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SUPPLEMENTARY INFORMATION

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Intersystem crossing in the exit channel

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Supplementary Information

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Supplementary Information Contents

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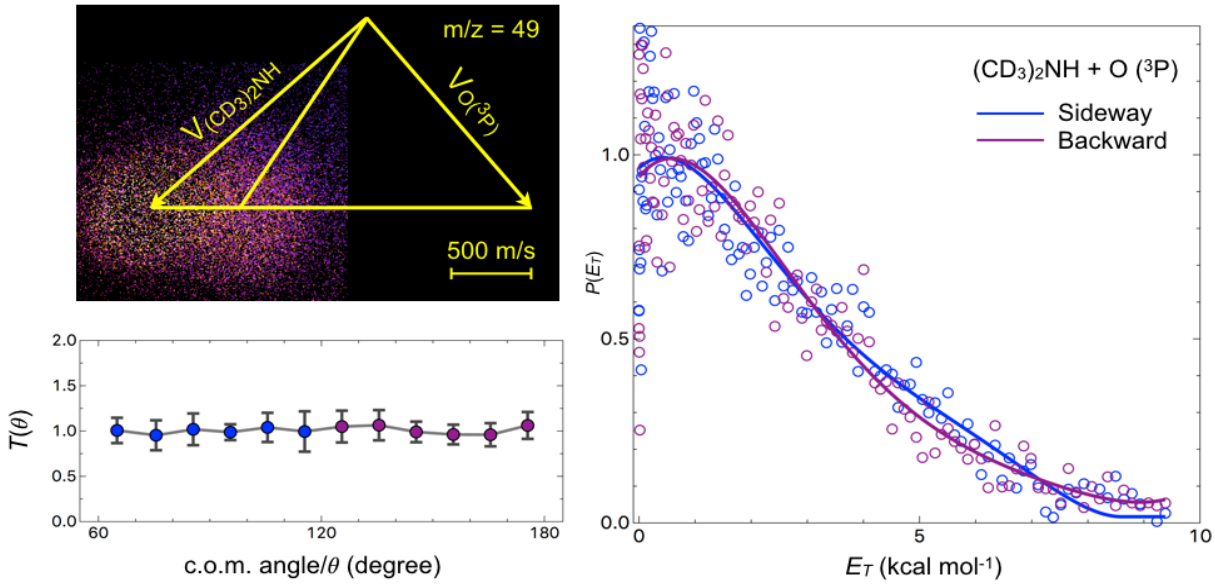
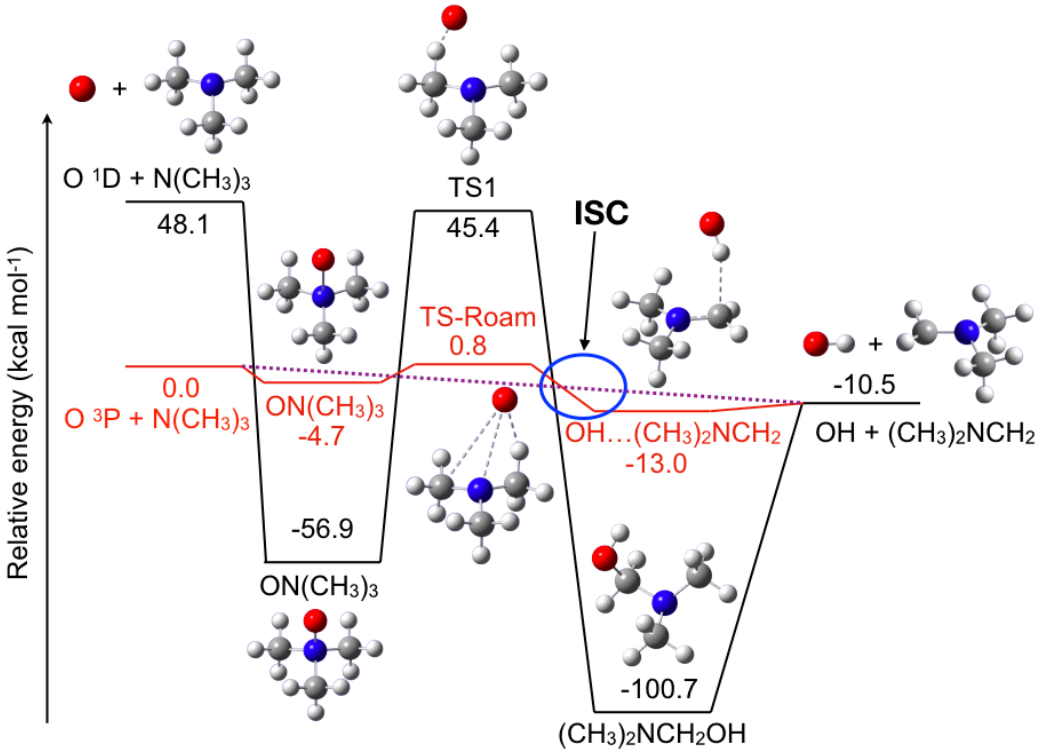
Supplementary Experimental Results



Supplementary Figure 1. Direct current slice images and center-of-mass (c.o.m.) distribution of the radical product for the reaction of $O(^3P)$ with $(CD_3)_2NH$ at collision energy of 8.0 kcal mol^{-1}. Image is shown after background subtraction and density-to-flux correction with Newton diagram superimposed. Both c.o.m. angular $T(\theta)$ and translational energy release $P(E_T)$ distributions are color-coded with the sideway component in blue (60-120°) and the backward component in purple (120-180°). Error bars ($\pm\sigma$) were estimated each 10° by mean absolute deviation of the raw data.

The reaction of O (^{3}P) with partially deuterated dimethylamine, $(CD_3)_2NH$, was also explored at collision energy of 8.0 kcal mol^{-1}. Only the CD_3NHCD_2 radical product was detected by our 7.9 eV probe that is consistent with the ionization energy calculations as mentioned in the main text. Supplementary Figure 1 shows experimental scattering results for this reaction. As what has been observed for the non-deuterated system in the main text, the angular distribution is isotropic. The translational energy release distribution also peaks at low energy region, ~10% of the collision energy. Both observations indicate the importance of the complex-elimination mechanism for this bimolecular reaction.

Supplementary Calculation Results



Supplementary Figure 1. Key points on the triplet (red) and singlet (black) PESs of the O(^{3}P) + TMA reaction. The diagram has been calculated at the CBS-QB3 level of theory. Relative energies are shown in kcal mol^{-1}. The purple dashed line illustrates the barrierless direct H abstraction pathway on the triplet surface. The blue circle suggests the region where ISC can occur.

The PES for the O (^{3}P) + TMA reaction calculated at same level of theory is analogous to the O (^{3}P) + TMA system as shown in Supplementary Fig. 2. No TS is found for the direct H abstraction channel, but a roaming-type TS is located between two shallow van der Waals complex wells along the reaction pathway on the triplet surface. However, again the roaming pathway may not play a key role due to the high collision energy and the possibility of barrierless H abstraction. On the singlet surface, two deep complex wells are present on the pathway forming the detected products, but the TS barrier on this pathway again is too high (45.4 kcal mol^{-1}) to surmount given the 8.0 kcal mol^{-1} experimental collision energy. Therefore, analogous to O (^{3}P) + DMA reaction, the O (^{3}P) + TMA reaction may proceed via direct H-abstraction from a methyl group on TMA, followed by ISC to singlet surface leading to the very deep exit channel complex well ($(CH_3)_2NCH_2OH$) before OH elimination to produce the detected radicals.

Supplementary Movie

This video contains animations of one trajectory starting from the transition state of the direct H abstraction process to $OH+CH_3NHCH_2$ products on the triplet surface, calculated using a Born-Oppenheimer molecular dynamics model at the B3LYP/6-31G(d) level of theory. Colour coding for atoms: carbon (grey), nitrogen (blue), oxygen (red), and hydrogen (white). A few snapshots for this trajectory is shown in Figure 5 in the main text.

Key stationary point geometry

The geometries of the key stationary point for both $O(^3P)$ + DMA and $O(^3P)$ + DMA reactions are listed below. All geometries here were optimized at the CBS-QB3 level of theory.

$O(^3P)$ + DMA reaction:

$(CH_3)_2NHO$
0 3
C 0.75665500 1.23459100 -0.13362900
N 0.20162000 -0.00002300 0.38605000
C 0.75060400 -1.23741200 -0.13349300
H 0.21420000 -2.08049800 0.30288400
H 0.60066000 -1.26988900 -1.21555700
H 1.82810300 -1.35333900 0.06740300
H 0.11470200 0.00021300 1.39337900
H 1.83470200 1.34530400 0.06727400
H 0.60688100 1.26766500 -1.21569800
H 0.22441600 2.08038400 0.30262800
O -1.98481900 0.00340600 -0.10024100

TS-Roam
0 3
C 0.00003200 0.00020800 0.00008700
N -0.00004600 0.00000300 1.45715800
C 1.29549000 -0.00013600 2.06874200
H 1.88944200 -0.84357700 1.70484200
H 1.21323700 -0.05301400 3.15593600
H -0.59174200 0.73161700 1.83425100
H -1.02736200 0.04714300 -0.36577000
H 0.56729400 0.84343800 -0.41876500
H 0.44489700 -0.93118200 -0.36229800
O 1.28916800 2.58803700 1.48210100
H 1.87470100 0.94126300 1.82797500

$CH_3NHCH_2…OH$
0 3
C -0.05169400 0.08422200 0.10602400
N 0.11232300 -0.50661000 1.42804400
C 1.16597100 -0.10689000 2.22978400
H 2.11423900 0.03770100 1.72105000
H 1.19528300 -0.53561800 3.22498800
H -0.75606000 -0.67199300 1.91784100
H -0.86045600 -0.42223200 -0.42286200
H -0.26569600 1.15800400 0.16410700
H 0.86902100 -0.05703500 -0.46596700

O 0.26486000 2.77194000 2.22994500
H 0.69377200 1.88993600 2.39905400

CH_3NHCH_2
0 2
C 1.19137500 -0.18647600 0.03330300
N -0.09362500 0.47138900 -0.13619800
C -1.25672500 -0.25294000 0.09097600
H -1.25365300 -1.28254200 -0.24749000
H -2.18589900 0.30105500 0.04520500
H -0.11528400 1.41407200 0.22782800
H 1.99251800 0.48273400 -0.28704700
H 1.38463600 -0.50157200 1.06960600
H 1.22516400 -1.07697400 -0.60039200

$(CH_3)_2NHO$
0 1
C -1.23779500 -0.61696400 0.10054600
N 0.00000100 0.11538900 -0.32229100
C 1.23779700 -0.61695900 0.10054600
H 2.07767200 -0.02797300 -0.25987500
H 1.24044500 -0.61820700 1.18853800
H 1.26254400 -1.63384500 -0.30347300
H 0.00000200 0.09575100 -1.35673100
O -0.00000400 1.38251600 0.14447900
H -1.26252400 -1.63386100 -0.30344600
H -1.24045400 -0.61818000 1.18853800
H -2.07767300 -0.02799800 -0.25990100

TS-C
0 1
C -0.00055800 0.00607300 -0.00162700
N 0.00377100 -0.00545600 1.44174300
C 1.26033200 -0.00175600 2.13760100
H 1.10120200 0.14461400 3.20686200
H 1.83133000 -0.93238900 1.98982000
H 1.87944600 0.81831200 1.75254300
H -0.78747800 -0.54354300 1.80873600
H 0.36660500 0.96007600 -0.39871500
H 0.54598900 -0.82532100 -0.45973400
H -1.07208400 -0.23256100 -0.26838400
O -1.68327300 -1.51337000 0.66585700

CH_3NHCH_2OH
0 1
C -0.00343500 -0.01925400 -0.00631400

N 0.00123800 -0.03428500 1.44405900
C 1.33050700 0.01232900 2.04603300
H 1.23685900 -0.01661200 3.13357300
H 2.00032100 -0.80829500 1.73901200
H 1.81820200 0.95543100 1.78236700
H -0.50747000 -0.85072300 1.76924600
H 0.66639500 0.79413400 -0.32477400
H 0.35356900 -0.95086400 -0.47140900
O -1.31779500 0.15366400 -0.48877400
H -1.68219100 0.89849700 0.00442400

O(^{3}P) + TMA reaction:

$ON(CH_3)_3$
0 3
C 0.59742400 1.22136900 -0.66417800
N 0.18810800 -0.00000900 0.00323700
C 0.59735800 -1.22366300 -0.66003100
H 1.69024700 -1.37408500 -0.62551400
H 0.10888500 -2.07385900 -0.18252800
H 0.28367000 -1.19391500 -1.70481100
C 0.39027100 0.00246200 1.43959600
H -0.07973800 0.88800100 1.87068600
H -0.07985000 -0.88149500 1.87380800
H 1.45961900 0.00286200 1.71239700
O -2.03662000 -0.00020400 -0.14129200
H 0.28383100 1.18806100 -1.70888300
H 0.10890500 2.07321000 -0.18966900
H 1.69031600 1.37190600 -0.63012700

TS-Roam
0 3
C 0.00000000 0.00000000 0.00000000
N 0.00000000 0.00000000 1.45035700
C 1.31833500 0.00000000 2.05523600
H 1.87341600 0.93505200 1.86671800
H 1.23107800 -0.13268600 3.13452900
H 1.90626700 -0.82790500 1.65495800
C -0.96209300 0.88398300 2.03609400
H -1.98793400 0.46685400 1.88738900
H -0.79590700 0.97437000 3.10907300
H -0.97431700 1.88873100 1.58166800
O -2.90334600 -1.02087800 1.59275700
H 0.62092800 -0.81699700 -0.37117100
H -1.01790100 -0.14892100 -0.36157800

H 0.38606900 0.94553200 -0.41843500

OH…$(CH_3)_2NCH_2$
0 3
C -0.07761700 -0.13487600 0.09644000
N 0.03148900 0.00690500 1.53645700
C 1.36048800 0.07220300 2.11126800
H 1.84880100 1.04098200 1.92180600
H 1.29928300 -0.07378000 3.19110100
H 1.99045200 -0.71742100 1.69418200
C -1.05615400 0.46996200 2.24551400
H -2.15174000 -1.30092500 2.04526600
H -0.87353100 0.81180500 3.25548500
H -1.86130400 0.92974400 1.68322500
O -2.54210300 -2.07392600 1.56240100
H 0.69228400 -0.81937900 -0.26590800
H -1.05189500 -0.56199900 -0.14533900
H 0.03726600 0.82642600 -0.42744200

$(CH_3)_2NCH_2$
0 2
C 0.00004700 -0.00003800 -0.00083000
N -0.00005800 0.00322100 1.45176600
C 1.31903500 0.00028300 2.05998600
H 1.86134800 0.94504000 1.89253600
H 1.22359600 -0.15228200 3.13677000
H 1.91465100 -0.81845600 1.64864600
C -0.98752400 0.74279400 2.08370700
H -1.95367300 0.77561900 1.59618800
H -0.95049100 0.77459700 3.16530500
H 0.62157800 -0.81994900 -0.36932600
H -1.01796100 -0.15102300 -0.36512400
H 0.38074700 0.94397500 -0.42334700

$ON(CH_3)_3$
0 1
C -0.01980300 -0.04147500 0.00730800
N -0.08084700 -0.18046600 1.50259000
C 1.30180100 -0.04038500 2.07500600
H 1.74486800 0.93190300 1.84027100
H 1.20731700 -0.18182300 3.14877700
H 1.89221700 -0.85327800 1.65966200
C -0.96773400 0.89249000 2.06895800
H -1.95724600 0.72904200 1.64939100
H -1.00503900 0.72755300 3.14288700
H -0.59778900 1.89490100 1.83406200

O -0.58350700 -1.40100500 1.82435600
H 0.60166500 -0.85729800 -0.35342200
H -1.03453600 -0.17907700 -0.35780700
H 0.38339100 0.92899600 -0.29682000

TS1
0 1
C 0.00000000 0.00000000 0.00000000
N 0.00000000 0.00000000 1.46189200
C 1.33721200 0.00000000 2.01714500
H 1.90207900 0.90100600 1.70471200
H 1.29515200 -0.01562200 3.10761000
H 1.88687800 -0.87915400 1.67506400
C -0.88369100 0.97230600 2.08575000
H -0.96768400 0.75177300 3.15208100
H -0.49568500 2.00087200 1.97261100
H -1.87193800 0.89830200 1.64050400
O -1.85360200 -1.19097700 0.54389500
H 0.52130700 -0.87699100 -0.37790800
H -1.08507300 -0.16404000 -0.30195700
H 0.42216700 0.92057100 -0.45149400

$(CH_3)_2NCH_2OH$
0 1
C 0.14538900 0.21585500 -0.08619600
N -0.00307600 0.42990600 1.34974900
C 0.98987800 -0.29860600 2.12719400
H 1.99322100 0.02770200 1.84161500
H 0.85819800 -0.07836800 3.19050400
H 0.94714200 -1.39378900 1.98968000
C -1.35209600 0.26912600 1.82227400
H -2.00174500 0.93172500 1.24827700
H -1.38193400 0.56867500 2.87684000
H 1.15268600 0.50705000 -0.39512600
H -0.02452000 -0.82909600 -0.38816600
H -0.56858300 0.84446700 -0.62414000
O -1.92938600 -1.03534200 1.66062800
H -1.54237200 -1.61922600 2.31982000