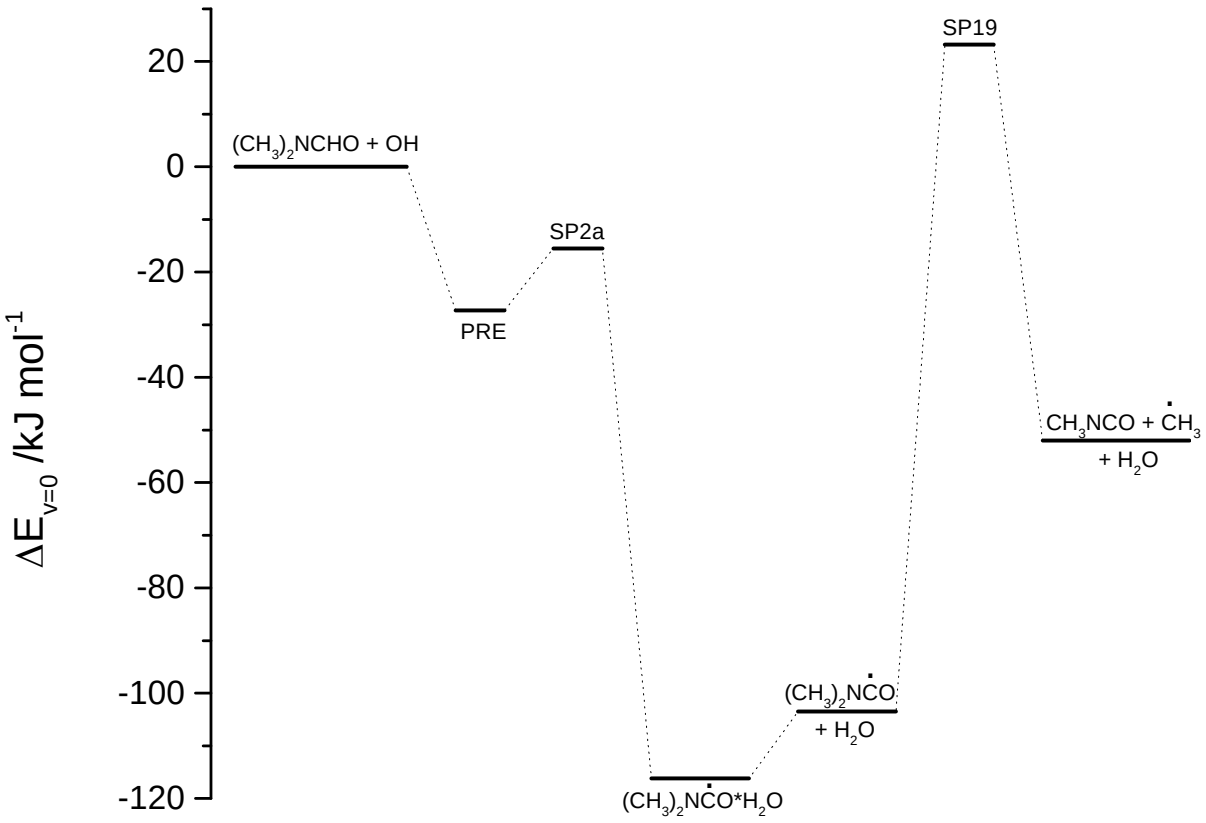



**Figure S9**. Relative energies of stationary points on the potential energy surface related to $(CH_3)2NH\dot{C}O$ radical formation and dissociation.

**Table S15**. Electronic energies of reactants, intermediates and products (/Hartree), and relative energies including Zero Point Energies, Δ (/kJ $mol^{-1}$), of stationary points on the potential energy surface of the $(CH_3)_2N\dot{C}(O)$ radical dissociation.

| | MP2/aTZ[a] | | CCSD(T*)-F12a/aTZ //MP2/aTZ | |
|---|---|---|---|---|
| Species | $E_{Elec}$ | $E_{ZPE}$ | $E_{Elec}$ | $\Delta E_{v=0}$ |
| $(CH_3)_2N\dot{C}O$ | -247.394946 | 0.090810 | -247.556894 | 0 |
| SP19 | -247.336288 | 0.085769 | -247.504294 | 23.2 |
| $CH_3NCO$ | -207.633560 | 0.051118 | -207.751257 | |
| $\dot{C}H_3$ | -39.738318 | 0.030227 | -39.777259 | |
| Sum Products | -247.371878 | 0.081344 | -247.528516 | -52.0 |

[a] aTZ, aug-cc-pVTZ; T* denotes scaled triples as recommended in the Molpro manual.

**Table S16**. Cartesian coordinates of stationary points on the potential energy surface of the $(CH_3)_2N\dot{C}(O)$ radical dissociation reaction. Results from MP2/aug-cc-pVTZ calculations.

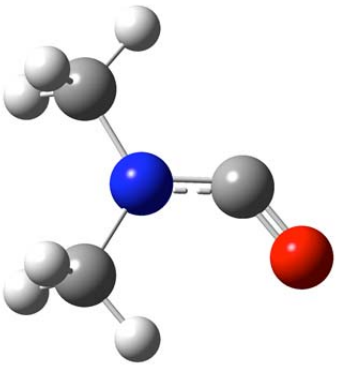
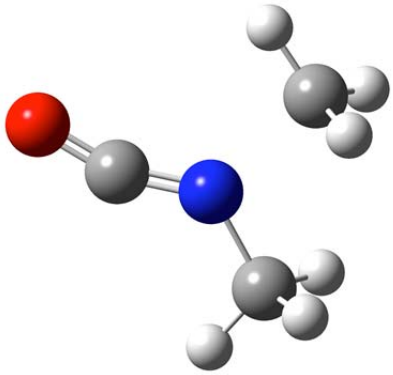
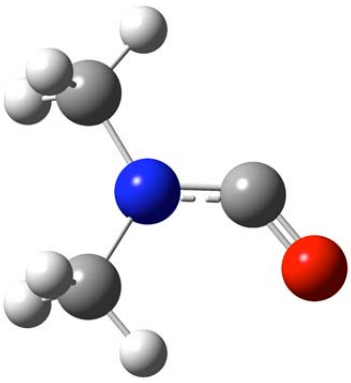
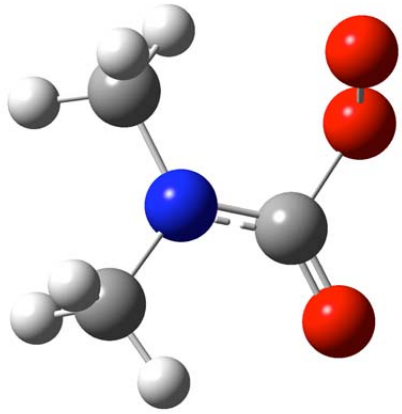
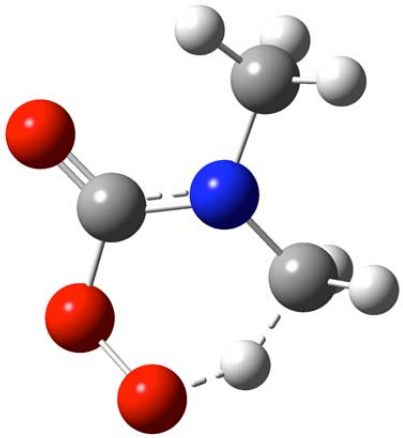
| | Atom | X | Y | Z |
|---|---|---|---|---|
| $(CH_3)_2N\dot{C}(O)$ | C | 0.850265 | -0.622724 | 0.004658 |
|  | O | 1.890402 | 0.010963 | -0.000903 |
| | N | -0.408197 | -0.072168 | 0.008120 |
| | H | 0.812263 | -1.721512 | 0.010174 |
| | C | -0.555862 | 1.373690 | -0.002813 |
| | H | 0.434240 | 1.812433 | 0.070938 |
| | H | -1.032259 | 1.692253 | -0.928848 |
| | H | -1.165137 | 1.685886 | 0.843819 |
| | C | -1.531750 | -0.869931 | -0.029230 |
| | H | -1.401967 | -1.936484 | 0.014327 |
| | H | -2.488895 | -0.401308 | 0.104282 |
| SP19 | C | -1.239658 | 1.421573 | 0.000011 |
|  | C | -1.112655 | -1.295454 | 0.000021 |
| | N | -0.185944 | -0.174053 | -0.000069 |
| | C | 1.044651 | -0.196203 | -0.000016 |
| | O | 2.165102 | 0.185232 | 0.000025 |
| | H | -0.479311 | 2.189669 | 0.000684 |
| | H | -1.810269 | 1.335739 | 0.914741 |
| | H | -1.809340 | 1.336414 | -0.915359 |
| | H | -0.585490 | -2.244684 | -0.000620 |
| | H | -1.744864 | -1.229712 | -0.883769 |
| | H | -1.743960 | -1.230402 | 0.884511 |
| $CH_3NCO$ | C | -1.735701 | 0.155747 | 0.000004 |
| | H | -2.471390 | -0.642112 | 0.000037 |
| | H | -1.881577 | 0.768246 | -0.887584 |
| | H | -1.881769 | 0.768489 | 0.887392 |
| | N | -0.419546 | -0.433485 | 0.000238 |
| | C | 0.726604 | -0.050461 | 0.000033 |
| | O | 1.885824 | 0.179075 | -0.000119 |
| $\dot{C}H_3$ | C | 0.000000 | 0.000000 | 0.000000 |
| | H | 0.000000 | 1.075068 | 0.000000 |
| | H | 0.931036 | -0.537534 | 0.000000 |
| | H | -0.931036 | -0.537534 | 0.000000 |

**Table S17**. Electronic energies of reactants, intermediates and products (/Hartree), and relative energies including Zero Point Energies, Δ (/kJ $mol^{-1}$), of stationary points on the potential energy surface of the $(CH_3)_2N\dot{C}(O) + O_2$ reaction.

| | MP2/aTZ[a] | | CCSD(T*)-F12a/aTZ //MP2/aTZ | |
|---|---|---|---|---|
| Species | $E_{Elec}$ | $E_{ZPE}$[b] | $E_{Elec}$ | $\Delta E_{v=0}$ |
| $(CH_3)_2N\dot{C}O$ | -247.394946 | 0.090124 | -247.556894 | |
| $O_2$ | -150.120938 | 0.003253 | -150.191209 | |
| Sum Reactants | -397.515884 | 0.093377 | -397.748103 | 0 |
| $(CH_3)_2NC(O)O\dot{O}$ | -397.561162 | 0.098584 | -397.802103 | -126.3 |
| SP20 | -397.520910 | 0.093167 | -397.760822 | -32.1 |
| $\dot{C}H_2(CH_3)NC(O)OOH$ | -397.556185 | 0.096665 | -397.790298 | -100.3 |
| SP21 | -397.505634 | 0.097406 | -397.745560 | 19.1 |
| $CH_2{=}NCH_3$ | -207.633560 | 0.068345 | -133.765368 | |
| $CO_2$ | -39.738318 | 0.011381 | -188.408300 | |
| OH | | 0.008584 | -75.670689 | |
| Sum Products | -247.371878 | 0.088310 | -397.844358 | -264.2 |

[a] aTZ, aug-cc-pVTZ; T* denotes scaled triples as recommended in the Molpro manual. [b] $E_{ZPE}$ from MP2/aug-cc-pVDZ calculations

**Table S18**. Cartesian coordinates of stationary points on the potential energy surface of the $(CH_3)_2N\dot{C}(O) + O_2$ reaction. Results from MP2/aug-cc-pVTZ calculations.

| | Atom | X | Y | Z |
|---|---|---|---|---|
| $(CH_3)_2N\dot{C}O$ | C | 0.850265 | -0.622724 | 0.004658 |
|  | O | 1.890402 | 0.010963 | -0.000903 |
| | N | -0.408197 | -0.072168 | 0.008120 |
| | H | 0.812263 | -1.721512 | 0.010174 |
| | C | -0.555862 | 1.373690 | -0.002813 |
| | H | 0.434240 | 1.812433 | 0.070938 |
| | H | -1.032259 | 1.692253 | -0.928848 |
| | H | -1.165137 | 1.685886 | 0.843819 |
| | C | -1.531750 | -0.869931 | -0.029230 |
| | H | -1.401967 | -1.936484 | 0.014327 |
| | H | -2.488895 | -0.401308 | 0.104282 |
| $O_2\,(X^3\Sigma_g^-)$ | O | 0.000000 | 0.000000 | 0.612212 |
| | O | 0.000000 | 0.000000 | -0.612212 |
| $(CH_3)_2NC(O)O\dot{O}$ | C | 2.074574 | 0.210027 | 0.294687 |
|  | C | 0.561450 | -1.646217 | -0.305658 |
| | N | 0.729814 | -0.225032 | -0.048256 |
| | C | -0.224189 | 0.711894 | -0.131038 |
| | O | -0.125884 | 1.911363 | -0.091480 |
| | O | -1.556860 | 0.167405 | -0.341701 |
| | O | -1.868513 | -0.704645 | 0.580980 |
| | H | 2.050957 | 1.263623 | 0.552254 |
| | H | 2.745679 | 0.058229 | -0.551255 |
| | H | 2.435759 | -0.369908 | 1.143929 |
| | H | -0.326476 | -1.830002 | -0.898746 |
| | H | 0.492269 | -2.206357 | 0.626187 |
| | H | 1.432159 | -1.987577 | -0.864911 |
| SP20 | C | -2.089567 | -0.271678 | -0.149977 |
|  | C | -0.071699 | -1.623207 | 0.280992 |
| | N | -0.636715 | -0.369920 | -0.105653 |
| | C | 0.064607 | 0.791890 | 0.028623 |
| | O | -0.382041 | 1.911798 | 0.061482 |
| | O | 1.436543 | 0.613387 | 0.208301 |
| | O | 1.915184 | -0.568205 | -0.363469 |
| | H | -2.353449 | 0.701760 | -0.551576 |
| | H | -2.520833 | -0.374327 | 0.847734 |
| | H | -2.478138 | -1.057399 | -0.794780 |
| | H | 1.139796 | -1.410035 | 0.091476 |
| | H | -0.325906 | -2.432199 | -0.398395 |
| | H | -0.182001 | -1.876226 | 1.336765 |

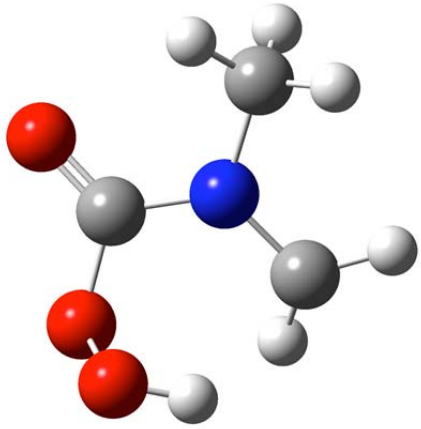
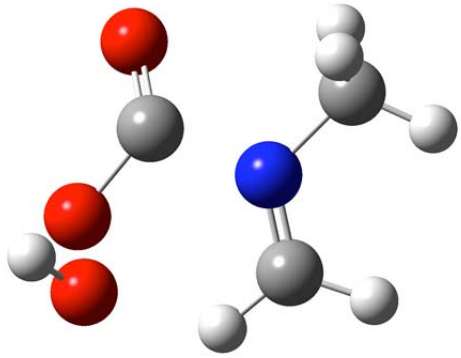
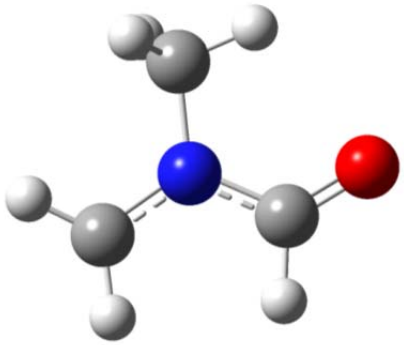
| | | | | |
|---|---|---|---|---|
| $\dot{C}H_2(CH_3)NC(O)OOH$ | C | -2.071848 | -0.000783 | -0.416853 |
|  | C | -0.455095 | -1.606676 | 0.493015 |
| | N | -0.728592 | -0.332804 | 0.042460 |
| | C | 0.164340 | 0.704712 | 0.168995 |
| | O | -0.128457 | 1.874399 | 0.162685 |
| | O | 1.475692 | 0.298438 | 0.388559 |
| | O | 1.888119 | -0.550540 | -0.715479 |
| | H | -2.017144 | 0.864260 | -1.069632 |
| | H | -2.720030 | 0.231101 | 0.427433 |
| | H | -2.469566 | -0.853162 | -0.962201 |
| | H | 1.503665 | -1.408206 | -0.457923 |
| | H | -1.241055 | -2.333694 | 0.394857 |
| | H | 0.337064 | -1.732568 | 1.213183 |
| SP21 | C | 2.133329 | -0.045345 | 0.441315 |
|  | C | 0.531611 | -1.517472 | -0.530532 |
| | N | 0.811103 | -0.401875 | -0.050237 |
| | C | -0.227728 | 0.768254 | 0.126254 |
| | O | 0.183446 | 1.858727 | -0.278978 |
| | O | -1.456132 | 0.296385 | -0.399304 |
| | O | -1.979979 | -0.713218 | 0.521879 |
| | H | 2.043787 | 0.235263 | 1.487414 |
| | H | 2.473731 | 0.818492 | -0.122245 |
| | H | 2.811228 | -0.887108 | 0.323481 |
| | H | -2.420758 | -0.132541 | 1.160327 |
| | H | 1.283333 | -2.298084 | -0.572362 |
| | H | -0.471000 | -1.690670 | -0.895952 |
| $CH_2=NCH_3$ | C | 1.142251 | 0.137831 | 0.000057 |
| | N | -0.138309 | -0.548275 | -0.000005 |
| | C | -1.176520 | 0.187832 | -0.000387 |
| | H | 1.706607 | -0.172935 | 0.878069 |
| | H | 1.044857 | 1.229576 | -0.000293 |
| | H | 1.706847 | -0.173470 | -0.877605 |
| | H | -1.130050 | 1.281812 | 0.000549 |
| | H | -2.154490 | -0.281035 | 0.001292 |
| $CO_2$ | O | 0.000000 | 0.000000 | 1.170266 |
| | C | 0.000000 | 0.000000 | 0.000000 |
| | O | 0.000000 | 0.000000 | -1.170266 |
| OH | O | 0.000000 | 0.000000 | 0.107715 |
| | H | 0.000000 | 0.000000 | -0.861717 |

**Table S19**. Electronic energies of reactants, intermediates and products (/Hartree), and relative energies including Zero Point Energies, Δ (/kJ mol$^{-1}$), of stationary points on the potential energy surface of the $\dot{C}H_2(CH_3)NCHO + O_2$ reaction. See Figure 12 in the main text.

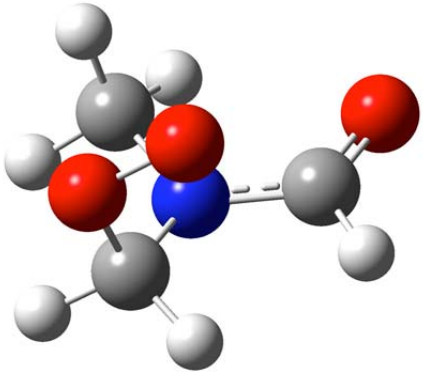
| | MP2/aTZ[a] | | CCSD(T*)-F12a/aTZ //MP2/aTZ | |
|---|---|---|---|---|
| Species | $E_{Elec}$ | $E_{ZPE}$ | $E_{Elec}$ | $\Delta E_{v=0}$ |
| $\dot{C}H_2(CH_3)NCHO$ | -247.394946 | 0.088743 | -247.556894 | |
| $O_2$ | -150.120938 | 0.003314 | -150.191209 | |
| Sum Reactants | -397.515884 | 0.092057 | -397.748103 | 0 |
| $\dot{O}OCH_2(CH_3)NCHO$ | -397.560879 | 0.099899 | -397.801365 | -119.2 |
| SP29a-1 | -397.514866 | 0.095372 | -397.759983 | -22.5 |
| $HOOCH_2(CH_3)N\dot{C}O$ | -397.556593 | 0.098992 | -397.790167 | -92.2 |
| SP29a-2 | -397.494283 | 0.094722 | -397.734911 | 41.6 |
| $HOOCH_2{*}CH_3NCO$ | -397.556593 | 0.098992 | -397.788456 | -87.7 |
| SP29b-1 | -397.519878 | 0.095627 | -397.762173 | -27.6 |
| $HOOCH_2N(CHO)\dot{C}H_2$ | -397.554269 | 0.097421 | -397.787933 | -90.5 |
| SP29b-2 | -397.468363 | 0.095202 | -397.716858 | 90.3 |

[a] aTZ, aug-cc-pVTZ; T* denotes scaled triples as recommended in the Molpro manual.

**Table S20**. Cartesian coordinates of stationary points on the potential energy surface of the $CH_3NH\dot{C}O$ radical dissociation reactions. Results from MP2/aug-cc-pVTZ calculations.

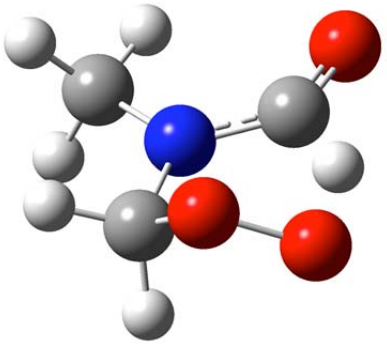
| | Atom | X | Y | Z |
|---|---|---|---|---|
| $\dot{C}H_2(CH_3)NCHO$ | C | 0.850265 | -0.622724 | 0.004658 |
|  | O | 1.890402 | 0.010963 | -0.000903 |
| | N | -0.408197 | -0.072168 | 0.008120 |
| | H | 0.812263 | -1.721512 | 0.010174 |
| | C | -0.555862 | 1.373690 | -0.002813 |
| | H | 0.434240 | 1.812433 | 0.070938 |
| | H | -1.032259 | 1.692253 | -0.928848 |
| | H | -1.165137 | 1.685886 | 0.843819 |
| | C | -1.531750 | -0.869931 | -0.029230 |
| | H | -1.401967 | -1.936484 | 0.014327 |
| | H | -2.488895 | -0.401308 | 0.104282 |
| $O_2\,(X^3\Sigma_g^-)$ | O | 0.000000 | 0.000000 | 0.612212 |
| | O | 0.000000 | 0.000000 | -0.612212 |

ȮOCH$_2$(CH$_3$)NCHO



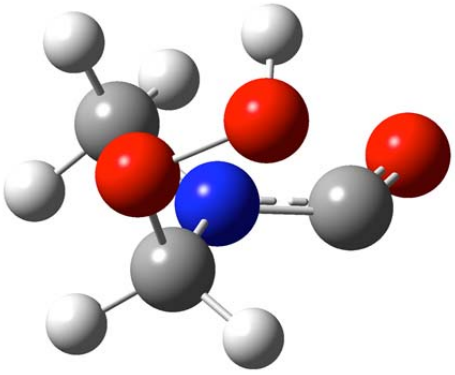
| | | | |
|---|---|---|---|
| C | -0.828695 | 1.500165 | -0.518237 |
| C | 0.871719 | 0.389032 | 0.872207 |
| N | -0.429881 | 0.400110 | 0.345559 |
| C | -1.180097 | -0.754431 | 0.359898 |
| O | -2.237011 | -0.893388 | -0.224023 |
| O | 1.896378 | 0.144588 | -0.164936 |
| O | 1.743105 | -1.045992 | -0.658228 |
| H | -1.899740 | 1.429278 | -0.680495 |
| H | -0.318595 | 1.447438 | -1.480045 |
| H | -0.588036 | 2.443619 | -0.031476 |
| H | 0.985805 | -0.398957 | 1.612203 |
| H | 1.160868 | 1.361335 | 1.266136 |
| H | -0.728467 | -1.533741 | 0.989047 |

SP29a-1



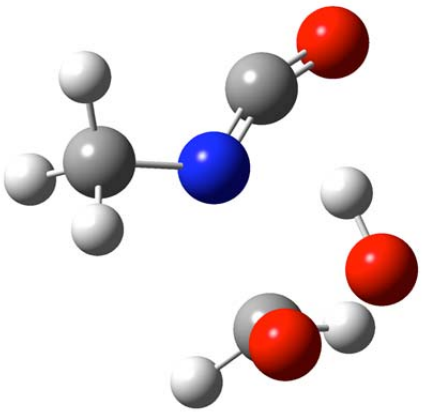
| | | | |
|---|---|---|---|
| C | 1.722292 | -1.232730 | -0.027909 |
| C | -0.772574 | -1.079247 | 0.208415 |
| N | 0.516917 | -0.423564 | 0.057392 |
| C | 0.575832 | 0.921826 | 0.017506 |
| O | 1.533199 | 1.652422 | -0.069777 |
| O | -1.749378 | -0.326676 | -0.467003 |
| O | -1.842996 | 0.863935 | 0.225418 |
| H | 2.566617 | -0.555667 | -0.127122 |
| H | 1.674549 | -1.889931 | -0.895701 |
| H | 1.845427 | -1.831599 | 0.874217 |
| H | -1.048032 | -1.180215 | 1.260351 |
| H | -0.731780 | -2.048634 | -0.286687 |
| H | -0.605089 | 1.294450 | 0.076019 |

HOOCH$_2$(CH$_3$)NĊO



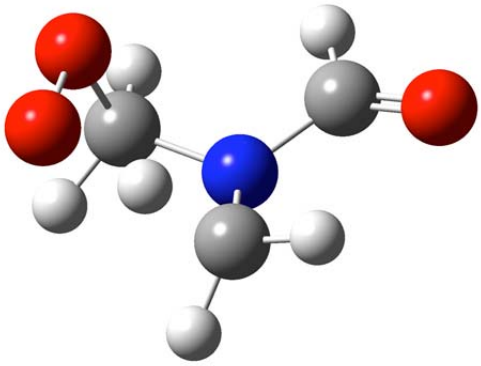
| | | | |
|---|---|---|---|
| C | -0.897252 | 1.471061 | -0.570939 |
| C | 0.797152 | 0.378792 | 0.883467 |
| N | -0.494481 | 0.341117 | 0.264019 |
| C | -1.265763 | -0.758879 | 0.376021 |
| O | -2.338625 | -0.999264 | -0.107424 |
| O | 1.858545 | 0.307229 | -0.050356 |
| O | 1.907469 | -1.069687 | -0.501488 |
| H | -1.881456 | 1.259664 | -0.978478 |
| H | -0.186338 | 1.614747 | -1.382968 |
| H | -0.938943 | 2.377993 | 0.031899 |
| H | 0.866320 | -0.435946 | 1.600868 |
| H | 0.958398 | 1.347737 | 1.359732 |
| H | 1.419451 | -1.004091 | -1.336335 |

SP29a-2



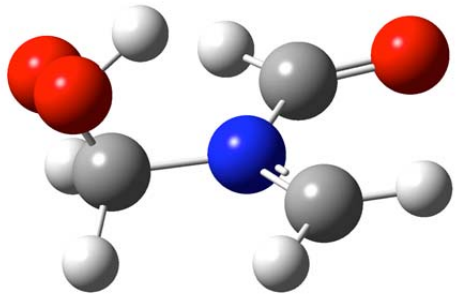
| | | | |
|---|---|---|---|
| C | -0.500446 | 1.825664 | -0.389689 |
| C | 0.959347 | -0.017749 | 1.065071 |
| N | -0.654164 | 0.443289 | 0.059655 |
| C | -1.668322 | -0.261559 | -0.056917 |
| O | -2.370338 | -1.206213 | 0.074905 |
| O | 1.958547 | 0.026520 | 0.136307 |
| O | 1.723018 | -1.062292 | -0.792089 |
| H | -0.981595 | 1.984556 | -1.350857 |
| H | 0.565004 | 2.023071 | -0.486624 |
| H | -0.924276 | 2.509451 | 0.343858 |
| H | 0.712262 | -1.001771 | 1.446843 |
| H | 1.082864 | 0.798650 | 1.765996 |
| H | 0.891600 | -0.759237 | -1.200576 |

SP29b-1



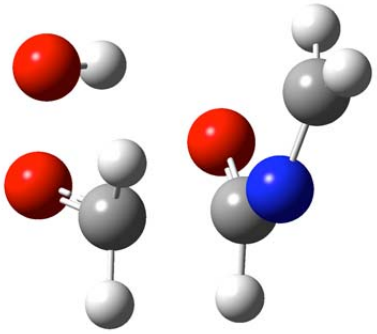
| | | | |
|---|---|---|---|
| C | 0.129396 | 1.341070 | 0.404119 |
| C | -0.741336 | -0.871884 | 0.654585 |
| N | 0.426480 | -0.035890 | 0.553924 |
| C | 1.543969 | -0.557769 | -0.086380 |
| O | 2.456813 | 0.109340 | -0.523093 |
| O | -1.476760 | -0.697373 | -0.552679 |
| O | -1.986170 | 0.584618 | -0.514763 |
| H | 0.920259 | 1.876799 | -0.108664 |
| H | -0.235062 | 1.807749 | 1.315705 |
| H | -0.923032 | 1.270893 | -0.282326 |
| H | -1.356512 | -0.567737 | 1.500551 |
| H | -0.460879 | -1.921349 | 0.702371 |
| H | 1.526625 | -1.656298 | -0.114773 |

$HOOCH_2(CHO)N\dot{C}H_2$



| | | | |
|---|---|---|---|
| C | 0.543573 | 1.499683 | 0.329572 |
| C | -0.725426 | -0.544195 | 0.807397 |
| N | 0.472783 | 0.121665 | 0.369218 |
| C | 1.530282 | -0.641078 | -0.094900 |
| O | 2.557459 | -0.177907 | -0.549025 |
| O | -1.641533 | -0.812446 | -0.233947 |
| O | -2.234240 | 0.463301 | -0.590498 |
| H | 1.474485 | 1.932145 | 0.013783 |
| H | -0.276017 | 2.055509 | 0.743955 |
| H | -1.706740 | 0.687180 | -1.373116 |
| H | -1.205808 | 0.056094 | 1.578528 |
| H | -0.474706 | -1.534511 | 1.185713 |
| H | 1.335246 | -1.718112 | 0.001952 |

SP29b-2



| | | | |
|---|---|---|---|
| C | 1.706719 | 0.700165 | -0.860180 |
| C | -0.801789 | 1.058295 | 0.608810 |
| N | 1.250980 | 0.635373 | 0.344825 |
| C | 0.841049 | -0.642954 | 0.775055 |
| O | 0.578991 | -1.603366 | 0.065411 |
| O | -1.683461 | 0.077492 | 0.349451 |
| O | -1.567198 | -0.242155 | -1.062091 |
| H | 1.715982 | -0.158666 | -1.526075 |
| H | 2.063053 | 1.653451 | -1.225569 |
| H | -0.882376 | -0.942768 | -0.990977 |
| H | -0.690337 | 1.814420 | -0.154849 |
| H | -0.844075 | 1.342381 | 1.651653 |
| H | 0.778360 | -0.705232 | 1.867768 |