# Supporting Information

## Reactions of Gas-phase Uranyl Formate/Acetate Anions: Intra-complex Hydride Attack to Convert Carboxylates to Aldehydes

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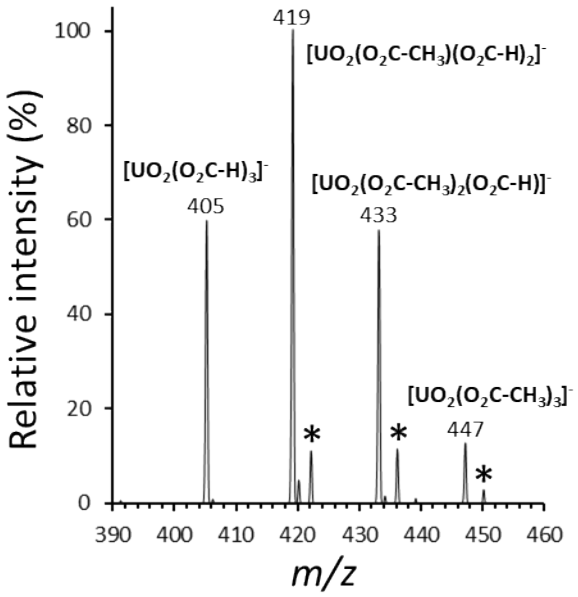
419
[UO2(O2C-CH3)(O2C-H)2]-
[UO2(O2C-H)3]-
405
[UO2(O2C-CH3)2(O2C-H)]-
433
[UO2(O2C-CH3)3]-
447
*
*
*
Relative intensity (%)
100
80
60
40
20
0
390
400
410
420
430
440
450
460
m/z

Figure S1.

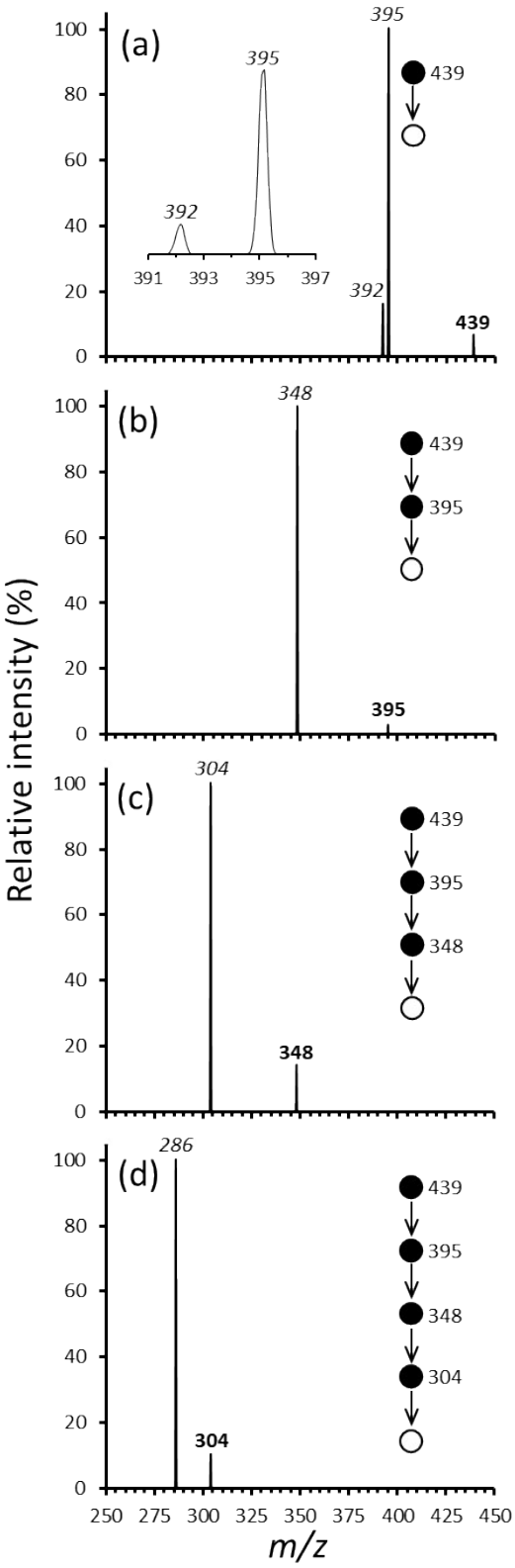
(a)
(b)
(c)
(d)
Relative intensity (%)
m/z
395
439
392
348
304
286
100
80
60
40
20
0
250 275 300 325 350 375 400 425 450
391 393 395 397

Figure S2.

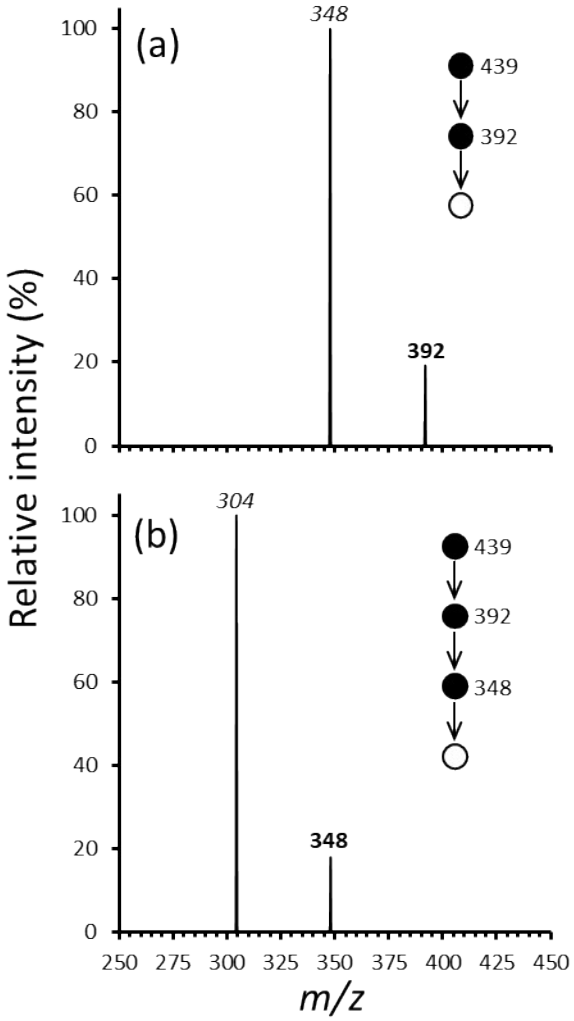
(a)
348
439
392
392
(b)
304
439
392
348
348
Relative intensity (%)
100
80
60
40
20
0
250 275 300 325 350 375 400 425 450
m/z

Figure S3.

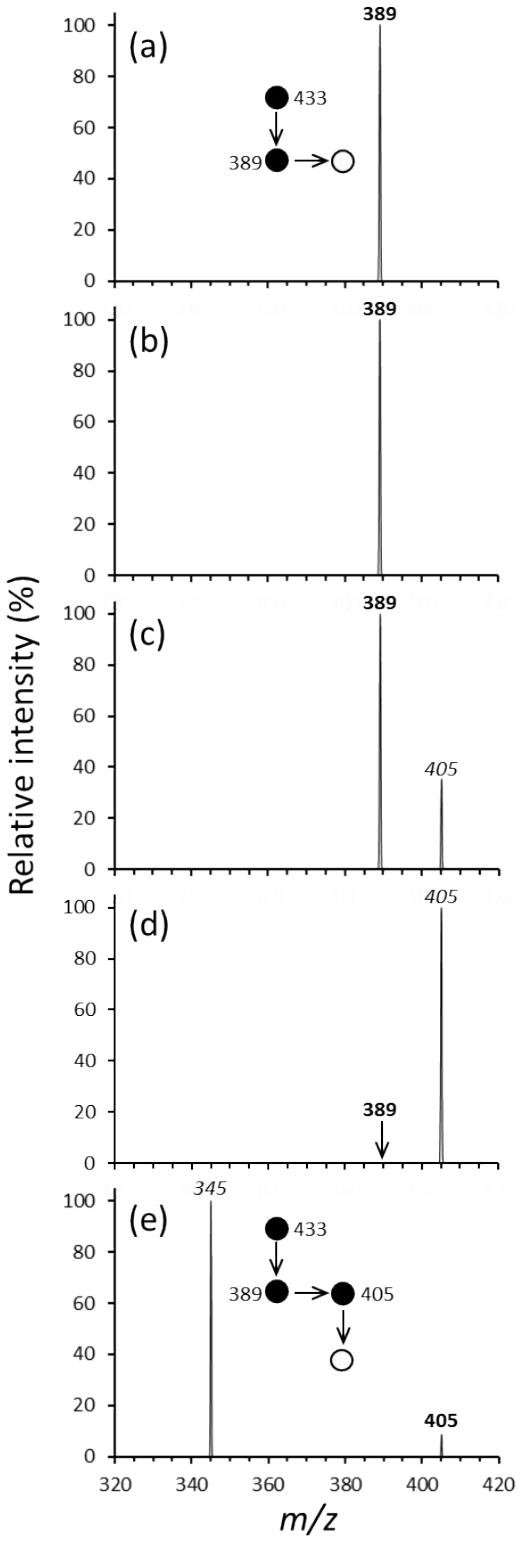
(a)
389
433
389
(b)
389
(c)
389
405
(d)
405
389
(e)
345
433
389
405
405
Relative intensity (%)
m/z
0
20
40
60
80
100
320
340
360
380
400
420

Figure S4.

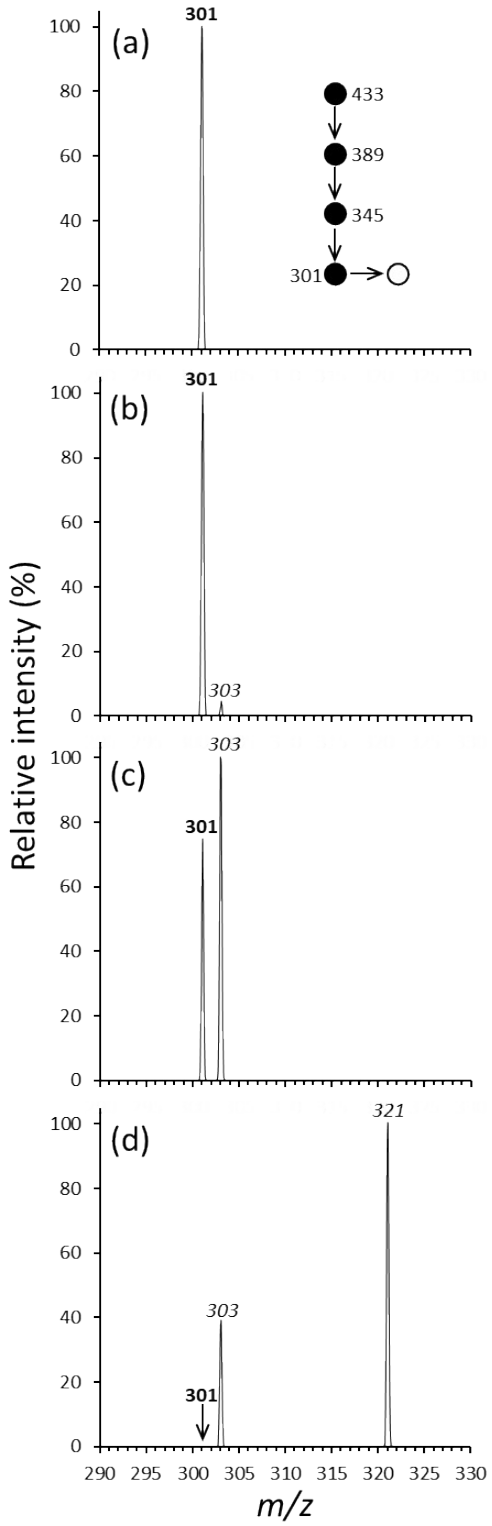
(a)
301
433
389
345
301
(b)
301
303
(c)
303
301
(d)
321
303
301
Relative intensity (%)
m/z

Figure S5.

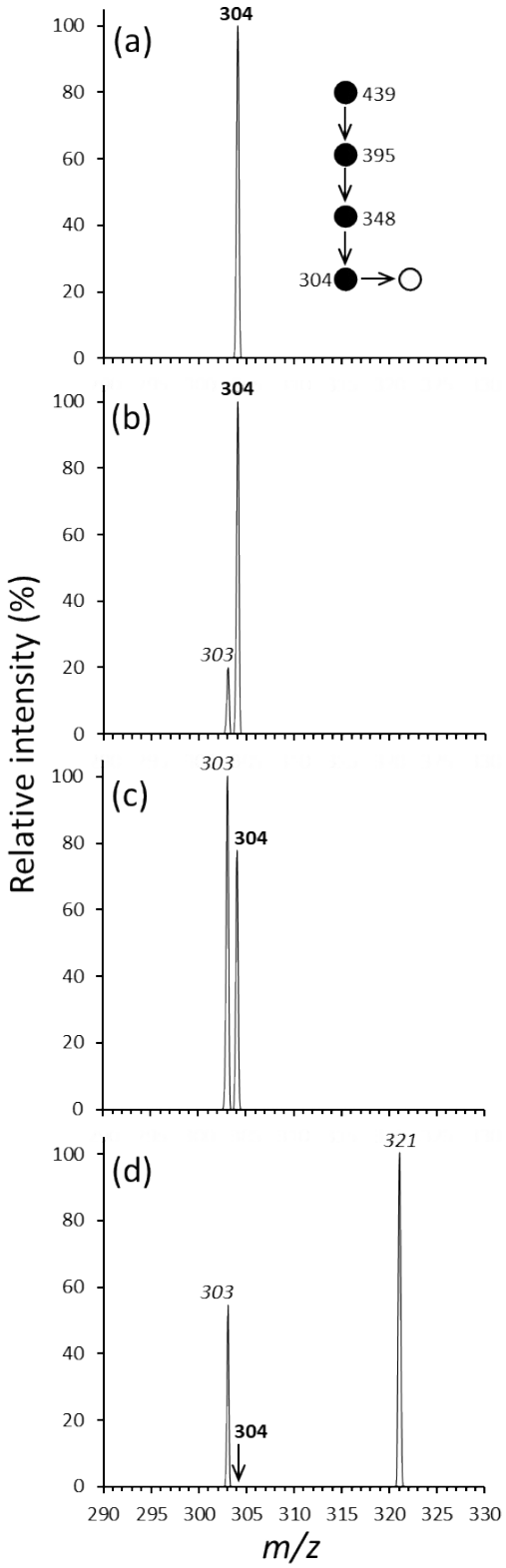
(a)
304
439
395
348
304
(b)
304
303
(c)
303
304
(d)
321
303
304
Relative intensity (%)
m/z
100
80
60
40
20
0
290 295 300 305 310 315 320 325 330

Figure S6.

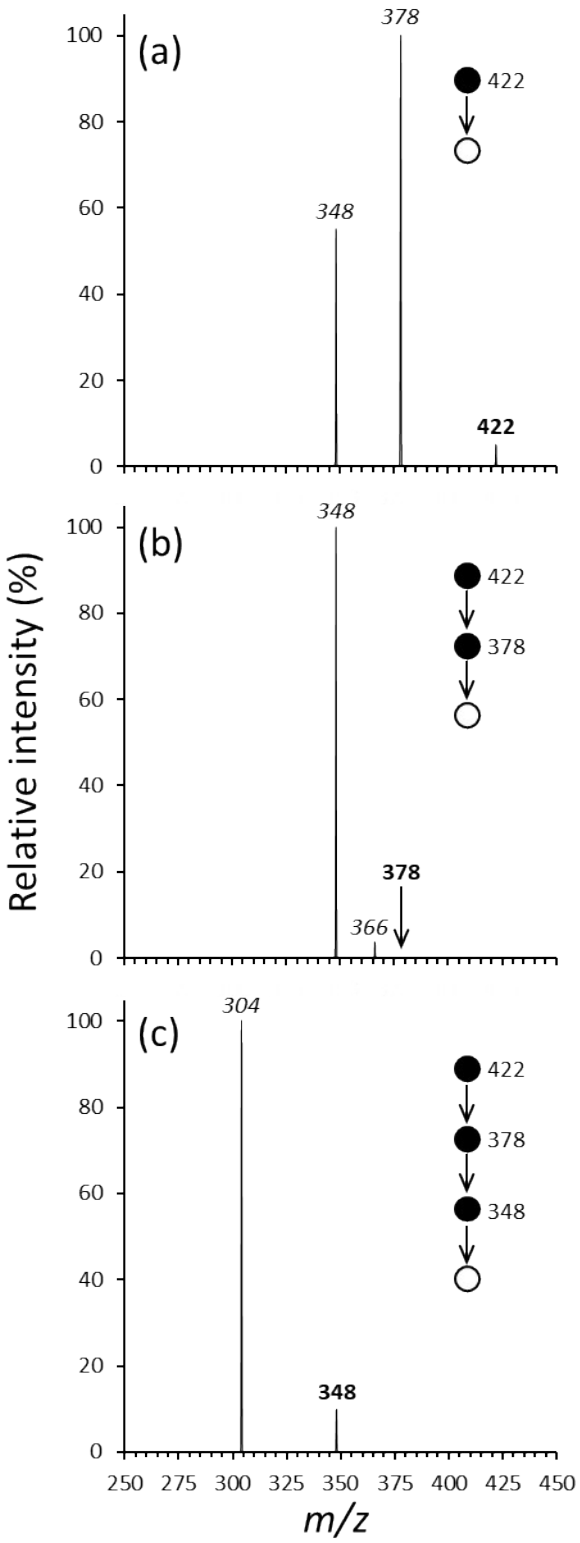
(a)
(b)
(c)
Relative intensity (%)
m/z
422
378
348
366
304
100
80
60
40
20
0
250 275 300 325 350 375 400 425 450

Figure S7.

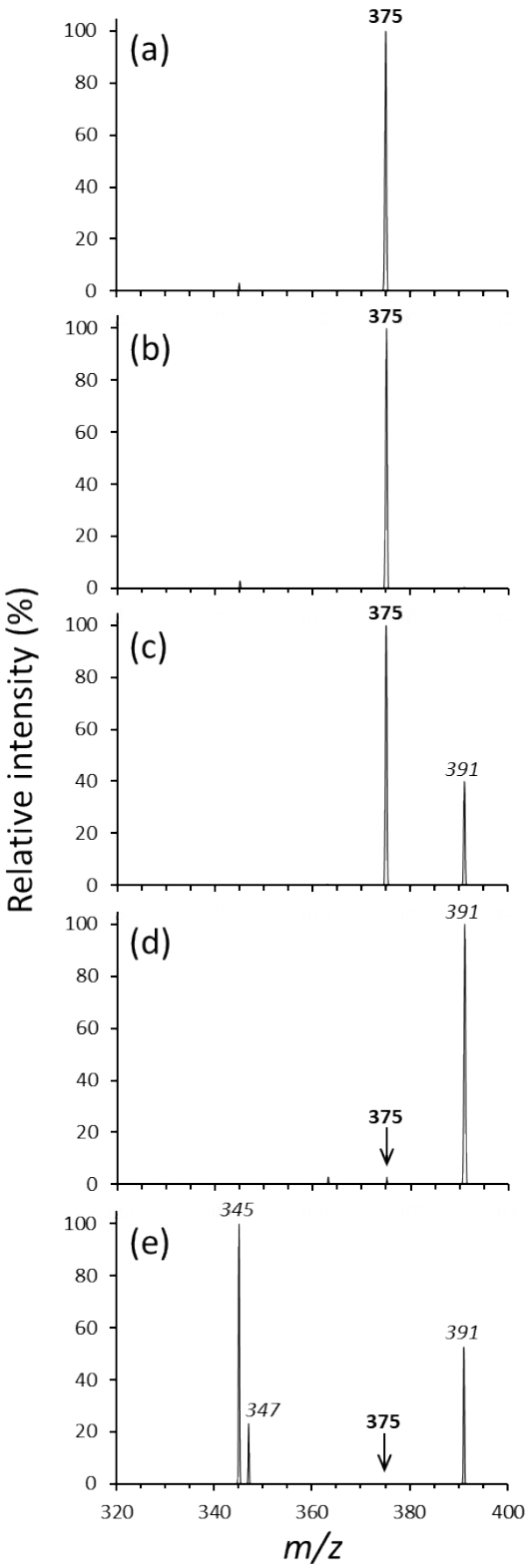
(a)
(b)
(c)
(d)
(e)
375
391
345
347
Relative intensity (%)
m/z
0
20
40
60
80
100
320
340
360
380
400

Figure S8.

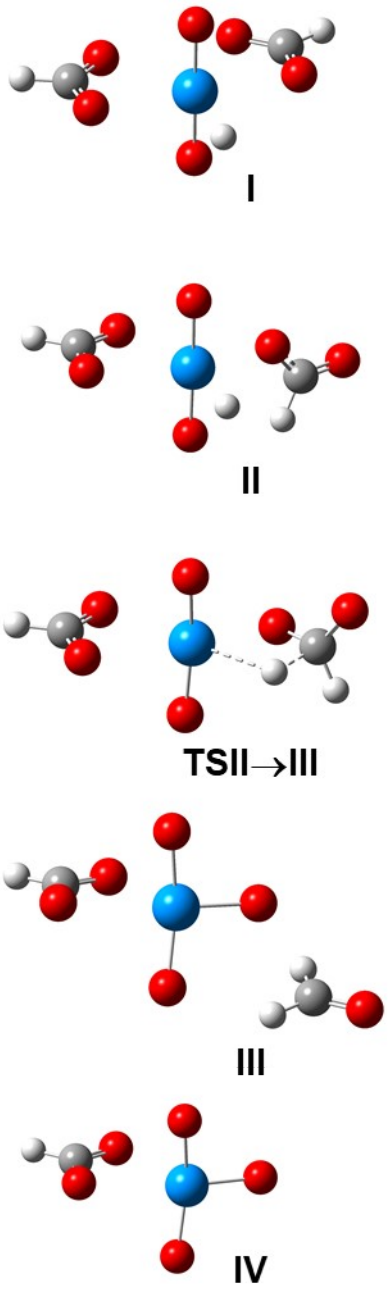


Figure S9.

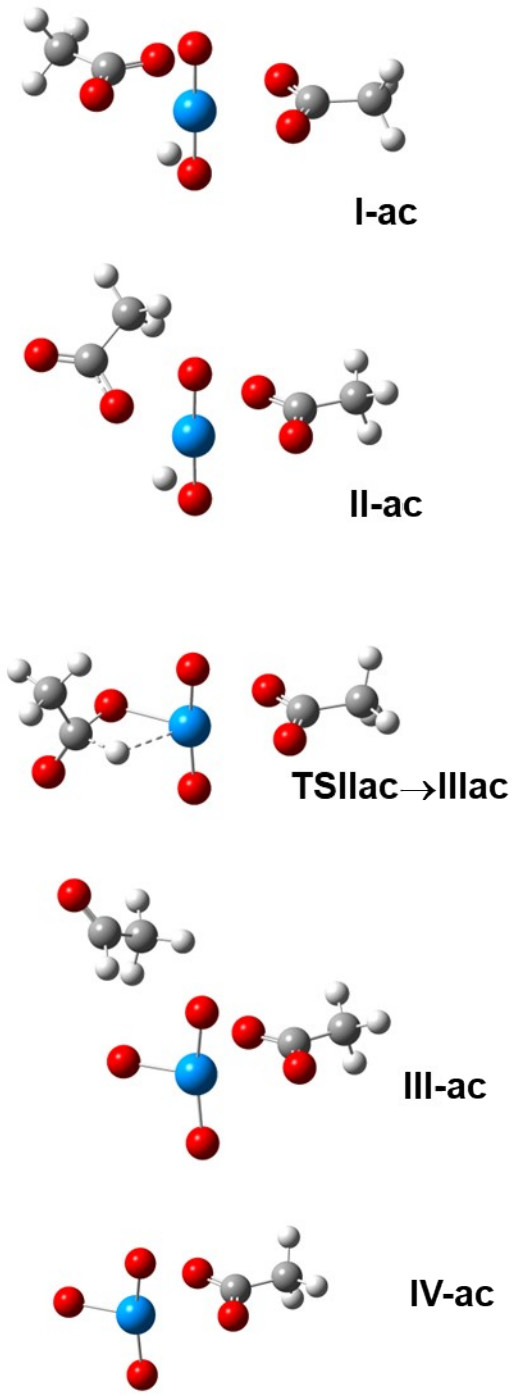


Figure S10.

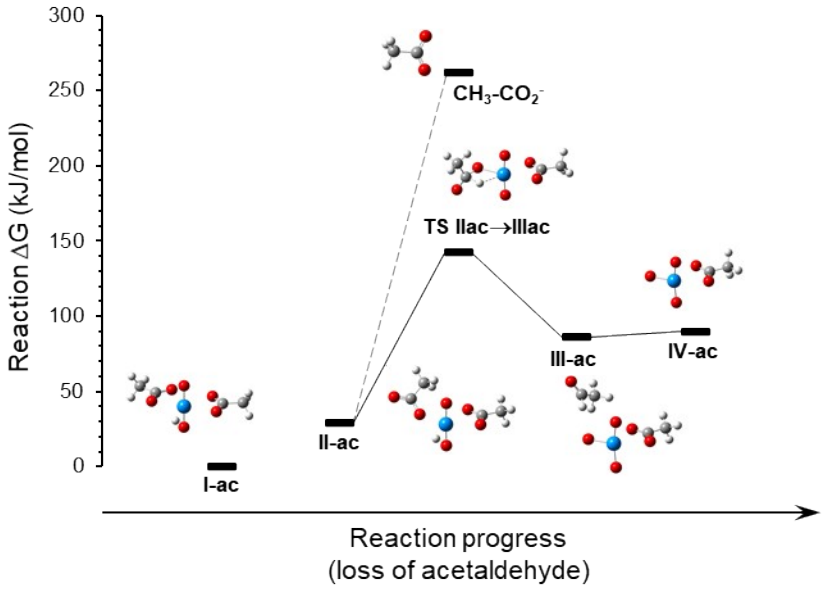
300
250
200
150
100
50
0
Reaction ΔG (kJ/mol)
CH3-CO2-
TS IIac→IIIac
I-ac
II-ac
III-ac
IV-ac
Reaction progress
(loss of acetaldehyde)

Figure S11.

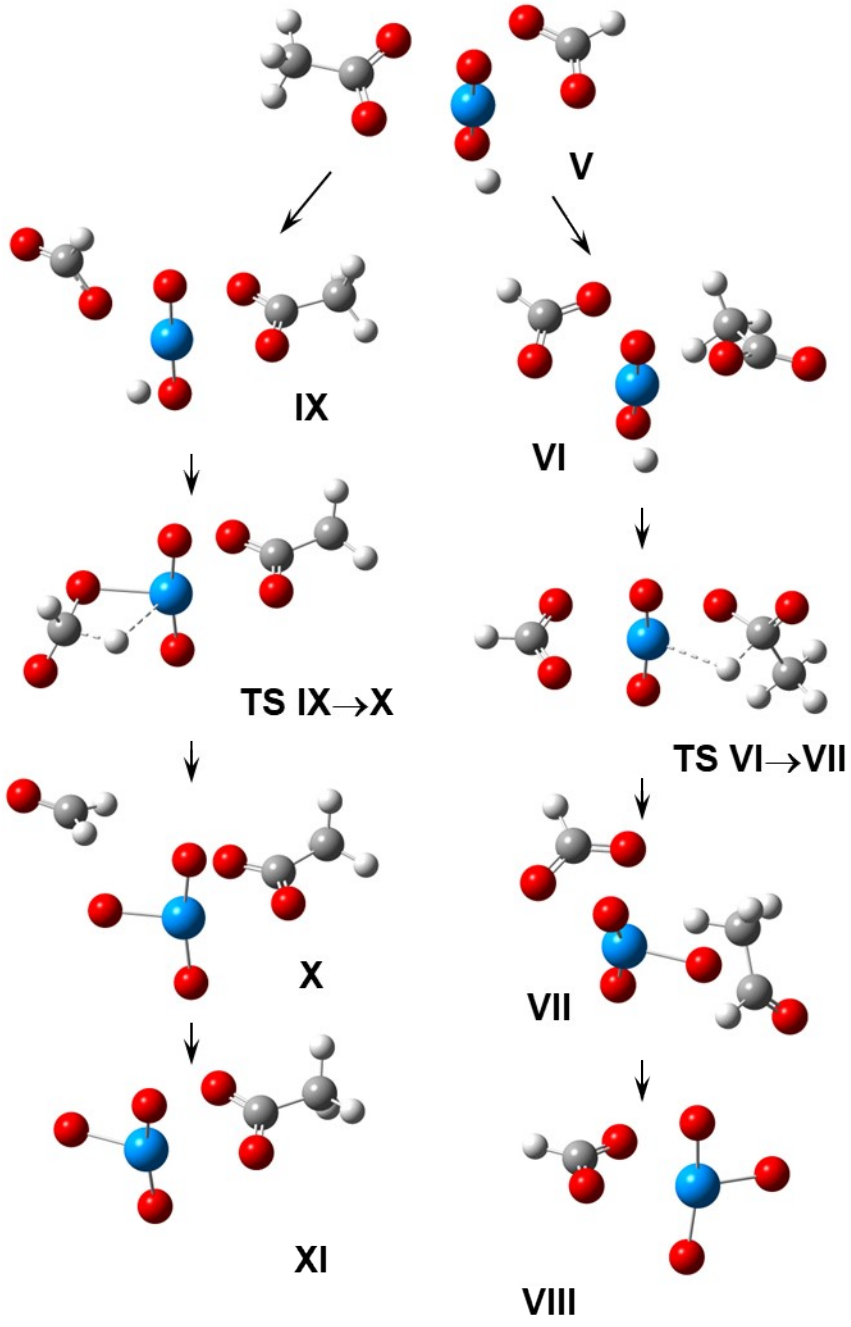


Figure S12

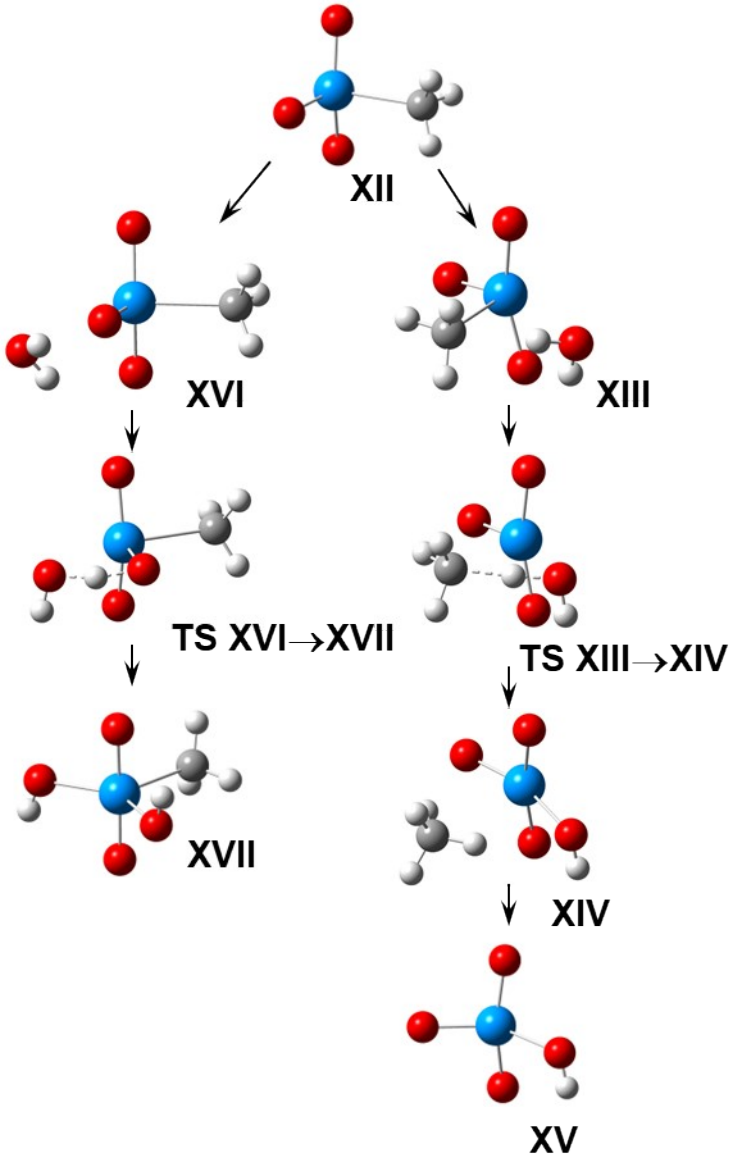


Figure S13.

Table S1.

| Structure | Zero-point corrected electronic energy | Thermally corrected free energy |
|---|---|---|
| I | -1004.615232 | -1004.654507 |
| II | -1004.604059 | -1004.644649 |
| TS II->III | -1004.565179 | -1004.604376 |
| III | -1004.574499 | -1004.615464 |
| IV | -890.057297 | -890.092941 |
| formaldehyde | -114.502636 | -114.524283 |

Table S2.

| Structure | Zero-point corrected electronic energy | Thermally corrected free energy |
|---|---|---|
| I-ac | -1083.221641 | -1083.264912 |
| II-ac | -1083.209669 | -1083.254063 |
| TS II-ac->III-ac | -1083.1684 | -1083.211674 |
| III-ac | -1083.186513 | -1083.232462 |
| IV-ac | -929.359691 | -929.397871 |
| acetaldehyde | -153.810131 | -153.835063 |

Table S3.

| Structure | Zero-point corrected electronic energy | Thermally corrected free energy |
|---|---|---|
| V | -1043.918513 | -1043.961161 |
| VI | -1043.906032 | -1043.947874 |
| TS VI->VII | -1043.864826 | -1043.905718 |
| VII | -1043.884324 | -1043.929082 |
| VIII | -890.057297 | -890.092941 |
| acetaldehyde | -153.810131 | -153.835063 |
| | | |
| IX | -1043.907696 | -1043.950918 |
| TS IX->X | -1043.868536 | -1043.910748 |
| X | -1043.877684 | -1043.922421 |
| XI | -929.359691 | -929.397871 |
| formaldehyde | -114.502636 | -114.524283 |

Table S4.

| Structure | Zero-point corrected electronic energy | Thermally corrected free energy |
|---|---|---|
| XII | -740.656324 | -740.690521 |
| $H_2O$ | -76.423266 | -76.440903 |
| XIII | -817.101013 | -817.138227 |
| TSXI II->XIV | -817.100974 | -817.137112 |
| XIV | -817.145404 | -817.184582 |
| V | -776.660695 | -776.694344 |
| $CH_4$ | -40.480523 | -40.497825 |
| | | |
| XVI | -817.101055 | -817.138367 |
| TSXVI->XVII | -817.094361 | -817.130389 |
| XVII | -817.143981 | -817.180702 |