**Supporting Information for**

**Synthesis of Interstellar Propen-2-ol (CH3C(OH)CH2) – The Simplest** **Enol Tautomer of a Ketone**

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**Ion signal of higher masses and assignment**

After the irradiation, several higher mass-to-charge ratios were observed at 9.43 eV, which were not present in the blank experiment. The ion signals at *m/z* = 72, 86, 100, 114, 116, and 158 in irradiated acetone ice shift to *m/z* = 80, 92, 108, 124, 128, and 172 in irradiated acetone-d6 ice respectively (Figs. S1 and S4), confirming their respective formulae C4H8O, C4H6O2, C5H8O2, C6H10O2, C6H12O2, and C8H14O3. Note that formula C12H14 is unlikely to be assigned to the signal at *m/z* = 158 due to the small dose (0.34 ± 0.05 eV molecule−1) used in the experiment. The tentatively assigned molecules are listed in Table S7 and the proposed pathways for their formation are shown in Figs. S5 and S6. Upon irradiation, the acetyl radical (**7**, CH3ĊO), acetonyl radical (**8**, CH3COĊH2) or methyl radical (**9**, ĊH3) can be produced via carbon-carbon single bond cleavage or H atom loss by acetone (**1**). Radical-radical reactions of two acetyl radicals (**7)** or two acetonyl radicals (**8**) can lead to the formation of 2,3-butanedione (**10**, C4H6O2; IE = 9.20 – 9.27 eV) or 2,5-hexanedione (**11**, C6H10O2). Our recent work demonstrated the recombination of two acetyl radicals (**7**) forms 2,3-butanedione (**10**) in irradiated acetaldehyde ice.1 The recombination of **7** and **8** radicals can form 2,4-pentanedione (**12**, C5H8O2; IE = 8.80 – 8.84 eV). Similarly, 2-butanone (**13**, C4H8O; IE = 9.45 – 9.53 eV) can be formed from the recombination reaction between acetonyl radical (**8**) and methyl radical (**9**). The ionization of 2-butanone (**13)** is possible as the lower limit of its ionization energy is only 0.02 eV higher than the energy of the ionizing photon (9.43 eV). Because the hydroxy (OH) group of propen-2-ol (**2**) is nucleophilic and the carbon of the carbonyl group (C=O) of acetone (**1**) or 2,4-pentanedione (**12**) acts as an electrophile, propen-2-ol (**2**) can react with acetone (**1**) or 2,4-pentanedione (**12**) via nucleophilic additions, forming the 2-prop-1-en-2-yloxypropan-2-ol (**14**, C6H12O2) or 4-hydroxy-4-(prop-1-en-2-yloxy)pentan-2-one (**15**, C8H14O3) (Fig. S5). Since each of the above molecular formulae has multiple isomers, further work is needed to provide confidence in their identification and better analyze their formation pathways, which is beyond the scope of the present work.

Chart

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**Fig. S1** Temperature programmed desorption profiles of higher mass-to-charge ratios (*m/z*) recorded at 9.43 eV in blank or unirradiated acetone (gray), irradiated acetone (black), and irradiated acetone-d6 (red) ices.

Chart

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**Fig. S2** QMS TPD profiles of acetone (top) at *m/z* = 58 and acetone-d6 (bottom) at *m/z* = 64. The dashed line indicates their peak sublimation temperature at 137 K.

A picture containing text, line, diagram, font

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**Fig. S3** The reduction and leveling of the reaction barrier of systems CH3COCH3 + n(H2O) (n = 0 − 5) leading to the formation of propen-2-ol (**2**), as more water molecules are involved in the reaction. The anticipated accuracy of the reaction barriers is within 10 kJ mol−1.



**Fig. S4** Mass spectra (integrated ion signals) of higher masses recorded at 9.43 eV in irradiated acetone (top) and acetone-d6 (bottom) ices.

**Chart, diagram

Description automatically generated Fig. S5** Proposed formation pathways for molecules **10** − **15** in irradiated acetone ice.

Chart, scatter chart

Description automatically generated **Fig. S6** Proposed formation pathways for molecules **10** − **15** in irradiated acetone-d6 ice.

**Table S1.** Conditions of ice studied in this work including the ice composition, thickness, irradiation parameters, and VUV photon energies.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Ice composition | Thickness (nm) | Current  (nA) | Irradiation  Time (s) | Dose (eV molecule−1) | Photon energy (eV) |
| CH3COCH3 | 720 ± 50 | - | - | - | 9.43 |
| CH3COCH3 | 710 ± 30 | 21 ± 1 | 300 ± 10 | 0.34 ± 0.05 | 9.43 |
| CD3COCD3 | 710 ± 30 | 22 ± 2 | 300 ± 10 | 0.40 ± 0.06 | 9.43 |
| CH3COCH3 −  CD3COCD3  (1.1 ± 0.2): 1 | 720 ± 50 | 15 ± 1 | 120 ± 10 | 0.10 ± 0.02 for CH3COCH3, 0.11 ± 0.02 for CD3COCD3 | 9.43 |
| CH3COCH3 | 710 ± 30 | 20 ± 2 | 300 ± 10 | 0.33 ± 0.05 | 8.90 |
| CH3COCH3 | 710 ± 30 | 20 ± 2 | 300 ± 10 | 0.33 ± 0.05 | 8.40 |

**Table S2.** Parameters for the generation of vacuum ultraviolet (VUV) light. The uncertainty for VUV photon energies is less than 0.001 eV.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| VUV photon energy (eV) | Nonlinear medium in four-wave mixing (2ω1 - ω2) | ω1 Dye laser wavelength (nm) | ω1 Dye | ω2 Dye laser wavelength (nm) | ω2 Dye |
| 9.43 | Krypton | 202.316 | Rhodamine 610 and 640 | 438.654 | Coumarin 440 |
| 8.90 | Xenon | 222.566 | Coumarin 450 | 553.180 | Pyrromethene  580 |
| 8.40 | Krypton | 202.316 | Rhodamine 610 and 640 | 321.497a | Rhodamine  640 |

a obtained from the second harmonic generation.

**Table S3.** Error analysis of adiabatic ionization energies (IE) of C3H6O isomers **1** to **6**. The IEs were computed at the CCSD(T)/CBS//B3LYP/cc-pVTZ level of theory including the zero-point vibrational energy (ZPVE) corrections. The IE ranges were corrected for the thermal and Stark effect by −0.03 eV and the combined error limits were determined to be -0.05/+0.03 eV.2 The computed Cartesian coordinates and vibrational frequencies are shown in Table S8.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Name | Isomer | Structure | Experimental IE (eV) 3 | Computed IE (eV) | IE range after error analysis (eV) | Corrected IE with electric field effect (eV) |
| acetone | **1** | D:\Dropbox\Astrochemistry\6 C3H6O-ACETONE\Figure\structures-andre\1.png | 9.703 ±  0.006 | 9.70 | 9.697 – 9.709 | 9.667 – 9.679 |
| propen-2-ol | **2a** | D:\Dropbox\Astrochemistry\6 C3H6O-ACETONE\Figure\structures-andre\2a.png | – | 8.80 | 8.75 – 8.83 | 8.72 – 8.80 |
| **2b** | A close-up of a stethoscope  Description automatically generated with medium confidence | – | 8.70 | 8.65 – 8.73 | 8.62 – 8.70 |
| propylene oxide | **3** | D:\Dropbox\Astrochemistry\6 C3H6O-ACETONE\Figure\structures-andre\3.png | 10.22 ±  0.02 | 10.20 | 10.20 – 10.24 | 10.17 – 10.21 |
| methyl vinyl ether | **4** |  | 8.95 ± 0.01 | – | 8.94 – 8.96 | 8.91 – 8.93 |
| methoxy methyl carbene | **5a** | A close-up of a stethoscope with balls  Description automatically generated with low confidence | – | 7.72 | 7.67 – 7.75 | 7.64 – 7.72 |
| **5b** | A picture containing indoor, device, accessory  Description automatically generated | – | 7.54 | 7.49 – 7.57 | 7.46 – 7.54 |
| **5t**  (triplet) | A picture containing indoor, device  Description automatically generated | – | 6.32 | 6.27 – 6.35 | 6.24 – 6.32 |
| – | 11.02 a  (q-state) | 11.97 – 11.05 | 11.94 – 11.02 |
| 1-methyleneoxyethyl | **6a** | A close-up of a stethoscope  Description automatically generated with low confidence | – | 7.05 | 7.00 – 7.08 | 6.97 – 7.05 |
| **6at**  (triplet) | A picture containing indoor, accessory, necklet  Description automatically generated | – | 6.53 | 6.48 – 6.56 | 6.45 – 6.53 |
| – | 10.79 a  (q-state) | 10.74 – 10.82 | 10.71 – 10.79 |
| **6b** | A picture containing indoor, accessory  Description automatically generated | – | 7.27 | 7.22 – 7.30 | 7.19 – 7.27 |
| **6bt**  (triplet) | A picture containing indoor, accessory, device  Description automatically generated | – | 6.53 | 6.48 – 6.56 | 6.45 – 6.53 |
| – | 10.76 a  (q-state) | 10.71 – 10.79 | 10.68 – 10.76 |

a These isomers are not observable in these experiments because their IEs are much higher than the maximum photon energy (9.43 eV) used in the experiment.

Table S4. Absorption peaks observed in acetone (CH3COCH3)ice before and after electron irradiation at 5 K.

|  |  |  |
| --- | --- | --- |
| Pristine acetone ice, before irradiation (cm−1) | Assignment4 | Approximate motion |
| 3002 | *ν*1, *ν*13 | CH3 asym. stretch |
| 2967 | *ν*9, *ν*20 | CH3 asym. stretch |
| 2921 | *ν*2, *ν*14 | CH3 sym. stretch |
| 2854 | 2*ν*21 | Overtone |
| 2781 | *ν*3+*ν*6 | Combination |
| 2581 | *ν*3+*ν*7 | Combination |
| 1708 | *ν*3 | C=O stretch |
| 1443 | *ν*21 | CH3 asym. def |
| 1419 | *ν*4 | CH3 asym. def |
| 1365 | *ν*16 | CH3 sym. def |
| 1351 | *ν*5 | CH3 sym. def |
| 1229 | *ν*17 | CCC asym. stretch |
| 1096 | *ν*22 | CH3 rock |
| 1071 | *ν*6 | CH3 rock |
| 899 | *ν*18 | CH3 rock |
| 793 | *ν*7 | CCC sym. stretch |
| New absorption after irradiation (cm−1) | Assignment4 |  |
| 2128 | *ν*(CO)/  *ν*2(H2CCO) | CO stretch |

Table S5. Absorption peaks observed in acetone-d6 (CD3COCD3) ice before and after electron irradiation at 5 K.

|  |  |  |
| --- | --- | --- |
| Pristine acetone-d6 ice, before irradiation (cm−1) | Assignment5 | Approximate motion |
| 2341 | *ν*4+*ν*15 | Combination |
| 2255 | *ν*9, *ν*20 | CD3 asym. stretch |
| 2222 | *ν*1, *ν*13 | CD3 asym. stretch |
| 2132 | *ν*4+*ν*5 | Combination |
| 2112 | *ν*2, *ν*14 | CD3 sym. stretch |
| 1733 | *ν*5+*ν*7 | Combination |
| 1697 | *ν*3 | C=O stretch |
| 1662 | *ν*5+*ν*8 | Combination |
| 1253 | *ν*15 | CD3 asym. def |
| 1092 | *ν*4 | CD3 asym. def |
| 1031 | *ν*16 | CD3 sym. def |
| 965 | 2*ν*19 | CD3 rock |
| 893 | *ν*6, *ν*22 | CD3 rock |
| New absorption after irradiation (cm−1) | Assignment6 |  |
| 2096 | *ν*5 (tentative) | CD3 sym. stretch (CD3C(OD)CD2) |

**Table S6.** Integrated ion signals and relative signal strengths of the different isotopologues of propen-2-ol (**2**) in irradiated CH3COCH3−CD3COCD3 ice.

|  |  |  |  |
| --- | --- | --- | --- |
| *m/z* | Molecular formula | Integrated signal | Relative signal |
| 58 | C3H6O | 329 ± 13 | 0.50 ± 0.03 |
| 59 | C3H5DO | 638 ± 29 | 1 |
| 60 | C3H4D2O | 33 ± 12 | 0.05 ± 0.02 |
| 61 | C3H3D3O | 10 ± 9 | 0.02 ± 0.01 |
| 62 | C3H2D4O | 7 ± 5 | 0.01 ± 0.01 |
| 63 | C3HD5O | 142 ± 37 | 0.22 ± 0.06 |
| 64 | C3D6O | 312 ± 13 | 0.48 ± 0.03 |

**Table S7**. Detected mass-to-charge ratios in the irradiated acetone and acetone-d6 ice and tentative assignments of molecules.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Mass-to-charge ratio | |  |  |  |  | |
| Acetone | Acetone-d6 | Formula | Tentative assignment | IE (eV) | | Corrected IE with electric field effect (eV) |
| 72 | 80 | C3H8O | 2-butanone | 9.52 ± 0.043 | | 9.45 – 9.53 |
| 86 | 92 | C4H6O2 | 2,3-butanedione | 9.23 – 9.301 | | 9.20 – 9.27 |
| 100 | 108 | C5H8O2 | 2,4-pentanedione | 8.85 ± 0.023 | | 8.80 – 8.84 |
| 114 | 124 | C6H10O2 | 2,5-hexanedione | – | | – |
| 116 | 128 | C6H12O2 | 2-prop-1-en-2-yloxypropan-2-ol | – | | – |
| 158 | 172 | C8H14O3 | 4-hydroxy-4-(prop-1-en-2-yloxy)pentan-2-one | – | | – |

**Table S8.** Cartesian coordinates for selected C3H6O structures. B3LYP/cc-pVTZ optimized geometry (distances in Å), electronic energies (in hartree), zero-point vibrational energies (ZPVE), extrapolated CCSD(T)/CBS energies (in hartree) and adiabatic ionization energies (IE) at CCSD(T)/CBS//B3LYP/cc-pVTZ level of theory.

|  |
| --- |
| **1**, Acetone (*C*2v)  C 0.000000 1.288092 –0.620789  C –0.000000 0.000000 0.175466  H –0.876805 1.331963 –1.270830  H 0.876805 1.331963 –1.270830  H 0.000000 2.140897 0.052651  C –0.000000 –1.288092 –0.620789  H –0.876805 –1.331963 –1.270830  H –0.000000 –2.140897 0.052651  H 0.876805 –1.331963 –1.270830  O –0.000000 0.000000 1.384697  E = –193.2331603  E[CCSD(T)/CBS] = –192.9201031  ZPVE = 52.2233 kcal mol–1  IE = 9.70 eV  Frequency Intensity  43.3611 0.0000  136.6537 0.0021  379.3676 1.4689  490.0400 0.3827  535.5428 14.7988  781.9256 1.8237  885.4521 9.9750  885.4690 0.0000  1085.1343 0.0258  1120.3492 2.5912  1233.9829 74.8958  1387.1958 18.7148  1387.8563 56.8165  1460.7372 0.6096  1466.3440 0.0000  1470.9001 27.9261  1488.3742 18.6373  1793.7782 175.0413  3025.4480 1.2215  3032.5185 7.1208  3077.3937 0.0000  3084.7486 19.7270  3138.5398 12.3851  3139.6114 7.4501 |
| **1+**, Acetone radical cation (*C*2)  C –0.001471 1.326832 –0.589947  C –0.000000 –0.000000 0.152284  H –0.910702 1.338692 –1.197145  H 0.872452 1.318096 –1.245695  H 0.025010 2.163548 0.100767  C 0.001471 –1.326832 –0.589947  H –0.872452 –1.318096 –1.245695  H –0.025010 –2.163548 0.100767  H 0.910702 –1.338692 –1.197145  O 0.000000 0.000000 1.356225  E = –192.8834063  E[CCSD(T)/CBS] = –192.5610784  ZPVE = 50.9363 kcal mol–1  Frequency Intensity  47.8843 0.0023  141.5308 0.5411  334.7063 1.8206  363.4011 3.8903  476.8309 0.0008  692.1956 1.7829  897.1665 0.0092  900.9593 0.4029  1006.5598 0.3124  1064.8662 14.5513  1079.3092 1.2411  1301.7499 8.7149  1347.5160 0.2416  1422.0634 11.5468  1429.8093 22.1708  1438.8125 0.3620  1462.0548 36.5236  1619.3022 0.0004  3023.1233 47.9646  3030.4842 21.2369  3097.6561 0.0256  3104.4229 33.1251  3173.5431 0.3054  3174.5477 20.0913 |
| **2a**, Acetone enol (*C*s)  C 0.884998 –1.113068 0.000000  C 0.009183 0.096873 0.000000  H 0.679520 –1.727319 –0.878845  H 0.679520 –1.727319 0.878845  H 1.935803 –0.834640 0.000000  C 0.436548 1.358491 0.000000  H –0.251272 2.194704 0.000000  H 1.491561 1.580920 0.000000  O –1.312053 –0.260683 0.000000  H –1.855755 0.534703 0.000000  E = –193.2145068  E[CCSD(T)/CBS] = –192.9018861  ZPVE = 52.9908 kcal mol–1  IE = 8.80 eV  Frequency Intensity  187.3283 1.1643  411.6287 1.5652  441.6040 100.7564  483.3059 17.7674  509.1547 0.2782  726.7750 0.8548  817.2377 70.0750  861.8940 4.9361  983.3085 17.6640  1023.2629 32.8677  1075.2204 0.4398  1204.1578 144.1494  1362.5961 13.7729  1415.9614 26.6198  1455.3824 3.9278  1474.4121 7.5757  1492.9396 7.9098  1717.3330 153.5019  3032.4016 18.5007  3079.2851 13.7439  3130.5369 14.5274  3143.4238 4.8778  3239.7196 8.8899  3798.7554 29.4014 |
| **2a+**, Acetone enol radical cation (*C*s)  C –0.116551 –1.420121 0.000000  C 0.000000 0.047012 0.000000  H –1.154734 –1.737476 0.000000  H 0.403462 –1.826872 0.873819  H 0.403462 –1.826872 –0.873819  C 1.248164 0.721810 0.000000  H 1.305829 1.803517 0.000000  H 2.167529 0.153657 0.000000  O –1.112705 0.708045 0.000000  H –1.013584 1.677482 0.000000  E = –192.8980634  E[CCSD(T)/CBS] = –192.5766502  ZPVE = 52.2404 kcal mol–1  Frequency Intensity  49.9316 2.1791  337.8396 0.0386  396.9033 0.8232  504.1019 10.0713  516.2239 13.5184  688.0623 101.4020  863.1349 6.5665  883.0662 52.6666  976.2592 4.0990  1031.4099 3.4012  1056.6947 3.8967  1177.8123 158.8569  1368.8930 92.0166  1433.7743 21.0690  1435.8196 17.5910  1460.3951 25.4498  1516.1887 73.0549  1540.7850 89.6238  3015.1288 50.1181  3057.4403 9.2174  3144.1412 21.5043  3161.6406 5.9289  3260.6477 10.8794  3666.3675 184.9125 |
| **2b**,Acetone enol (*C*s)  C 0.776425 –1.166010 0.000000  C 0.013967 0.122323 0.000000  H 0.527893 –1.763239 –0.882473  H 0.527893 –1.763239 0.882473  H 1.849012 –0.988840 0.000000  C 0.560752 1.334031 0.000000  H –0.054609 2.221439 0.000000  H 1.632750 1.448615 0.000000  O –1.353680 –0.003049 0.000000  H –1.593024 –0.933782 0.000000  E = –193.2115300  E[CCSD(T)/CBS] = –192.8992280  ZPVE = 52.7952 kcal mol–1  IE = 8.7 eV  Frequency Intensity  202.8336 4.6008  249.9783 81.4330  413.3069 1.2100  472.7419 3.1359  503.2637 6.0558  740.5189 10.0632  847.6581 59.5270  853.3020 17.2559  979.5839 44.3935  1023.9128 2.2774  1074.0002 0.2970  1235.1715 35.8829  1327.2109 204.5558  1413.6977 7.4950  1440.9338 13.2862  1480.4724 7.2447  1491.1741 5.0486  1742.9148 93.7090  3008.2914 29.3854  3049.4967 19.9916  3125.5839 11.8057  3166.1677 0.2301  3255.5412 6.1575  3833.0242 55.4445 |
| **2b+**, Acetone enol radical cation (*C*s)  C 0.170487 –1.404240 0.000000  C 0.000000 0.062418 0.000000  H –0.777365 –1.938630 0.000000  H 0.756572 –1.703459 0.874699  H 0.756572 –1.703459 –0.874699  C 1.085928 0.969942 0.000000  H 0.895576 2.034655 0.000000  H 2.101816 0.602501 0.000000  O –1.170342 0.619379 0.000000  H –1.908927 –0.015364 0.000000  E = –192.9000084  E[CCSD(T)/CBS] = –192.5784944  ZPVE = 52.3623 kcal mol–1  Frequency Intensity  41.3179 0.7449  380.9711 0.1493  395.7799 0.6806  499.7314 13.4746  524.0014 3.8402  674.2079 116.3003  856.0381 6.4449  901.9067 6.1938  985.4888 10.7773  1033.9370 29.1984  1058.8680 17.0411  1176.9209 102.3452  1377.3590 44.9495  1434.7348 16.2037  1438.1265 138.5743  1453.5257 14.9907  1505.9555 85.7278  1562.2445 56.3008  3017.9836 40.4807  3065.6771 10.7328  3131.9248 2.3822  3157.1443 26.7637  3276.1903 15.3731  3677.9094 235.2477 |
| **3**, Propylene oxide (*C*1)  O 0.828151 –0.788103 –0.239678  C –0.151978 –0.036276 0.485663  C 1.039391 0.616002 –0.061056  H 0.949431 1.214820 –0.962147  H 1.863181 0.881727 0.593531  C –1.507102 0.097896 –0.148350  H –2.072435 0.904642 0.322842  H –2.078890 –0.824440 –0.033483  H –1.414651 0.312331 –1.212823  H –0.153708 –0.249991 1.551964  E = –193.1848099  E[CCSD(T)/CBS] = –192.8734273  ZPVE = 53.4227 kcal mol–1  IE = 10.20 eV  Frequency Intensity  206.8626 0.4530  366.6999 3.6260  410.5787 4.5829  771.9818 7.1502  845.3082 40.6571  908.1404 2.5280  974.1144 15.3056  1042.4171 8.6802  1130.4220 6.6258  1156.5150 1.0942  1165.4396 4.0121  1188.4077 0.6584  1294.6846 5.9149  1407.1784 3.4512  1440.1552 21.7397  1483.5629 5.0692  1497.8997 5.4985  1531.4050 5.0971  3027.9961 18.1314  3077.7230 29.2458  3085.1945 22.1969  3086.4761 9.1150  3109.3152 38.1208  3161.2533 31.8449 |
| **3+**, Propylene oxide radical cation (*C*1)  O –0.812977 0.825585 –0.170935  C 0.176116 –0.080792 0.488006  C –1.063539 –0.603419 –0.101799  H –1.122401 –1.034899 –1.100128  H –1.912728 –0.827742 0.546067  C 1.520712 –0.074656 –0.171100  H 2.053903 –0.946042 0.224208  H 2.088834 0.814749 0.097370  H 1.443780 –0.162172 –1.252650  H 0.152698 0.104636 1.561969  E = –192.8151624  E[CCSD(T)/CBS] = –192.4931845  ZPVE = 51.0130 kcal mol–1  Frequency Intensity  171.0917 1.0275  265.0722 6.2472  337.4290 0.9421  399.6757 7.4099  637.9161 5.9540  741.1917 27.1708  909.9490 10.0678  928.8572 7.2026  1019.1844 26.9892  1100.6388 6.2430  1151.0243 22.8081  1172.3911 0.9912  1246.3029 8.3529  1344.6340 5.5320  1392.0829 28.4475  1425.9301 42.2753  1436.6627 9.7465  1483.7257 16.5636  3016.3457 35.4920  3037.1040 106.5865  3082.3838 11.5075  3103.1771 10.1779  3135.9039 35.4710  3145.4364 3.78350 |
| **5a**, methoxy methyl carbene  C –1.834310 0.119978 0.000000  C –0.422597 0.613974 0.000000  H –2.336536 0.556213 –0.868084  H –2.336536 0.556213 0.868084  H –1.951761 –0.968260 0.000000  O 0.368176 –0.422620 0.000000  C 1.787398 –0.162473 0.000000  H 2.208044 –0.626648 –0.889807  H 2.208044 –0.626648 0.889807  H 1.951377 0.912212 0.000000  E = –193.1294754  E[CCSD(T)/CBS] = –192.8259877  ZPVE = 51.6760 kcal mol–1  Frequency Intensity  96.4397 3.7746  144.0836 4.5811  247.9529 5.2190  329.9715 13.3721  557.3315 10.2882  879.9765 9.6493  907.9582 1.8274  1013.4830 6.7496  1119.3066 11.3806  1178.7087 1.2988  1181.2616 69.8272  1315.1482 167.9477  1361.6062 12.8495  1448.2786 11.1378  1451.6717 5.2039  1475.3827 9.4937  1490.9292 4.4204  1500.0949 14.5144  2989.8054 25.9075  3045.4078 41.6049  3067.4877 2.9670  3074.0230 30.3611  3127.6556 17.3186  3143.9347 6.4613 |
| **5a+**, methoxy methyl carbene radical cation  C –1.345321 –1.367745 0.000000  C –0.138649 –0.562750 0.000000  H –1.318053 –2.025454 0.875388  H –1.318053 –2.025454 –0.875388  H –2.242849 –0.743855 0.000000  O 0.002157 0.649240 0.000000  C 1.344648 1.353676 0.000000  H 1.328187 1.957173 0.900051  H 1.328187 1.957173 –0.900051  H 2.120983 0.597370 0.000000  E = –192.8538541  E[CCSD(T)/CBS] = –192.5424418  ZPVE = 51.7487 kcal mol–1  Frequency Intensity  95.5055 1.7763  143.9092 0.2521  206.5568 6.3309  236.3693 10.4435  476.0835 8.4180  736.1612 70.5382  949.4676 15.3715  957.8452 5.7378  1106.3270 5.0296  1155.1684 0.1243  1181.1532 5.8559  1356.8490 67.9303  1395.1234 21.9253  1413.4977 63.6228  1438.3015 6.5435  1462.9248 15.5603  1477.7192 27.2187  1731.7704 312.9276  3001.8939 50.7238  3067.4975 23.9788  3087.3813 0.9066  3096.3889 18.3536  3210.1442 4.9045  3214.7029 4.3192 |
| **5b**, methoxy methyl carbene  C –1.967297 –0.009938 0.086807  C –0.561144 –0.495334 0.303981  H –2.671119 –0.757881 0.442718  H –2.112051 0.079274 –0.998785  H –2.207301 0.961828 0.531498  O 0.358521 0.419037 0.199574  C 0.114972 1.839428 –0.097230  H –0.448434 1.945139 –1.021268  H 1.102252 2.275793 –0.204388  H –0.415857 2.310772 0.726712  E = –193.1164876  E[CCSD(T)/CBS] = –192.8133171  ZPVE = 51.3223 kcal mol–1  Frequency Intensity  56.8599 0.8443  169.0002 0.4241  340.8810 0.7486  378.9863 0.8921  573.2025 0.5111  783.7655 3.8064  810.9238 5.3502  948.1938 2.9040  1049.9960 33.8844  1118.7530 1.2926  1162.8999 0.2201  1308.7404 78.1168  1347.4503 45.1136  1435.7419 14.7232  1454.3453 0.2847  1481.0182 12.4335  1493.3063 3.9611  1500.1037 18.0625  2978.2132 5.8170  3033.9842 15.6102  3055.5562 14.4785  3120.2133 9.1297  3137.6556 15.8834  3160.6961 12.3819 |
| **5b+**, methoxy methyl carbene radical cation  C 1.631653 0.514275 0.218985  C 0.637480 –0.518952 –0.003520  H 2.375675 0.442195 –0.581605  H 2.162138 0.276400 1.147145  H 1.204950 1.519691 0.262539  O –0.560365 –0.602081 –0.163446  C –1.606348 0.519368 –0.191571  H –1.098455 1.464413 –0.040025  H –2.285399 0.256745 0.610827  H –2.060513 0.421606 –1.170382  E = –192.8480813  E[CCSD(T)/CBS] = –192.5364994  ZPVE = 51.5962 kcal mol–1  Frequency Intensity  49.9728 1.0627  87.5585 3.2724  229.0026 1.7788  363.3434 0.6138  518.5413 21.4952  633.4510 40.5322  905.2366 0.7924  974.0019 5.9095  1089.1775 11.8098  1126.5234 2.7437  1130.2990 0.9726  1357.9320 66.2982  1397.7987 18.0950  1399.2409 51.4471  1438.8174 13.8859  1451.9227 15.1939  1476.1662 25.8152  1777.7934 252.7488  3002.1574 44.1903  3068.3113 27.3737  3088.6102 0.9446  3092.2211 19.2826  3215.2555 6.6177  3218.7121 1.9833 |
| **5t**, methoxy methyl carbene, triplet  C 1.748119 0.462146 0.153742  C 0.562437 –0.279832 –0.340131  H 2.579779 0.338336 –0.538175  H 2.067438 0.092314 1.137002  H 1.552263 1.539281 0.252384  O –0.600105 –0.381062 0.297264  C –1.673696 0.476586 –0.143586  H –1.382462 1.524951 –0.060933  H –2.519120 0.272398 0.508413  H –1.933749 0.248314 –1.176951  E = –193.0829400  E[CCSD(T)/CBS] = –192.7739003  ZPVE = 51.1986 kcal mol–1  Frequency Intensity  87.1747 3.0628  137.4062 2.1173  147.6986 2.0881  406.6671 2.1171  428.4762 7.7781  846.6401 10.4910  970.5690 51.7888  1018.3177 1.6745  1079.7001 7.3052  1153.9042 1.7348  1185.8253 0.6120  1312.1986 139.1539  1382.2459 1.5666  1459.1392 4.4761  1462.3981 5.1591  1475.3775 0.4072  1487.8498 6.2098  1495.1653 10.6581  2943.5269 40.3305  2980.3417 32.0417  3024.7898 43.9049  3095.0809 31.1062  3100.7100 9.8808  3132.7414 19.4783 |
| **5t+**, methoxy methyl carbene radical cation, triplet  C 1.945377 0.183741 0.141902  C 0.551708 0.306333 –0.242016  H 2.397015 –0.611908 –0.460243  H 2.048707 –0.020281 1.210808  H 2.460999 1.108232 –0.138672  O –0.463273 0.215825 0.429127  C –1.867438 0.369198 –0.121224  H –2.285814 1.193983 0.443850  H –2.348404 –0.573934 0.110688  H –1.791816 0.566850 –1.184201  E = –192.8538544  E[CCSD(T)/CBS] = –192.5424418  ZPVE = 51.7478 kcal mol–1  Frequency Intensity  94.9016 1.7488  143.6276 0.2799  206.4249 6.3210  236.4269 10.4320  476.1502 8.3877  736.4979 70.4535  949.1946 15.4197  957.8013 5.7183  1106.2516 5.1006  1155.2380 0.1252  1181.2397 5.8764  1356.6029 67.6154  1395.1081 21.9085  1413.4565 63.6970  1438.3149 6.5643  1462.9235 15.5514  1477.7484 27.2402  1731.5786 312.5163  3002.0938 50.5012  3068.3334 23.9973  3087.2200 0.9038  3096.4501 18.5285  3209.9194 4.9023  3214.5891 4.3213 |
| **5t+**, methoxy methyl carbene radical cation, tripletq-state  C 1.830365 0.248197 0.128868  C 0.599571 –0.193367 –0.507161  H 2.568755 0.405117 –0.669147  H 2.218509 –0.500966 0.827349  H 1.725570 1.218161 0.638283  O –0.601211 –0.384942 0.314981  C –1.714160 0.345680 –0.004757  H –1.442769 1.374410 –0.325309  H –2.455732 0.273814 0.782626  H –2.081835 –0.048064 –0.995715  E = –192.6845330  E[CCSD(T)/CBS] = –192.3634925  ZPVE = 47.8669 kcal mol–1  Frequency Intensity  70.2827 4.1422  107.2506 5.1729  134.9396 14.3491  332.7074 2.9236  392.0071 2.9162  678.9430 7.7607  817.2803 8.8738  901.4497 241.8780  997.2504 5.5268  1022.4438 39.3760  1133.9441 5.3261  1161.1857 7.8787  1228.8157 127.4985  1272.8334 46.9087  1328.5364 108.5492  1366.4682 15.2269  1412.4624 9.6033  1459.2887 3.7782  2664.4944 260.8535  2839.5885 164.8977  2937.5075 72.2139  2996.8683 69.3914  3041.5609 31.6849  3185.2598 12.4669 |
| **6a**,1-methyleneoxyethyl  C 1.849170 –0.035737 0.000000  C 0.452807 –0.532823 0.000000  H 2.410972 –0.373173 0.878625  H 1.852544 1.053931 0.000000  H 2.410972 –0.373173 –0.878625  O –0.508597 0.338288 0.000000  C –1.811328 0.191523 0.000000  H –2.237102 –0.799962 0.000000  H –2.369795 1.107463 0.000000  H 0.182808 –1.581922 0.000000  E = –193.1132045  E[CCSD(T)/CBS] = –192.8057130  ZPVE = 50.7849 kcal mol–1  Frequency Intensity  23.0379 0.5168  206.1886 0.0027  296.8997 2.7754  319.5769 112.0657  522.4038 6.4814  569.0577 7.8448  662.6667 16.1524  907.9233 31.4272  1037.5790 0.0740  1118.6766 4.6642  1172.6609 5.9020  1228.4298 71.3299  1375.5148 171.8412  1429.8952 23.3940  1453.1101 95.6229  1463.4629 6.2991  1489.1758 2.8655  1535.6161 44.6074  2980.4972 75.7292  3001.5530 30.1943  3099.6532 8.7135  3151.5320 14.0284  3159.2684 25.1375  3320.1775 5.3144 |
| **6a+**,1-methyleneoxyethyl radical cation  C 0.986042 –1.510508 0.000000  C –0.137066 –0.589174 0.000000  H 0.905587 –2.175329 0.870065  H 1.944137 –0.998350 0.000000  H 0.905587 –2.175329 –0.870065  O 0.087084 0.688251 0.000000  C –0.845742 1.637396 0.000000  H –1.890539 1.356992 0.000000  H –0.456670 2.641833 0.000000  H –1.176518 –0.911184 0.000000  E = –192.8628855  E[CCSD(T)/CBS] = –192.5471165  ZPVE = 51.1827 kcal mol–1  Frequency Intensity  135.4274 0.3663  215.3904 4.4072  307.0168 9.2775  433.0774 9.2929  535.5964 1.7544  731.7787 34.1669  811.3312 12.8492  886.5432 81.7371  1032.2226 0.8920  1059.1482 123.0415  1151.2434 7.5950  1206.2477 4.3215  1293.6695 40.0952  1382.0509 70.9304  1425.0538 11.9950  1426.2041 19.3296  1473.0470 12.9586  1535.5679 17.3439  2992.5648 69.1800  3024.1071 11.1185  3132.7030 54.5609  3141.5258 20.4948  3154.4341 9.0617  3316.8403 19.0392 |
| **6at**,1-methyleneoxyethyl, triplet  C 1.348162 –1.197781 –0.025289  C –0.023091 –0.663420 –0.156249  H 1.668687 –1.263467 1.024364  H 2.068070 –0.554868 –0.537200  H 1.406326 –2.197519 –0.454275  O –0.168010 0.650101 0.255816  C –1.398018 1.203719 0.021447  H –1.957378 0.841180 –0.831931  H –1.488012 2.217129 0.378893  H –0.904745 –1.285038 –0.033110  E = –193.0948875  E[CCSD(T)/CBS] = –192.7848177  ZPVE = 49.8580 kcal mol–1  Frequency Intensity  89.0645 4.4431  173.5962 0.5584  222.3677 6.9915  295.1746 0.9084  481.7065 1.7534  591.7096 21.3715  614.7865 36.4555  889.7726 8.0580  1020.0611 3.2008  1113.5290 10.3183  1125.7160 5.4083  1204.7918 64.2019  1258.3356 237.3613  1366.8562 40.8209  1418.0871 34.8732  1461.4508 9.3651  1467.0128 0.4222  1486.3325 2.8857  2953.1110 34.8164  3042.0943 15.3439  3101.1092 4.1561  3111.3365 34.0937  3125.1575 37.4654  3263.0300 9.5003 |
| **6at+**,1-methyleneoxyethyl radical cation, triplet  C 1.795666 –0.167959 0.015016  C 0.460843 0.387478 –0.127268  H 2.288311 –0.175046 –0.966119  H 1.786975 –1.166332 0.443360  H 2.402886 0.508862 0.630264  O –0.564044 –0.313641 0.246703  C –1.835103 0.073515 0.171895  H –2.071487 1.049807 –0.229641  H –2.542411 –0.653586 0.534302  H 0.263674 1.376195 –0.536867  E = –192.8628850  E[CCSD(T)/CBS] = –192.5471210  ZPVE = 51.1804 kcal mol–1  Frequency Intensity  134.3215 0.3604  215.2514 4.4114  306.8848 9.2799  433.1487 9.2761  535.4907 1.7536  731.7443 34.1972  811.3209 12.8303  886.4524 81.5571  1032.3252 0.8875  1059.1238 123.0695  1151.2328 7.5629  1206.1469 4.3320  1293.8439 40.0900  1381.9560 70.7666  1424.9917 11.9919  1426.2279 19.3214  1472.9701 12.9515  1535.5729 17.2960  2992.8886 69.1229  3024.7181 11.1333  3132.3987 53.9471  3141.3007 21.0942  3154.1824 9.0451  3316.7098 19.0546 |
| **6at+**,1-methyleneoxyethyl radical cation, triplet, q-state  C 1.655344 –0.241697 0.056224  C 0.488344 0.730186 –0.032778  H 1.984342 –0.541490 –0.942748  H 1.356033 –1.119184 0.629306  H 2.453184 0.299133 0.563071  O –0.639845 0.232933 –0.639218  C –1.796790 –0.045843 0.041246  H –2.419444 0.819198 0.273452  H –1.785316 –0.962323 0.632305  H 0.689460 1.748378 –0.399214  E = –192.7087577  E[CCSD(T)/CBS] = –192.3844963  ZPVE = 47.5123 kcal mol–1  Frequency Intensity  144.8821 3.4012  164.0218 2.2568  286.6558 6.9277  363.4720 45.6959  469.8462 6.5272  491.4564 10.4745  636.2938 144.3598  794.7816 91.8971  857.4964 13.9691  950.0922 5.8398  976.3812 0.8635  989.2137 4.9183  1034.1449 4.5591  1172.0870 24.7049  1310.4139 39.9024  1358.0011 14.1113  1425.5162 32.1606  1443.9948 14.6361  2952.8459 205.7888  3011.7653 172.4843  3016.3455 20.8433  3099.2695 7.5398  3132.3481 11.0413  3153.9932 63.8612 |
| **6b**,1-methyleneoxyethyl  C 1.429739 –0.644198 0.000000  C 0.659138 0.606942 0.000000  H 2.498036 –0.440438 0.000000  H 1.192188 –1.266160 –0.877668  H 1.192188 –1.266160 0.877668  O –0.641995 0.574564 0.000000  C –1.437441 –0.470696 0.000000  H –1.031561 –1.467043 0.000000  H –2.484274 –0.233590 0.000000  H 1.065801 1.602739 0.000000  E = –193.1194698  E[CCSD(T)/CBS] = –192.8136406  ZPVE = 51.3465 kcal mol–1  Frequency Intensity  230.2630 4.4944  279.2240 0.1121  301.5178 24.1596  398.6635 55.4454  548.3303 52.3548  592.1802 4.1683  645.6668 2.1549  937.8283 8.4751  1027.1509 0.1573  1120.9249 44.2542  1156.8990 7.4211  1213.0137 33.1919  1390.2059 38.1856  1429.6286 135.3225  1449.2262 38.5075  1454.0217 9.7268  1480.7322 12.2494  1514.1884 4.7781  2930.2562 38.9185  2942.2856 42.7964  3118.6876 9.6412  3181.2097 7.7450  3246.7160 4.8384  3328.5677 5.1193 |
| **6b+**,1-methyleneoxyethyl radical cation  C –1.441133 0.534417 0.000000  C –0.021174 0.868893 0.000000  H –2.040008 1.440573 0.000000  H –1.702257 –0.066963 0.880685  H –1.702257 –0.066963 –0.880685  O 0.939901 –0.016308 0.000000  C 0.800786 –1.330033 0.000000  H –0.180900 –1.779945 0.000000  H 1.733253 –1.871240 0.000000  H 0.375108 1.876108 0.000000  E = –192.8609005  E[CCSD(T)/CBS] = –192.5464685  ZPVE = 51.4455 kcal mol–1  Frequency Intensity  121.0535 1.8860  273.7486 4.6257  293.8845 2.4211  504.9968 12.3757  585.8411 6.1165  703.1492 15.2404  786.9320 35.1146  931.8280 13.5264  1040.6974 0.0051  1057.3183 117.8034  1117.1836 7.0607  1195.0183 3.1213  1275.9854 35.2110  1369.7773 19.0440  1446.8448 19.7408  1453.4462 13.8444  1472.1198 43.6517  1519.8502 9.6546  2987.1359 25.6550  3026.4026 3.8506  3149.9394 7.9123  3151.5561 54.8239  3205.7604 29.6204  3316.1890 14.6591 |
| **6bt**, 1-methyleneoxyethyl, triplet  C –1.712029 0.824489 0.327697  C –0.427147 0.332181 –0.209490  H –2.132179 1.582897 –0.331823  H –1.597240 1.271541 1.325845  H –2.433312 0.009885 0.426540  O 0.150043 –0.692382 0.522823  C 1.229807 –1.273945 –0.086384  H 1.650324 –2.098976 0.464947  H 1.817632 –0.670900 –0.765656  H 0.272569 0.978957 –0.730592  E = –193.0941805  E[CCSD(T)/CBS] = –192.7846289  ZPVE = 49.7378 kcal mol–1  Frequency Intensity  93.2074 3.4117  170.4327 0.5613  206.0163 3.3482  298.2683 3.0813  480.2045 0.2452  525.0949 31.9584  578.8678 36.2038  894.5851 9.1964  1016.9600 3.8095  1112.9386 7.1655  1128.7505 5.4925  1208.7387 63.6849  1261.4890 240.5474  1368.7635 40.4161  1419.2883 38.3129  1461.7983 7.5836  1472.2464 1.8357  1486.8298 3.3653  2950.9580 34.8010  3041.8042 15.5088  3101.2670 4.2814  3119.2037 24.2336  3123.1627 40.5538  3271.2485 10.3874 |
| **6bt+**, 1-methyleneoxyethyl radical cation, triplet  C –1.792090 –0.155763 –0.017984  C –0.462371 0.401340 0.160652  H –2.385249 0.523491 –0.644161  H –2.308996 –0.169283 0.950563  H –1.770813 –1.151726 –0.451426  O 0.572937 –0.295949 –0.191072  C 1.840954 0.093056 –0.082249  H 2.558527 –0.630777 –0.430747  H 2.065305 1.067598 0.330290  H –0.277499 1.388229 0.580271  E = –192.8628850  E[CCSD(T)/CBS] = –192.5471204  ZPVE = 51.1808 kcal mol–1  Frequency Intensity  134.5331 0.3617  215.2243 4.4110  306.8729 9.2794  433.1392 9.2753  535.4984 1.7543  731.7369 34.1983  811.3300 12.8339  886.4867 81.5601  1032.2995 0.8894  1059.2040 123.0845  1151.2528 7.5691  1206.1949 4.3354  1293.8731 40.0825  1381.9692 70.8260  1425.0049 11.9942  1426.1870 19.3227  1472.9845 12.9505  1535.6029 17.2930  2992.7875 69.1332  3024.5317 11.1320  3132.4055 54.0330  3141.3171 20.9868  3154.3051 9.0527  3316.7234 19.0544 |
| **6bt+**,1-methyleneoxyethyl radical cation, triplet, q-state  C –1.683433 –0.221780 –0.066425  C –0.537255 0.768439 0.058490  H –2.515086 0.339181 –0.490030  H –1.962307 –0.616952 0.914511  H –1.389898 –1.036797 –0.727878  O 0.626258 0.254657 0.578141  C 1.738999 0.064491 –0.203512  H 1.951717 –0.990466 –0.399330  H 2.552303 0.754064 0.040910  H –0.740595 1.755381 0.499260  E = –192.7104871  E[CCSD(T)/CBS] = –192.3862877  ZPVE = 47.8024 kcal mol–1  Frequency Intensity  143.9840 2.5162  163.7291 2.3738  300.1649 5.7358  434.6810 16.4097  449.0680 24.5153  595.9410 177.6518  692.4751 59.2398  787.9562 103.4722  861.4352 4.9904  943.7548 1.5430  971.4944 1.2630  1004.6999 4.6518  1051.4545 6.8810  1179.3041 15.9405  1315.6496 43.9413  1360.3642 19.6637  1427.1415 32.1179  1444.7458 12.4923  2958.2485 301.8091  2993.1606 141.3534  3016.1739 9.9116  3099.2120 6.4473  3110.1069 65.1820  3133.3235 9.8122 |

**Table S9.** The ωB97X-D/6-311G(d,p) optimized geometries and harmonic frequencies of the reactants, transition states, and products depicted in Fig. 5.

|  |
| --- |
| **R0**, Acetone, CH3C(O)CH3  C 0.000000 1.285376 0.612598  C 0.000000 0.000000 -0.187852  O 0.000000 0.000000 -1.392832  C 0.000000 -1.285376 0.612598  H 0.943971 1.377015 1.159027  H -0.802116 1.278292 1.356041  H -0.116116 2.137148 -0.055773  H 0.116116 -2.137148 -0.055773  H -0.943971 -1.377015 1.159027  H 0.802116 -1.278292 1.356041  Frequencies  53.4499 133.5866 383.5578  492.7647 541.1902 795.5710  884.8346 894.6565 1086.0112  1122.8809 1244.2777 1387.7351  1397.4726 1463.9048 1468.6523  1473.9393 1491.5856 1852.1136  3043.4252 3048.6544 3112.8430  3118.9099 3165.8703 3167.3884 |
| **P0**, propen-2-ol, CH3C(OH)CH2  C -0.980498 -1.033274 0.000000  C -0.085172 -0.046750 0.000000  O -0.406360 1.275492 0.000000  C 1.397703 -0.231494 0.000000  H -2.048070 -0.838031 0.000000  H -0.659492 -2.065263 0.000000  H -1.361527 1.363465 0.000001  H 1.832950 0.246697 -0.881555  H 1.661868 -1.288384 -0.000004  H 1.832948 0.246689 0.881560  Frequencies  181.8918 419.4738 443.1288  494.3902 512.8506 734.1046  823.6144 877.8479 991.3134  1032.9915 1078.5027 1228.4877  1381.6810 1425.3841 1464.6694  1476.6993 1497.6885 1750.3240  3052.1622 3117.6329 3158.2009  3159.0225 3259.8322 3902.2729 |
| **TS0**  C 1.462468 0.264308 -0.018764  C 0.002851 -0.024197 -0.007499  O -0.430997 -1.226760 0.012078  C -1.106807 0.861681 0.044471  H 1.681870 1.004276 0.755286  H 1.737588 0.714953 -0.975914  H 2.047885 -0.637303 0.154511  H -1.460330 -0.560291 0.289328  H -1.699207 0.813470 -0.871004  H -1.010895 1.868228 0.441923  Frequencies  -2183.3396 111.1829 372.6432  423.8953 565.8434 671.0433  773.4529 906.3437 990.2182  1027.8534 1111.6509 1190.2282  1344.1638 1408.1479 1459.7540  1476.4764 1501.9741 1576.2689  1975.9951 3064.1761 3109.0196  3133.9494 3174.7429 3195.0570 |
| **R1**, CH3C(O)CH3·H2O  C -0.233169 1.335134 -0.033484  C -0.723346 -0.092043 -0.024373  O 0.033734 -1.035326 -0.099271  C -2.214958 -0.300450 0.078235  H -0.709838 1.910779 0.764527  H -0.523495 1.800900 -0.980954  H 0.852145 1.360855 0.061755  H -2.457239 -1.351287 -0.071462  H -2.740871 0.318618 -0.653544  H -2.556025 0.015010 1.069345  O 2.749788 -0.075538 -0.029128  H 2.964601 -0.253201 0.886700  H 1.931389 -0.570613 -0.171449  Frequencies  44.8599 96.9296 127.4351  134.5612 166.8138 223.5359  318.3338 398.4345 498.1665  559.9697 654.0177 805.8163  891.1885 913.3768 1097.5411  1129.2106 1264.4333 1394.3161  1405.1294 1465.7502 1472.1872  1477.8583 1501.4934 1674.7694  1825.5976 3041.7677 3049.2668  3113.7875 3120.5699 3161.5391  3169.4080 3763.7976 3957.4475 |
| **P1**, CH3C(OH)CH2·H2O  C -0.328959 1.348812 -0.162279  C -0.757938 0.085023 -0.083547  O 0.012088 -1.002449 -0.311123  C -2.159883 -0.308327 0.261524  H -1.006138 2.167098 0.039699  H 0.680263 1.590222 -0.476284  H 2.308818 0.484931 0.859912  H -2.163285 -0.943714 1.151420  H -2.589365 -0.892233 -0.557237  H -2.785677 0.565587 0.440807  O 2.597832 -0.038029 0.108381  H 3.218003 -0.676350 0.463240  H 0.938695 -0.724764 -0.393811  Frequencies  35.8064 106.0116 153.5592  183.1496 204.0923 286.2667  362.1544 428.4540 518.0219  539.8549 716.7164 786.4634  835.6364 884.9228 1000.6809  1038.2082 1077.0688 1304.2188  1411.9283 1428.5300 1476.0123  1494.1734 1505.9885 1632.6027  1736.9915 3049.5509 3114.3444  3154.4317 3166.6708 3260.5593  3688.8976 3875.7821 3983.3154 |
| **TS1**  C 0.040877 1.272258 -0.197644  C -0.589685 0.009702 -0.150292  O 0.054750 -1.054115 -0.428403  C -2.002503 -0.160158 0.327468  H -0.522693 2.127830 0.156786  H 0.628187 1.469462 -1.094496  H 1.288482 0.754934 0.343588  H -2.121745 -1.117524 0.835300  H -2.662691 -0.152244 -0.545676  H -2.304717 0.661338 0.978492  O 2.121703 -0.104932 0.245962  H 2.357307 -0.455360 1.107835  H 1.234113 -0.746864 -0.199501  Frequencies  -1894.9220 118.4046 124.7542  373.9518 465.3423 501.2940  559.3909 587.7429 619.6087  721.9188 764.2422 829.0781  882.6548 1002.5008 1042.7039  1096.9712 1168.9084 1327.9344  1382.5812 1420.0360 1466.2941  1480.7788 1499.4627 1530.0218  1591.4864 1679.9564 1933.1042  3056.9981 3123.1253 3131.4291  3165.6345 3220.4339 3909.4875 |
| **R2**, CH3C(O)CH3·(H2O)2  O -2.263614 1.412655 -0.427760  H -2.327652 1.435391 -1.382350  C 0.535345 0.773541 1.020602  C 1.248155 -0.139752 0.061082  O 0.753577 -1.185828 -0.310675  C 2.593685 0.301968 -0.450684  H 0.065325 0.183935 1.809544  H 1.197512 1.522522 1.456281  H 2.959203 -0.391841 -1.205826  H 3.301153 0.353400 0.382795  H 2.518566 1.311344 -0.865966  H -0.275730 1.275074 0.474465  O -2.007728 -1.312214 0.092698  H -2.187220 -1.677763 0.958365  H -2.323144 0.467063 -0.209370  H -1.049003 -1.410571 -0.038049  Frequencies  30.0781 58.8940 85.7965  123.9783 148.7993 182.6117  195.5879 200.1645 234.7920  262.1524 367.0018 398.5877  463.5375 513.0912 550.6592  664.6726 806.0459 838.7264  896.0110 944.6303 1090.2869  1121.6400 1263.3110 1394.6422  1412.9517 1465.1046 1476.2672  1487.1753 1500.6418 1666.1749  1687.2565 1809.3342 3011.2794  3046.6576 3111.3427 3116.2511  3155.6562 3170.2891 3636.5479  3690.6747 3957.9040 3967.6404 |
| **P2**, CH3C(OH)CH2·(H2O)2  O -1.653957 1.577689 -0.423159  H -1.394947 1.602955 -1.345823  C 0.632589 0.319045 1.320780  C 1.107670 -0.173235 0.165437  O 0.444110 -1.013502 -0.642898  C 2.459360 0.159880 -0.385169  H -0.327893 0.006138 1.712355  H 1.240953 0.977215 1.925347  H 2.361643 0.586471 -1.387075  H 3.048849 -0.755821 -0.479550  H 2.991460 0.862003 0.255983  H -0.817437 1.534451 0.062968  O -2.170715 -1.075058 0.075925  H -2.561412 -1.254956 0.930482  H -2.240045 -0.112548 -0.063174  H -0.454390 -1.193077 -0.296745  Frequencies  39.0128 77.2780 131.0755  158.4091 181.0715 214.5886  235.3113 245.8895 293.5566  309.5852 430.8060 493.6229  523.4601 537.9877 547.8276  747.1400 792.5144 831.0555  884.3404 981.0690 1001.7590  1041.8680 1076.6585 1307.2852  1410.2061 1430.5352 1475.4661  1490.5588 1498.4115 1653.3251  1659.6700 1716.3100 3052.4545  3118.5595 3157.0709 3172.0934  3266.9438 3506.2836 3624.5507  3739.9379 3946.4957 3968.8197 |
| **TS2**  O -1.699005 1.267331 -0.489782  H -1.587741 1.418717 -1.430842  C 0.472480 0.914578 0.929730  C 1.044866 -0.125316 0.177047  O 0.475472 -1.233074 -0.062514  C 2.394853 0.065883 -0.468978  H -0.216019 0.614201 1.718662  H 1.106914 1.757669 1.182113  H 2.379779 -0.332782 -1.484748  H 3.129227 -0.512119 0.099908  H 2.708717 1.110274 -0.475342  H -0.679208 1.291457 0.022687  O -1.928135 -1.054162 0.032183  H -2.325906 -1.212767 0.888822  H -1.940668 0.125642 -0.267686  H -0.834948 -1.231919 0.080527  Frequencies  -1563.4525 69.2758 102.3644  106.3293 173.4542 376.1070  395.6707 418.1767 496.5235  528.5967 562.0996 615.0470  633.7429 643.8013 706.8317  767.4122 849.1832 871.3277  999.1052 1047.2176 1089.8015  1172.9196 1313.7276 1362.4772  1397.2215 1435.1531 1467.2191  1481.6594 1508.2975 1541.5129  1589.1343 1660.3841 1710.9307  1779.0309 1843.5946 3059.1341  3123.1621 3134.0731 3158.6736  3212.5358 3914.8460 3946.4875 |
| **R3**, CH3C(O)CH3·(H2O)3  O 0.132863 2.040051 -0.505067  H 0.081234 1.912367 -1.452584  H 0.986379 0.661928 1.877864  C 0.624698 -0.261499 1.426789  C 1.255081 -0.497987 0.077023  O 0.706158 -1.171432 -0.774422  C 2.618478 0.087925 -0.151346  H -0.458176 -0.222048 1.324398  H 0.893675 -1.100301 2.078641  H 3.039165 -0.281397 -1.085408  H 3.282752 -0.144226 0.685956  H 2.496570 1.173393 -0.193048  O -1.982535 -1.579839 -0.383045  H -2.084322 -2.310109 0.226315  H -1.029292 -1.547285 -0.595160  H -2.382439 0.106888 -0.009487  O -2.383358 1.063085 0.187746  H -2.842542 1.162058 1.020540  H -0.757570 1.803188 -0.194522  Frequencies  41.1800 65.7447 76.2892  97.0629 108.6944 118.9635  148.9966 169.1855 197.5638  206.7886 228.1717 246.4648  252.8162 276.4639 368.4378  400.6943 447.6077 491.0581  546.8672 562.6565 680.4393  754.6271 806.4284 877.6061  906.5640 940.7528 1094.8088  1123.6783 1266.8688 1387.8148  1405.0098 1466.2002 1471.5532  1482.2599 1498.4477 1670.8468  1687.3373 1697.6131 1806.9347  3048.6062 3052.1206 3130.3434  3139.9165 3169.1433 3184.4865  3545.4079 3613.3910 3680.4300  3952.7815 3967.8299 3973.9560 |
| **P3**, CH3C(OH)CH2·(H2O)3  O -0.684412 1.868316 -0.593280  H -0.320740 1.296997 -1.277276  H -0.091490 1.700105 0.149661  C 0.873794 -0.135687 1.396447  C 1.484630 -0.210304 0.205837  O 0.889967 -0.647207 -0.923676  C 2.893244 0.225567 -0.047589  H -0.150120 -0.468498 1.515933  H 1.412888 0.207735 2.268591  H 2.908804 1.004617 -0.815143  H 3.476005 -0.616742 -0.428896  H 3.363007 0.607765 0.858315  O -1.489363 -1.738148 -0.352745  H -1.548190 -2.451630 0.281571  H 0.031821 -1.083289 -0.712619  H -2.107269 -1.040271 -0.052226  O -2.870815 0.478564 0.330955  H -3.037029 0.772603 1.226088  H -2.210714 1.100945 -0.032197  Frequencies  34.6909 56.2036 60.0889  100.5997 130.5001 180.8361  183.2893 224.3933 242.8117  256.7564 259.2569 277.1800  290.3716 365.9861 428.6054  497.9260 528.4641 540.9207  560.4671 624.3563 725.9231  751.7994 820.2907 855.2427  885.1849 1000.2483 1033.9505  1053.4576 1079.1137 1314.7901  1411.8355 1422.2280 1476.2327  1491.7317 1503.9942 1677.8933  1684.5655 1703.1489 1722.0918  3050.9458 3117.3434 3156.0753  3171.9182 3268.4103 3389.6866  3529.1923 3597.5796 3806.5648  3891.5462 3966.0377 3970.5331 |
| **TS3**  O 0.836883 1.951816 0.209325  H 0.477792 2.150469 1.076955  H 0.064821 1.422862 -0.345816  C -0.854219 0.432919 -1.205677  C -1.425887 -0.237689 -0.120313  O -0.877037 -1.170285 0.538884  C -2.773244 0.215119 0.399369  H -0.036051 -0.057613 -1.729382  H -1.490267 1.064945 -1.816110  H -2.710568 0.378487 1.477824  H -3.495704 -0.589598 0.238214  H -3.135685 1.118323 -0.093426  O 1.413401 -1.761654 -0.090679  H 1.411594 -2.136595 -0.971316  H 0.393268 -1.549325 0.166646  H 2.113517 -0.648147 0.081114  O 2.587546 0.321342 0.286756  H 3.273367 0.505662 -0.355877  H 1.767672 1.148680 0.276615  Frequencies  -1101.1789 41.8804 78.0259  93.3127 112.7206 136.7226  156.1908 325.3637 362.9665  387.3985 402.9528 471.2057  484.2237 547.4066 564.4771  594.8418 633.2741 655.7461  687.0627 702.5376 800.5369  858.8160 873.3081 1004.9825  1056.3676 1088.7940 1121.2025  1235.0970 1296.1367 1361.3028  1406.3400 1475.4764 1484.5599  1492.4828 1545.2745 1561.5631  1619.2598 1679.6432 1727.3953  1773.2438 1830.7405 1898.9257  2095.9545 3057.2735 3121.4497  3130.1715 3154.0591 3212.7055  3915.6591 3946.6844 3950.9369 |
| **R4**, CH3C(O)CH3·(H2O)4  O 0.093465 1.838235 1.213973  H 0.017188 2.709998 1.601186  H 0.931909 -0.405856 1.841861  C 1.239194 -1.223550 1.181342  C 1.376098 -0.627852 -0.189899  O 0.578295 -0.870615 -1.080790  C 2.496394 0.348716 -0.404860  H 0.480359 -2.004481 1.196340  H 2.197257 -1.603783 1.542700  H 2.546599 0.648998 -1.450358  H 3.450655 -0.075843 -0.083856  H 2.287913 1.219845 0.223813  O -1.662612 -2.126443 -0.050770  H -2.201089 -2.658732 -0.635799  H -0.906387 -1.817075 -0.578470  O -2.409590 0.511138 0.496099  H -1.728003 0.800560 1.114522  H -2.287693 -0.448969 0.416721  H -0.102842 1.955096 0.260363  O -0.784930 1.703482 -1.367311  H -0.313427 0.948089 -1.731695  H -1.559577 1.301889 -0.926431  Frequencies  36.6384 52.5336 71.3077  95.4330 105.5281 110.6062  145.9467 150.0704 156.9933  178.6942 201.1180 219.7177  230.8657 256.5956 266.9663  281.9999 401.7244 410.2301  413.4460 451.2319 500.0349  556.1242 564.3747 582.5914  603.4230 661.7375 768.2035  819.8193 857.8502 886.3902  929.2765 1045.1527 1105.1158  1134.9303 1275.8934 1394.1418  1403.6386 1468.2343 1473.1791  1483.8306 1496.5961 1657.7996  1673.3370 1691.0281 1707.0452  1793.0343 3047.2824 3052.6609  3124.4442 3131.3136 3168.7571  3171.7043 3483.0001 3588.3273  3643.4194 3707.0849 3830.1673  3877.7119 3960.5077 3966.0009 |
| **P4**, CH3C(OH)CH2·(H2O)4  O -0.638637 2.902178 -0.409758  H -1.310321 3.205439 0.202616  H -0.995542 2.089167 -0.789713  C -0.735729 -0.159586 -1.226819  C -1.339227 -0.510548 -0.076108  O -0.788308 -0.380538 1.139441  C -2.698757 -1.134204 -0.008208  H 0.274116 0.234593 -1.230366  H -1.241055 -0.299173 -2.173069  H -3.359334 -0.517601 0.606593  H -2.628575 -2.111674 0.476838  H -3.135960 -1.258423 -0.998607  O 1.269864 -2.307107 0.072253  H 0.592347 -2.143866 -0.592647  H 0.834706 -2.032082 0.885440  O 2.905363 -0.128673 -0.468383  H 3.140974 -0.114120 -1.394976  H 2.474870 -0.988459 -0.308325  H 0.756447 2.070858 0.551700  O 1.169719 1.344335 1.044106  H -0.003813 0.240317 1.116687  H 1.899412 1.009476 0.493370  Frequencies  39.0847 58.5108 64.1985  72.5896 91.4771 131.6118  146.7840 175.6413 181.2073  194.8942 218.7389 222.0621  229.0549 241.9050 255.6430  269.2900 309.3426 359.9764  435.5946 478.5246 491.5743  536.8032 557.1292 574.3137  659.3219 713.5709 755.1933  767.5362 839.8882 858.8399  887.7069 1007.2441 1041.0440  1073.2514 1161.5568 1334.9533  1420.3957 1429.1917 1475.1501  1492.6574 1525.1660 1642.0457  1674.7969 1675.6713 1692.7426  1705.2612 3052.6233 3095.1296  3119.2647 3156.7811 3165.1752  3263.5659 3603.0242 3657.3639  3721.8960 3788.2795 3836.4065  3903.8896 3955.8399 3975.1935 |
| **TS4**  O 0.218480 2.285063 0.552848  H 0.895680 2.889629 0.242121  H 0.707267 1.348193 0.931576  C 1.100301 -0.093681 1.317702  C 1.493442 -0.494188 0.034519  O 0.682968 -0.833511 -0.882492  C 2.954173 -0.438960 -0.353680  H 0.104819 -0.395901 1.638095  H 1.853715 -0.025245 2.095922  H 3.061561 0.116546 -1.288371  H 3.296291 -1.459092 -0.548396  H 3.584476 0.003287 0.419156  O -1.458937 -2.086450 0.199327  H -1.137761 -2.627285 0.919807  H -0.656162 -1.727378 -0.241939  O -2.996356 0.101209 0.172089  H -3.096375 0.454764 1.056144  H -2.583493 -0.783135 0.281193  H -0.420712 1.837893 -0.340132  O -1.020197 1.192821 -1.181787  H -0.446193 0.391768 -1.277182  H -1.858287 0.863872 -0.759111  Frequencies  -1151.5063 24.1463 48.3123  75.2119 81.4212 108.8189  121.4316 138.2970 198.0650  226.1843 262.7775 293.4725  319.5084 331.2552 417.7887  452.4439 473.8235 512.3051  541.5494 554.4991 576.2654  617.4626 643.9794 683.3142  741.4538 825.8465 855.7029  868.4678 893.1177 949.7393  997.6621 1033.5744 1056.9173  1089.1840 1238.1733 1330.9252  1399.5378 1471.3381 1483.6717  1491.6583 1512.9082 1583.8613  1659.0255 1676.2361 1693.7332  1702.1649 1753.8708 1810.7023  3058.4548 3125.9694 3131.9185  3154.2571 3219.5527 3249.2962  3357.8431 3431.0681 3513.6859  3917.6492 3956.3965 3967.8667 |
| **R5**, CH3C(O)CH3·(H2O)5  O 0.699002 1.108780 1.658158  H 0.712289 1.643453 2.451858  H 1.117183 -2.610708 1.165651  C 0.513621 -2.048926 0.453545  C 1.316475 -1.036440 -0.306344  O 0.836873 -0.449894 -1.267916  C 2.710486 -0.743104 0.155583  H -0.283206 -1.523632 0.994982  H 0.024817 -2.731272 -0.245504  H 3.183846 -0.001713 -0.486623  H 3.299134 -1.664713 0.170591  H 2.646188 -0.364534 1.178833  O 0.928420 2.412051 -0.731888  H -0.038476 2.460417 -0.649979  H 1.069962 1.607256 -1.243915  H 0.994310 1.692407 0.930695  O -1.658573 1.675750 0.150774  H -1.856545 0.982791 -0.495499  H -1.043423 1.262096 0.775188  O -2.531325 -1.048596 1.212224  H -2.736363 -0.120807 1.348520  H -2.504704 -1.126319 0.250452  O -1.865901 -0.602029 -1.518438  H -0.891162 -0.646558 -1.574221  H -2.205303 -0.655840 -2.411048  Frequencies  45.6764 62.1323 64.1537  70.0399 84.4352 112.7429  118.2946 120.6913 153.0717  159.1789 173.5995 182.6938  190.0953 208.5263 218.5322  226.6573 253.3835 260.3037  302.7774 330.0075 376.6258  396.3333 406.8030 431.0414  443.0437 513.9710 556.1186  571.6776 599.1736 652.1645  697.4227 701.5776 759.4539  816.4975 858.0422 892.0539  960.9949 1026.3506 1093.5940  1122.9064 1276.9979 1394.2733  1400.3853 1465.5775 1479.5976  1488.3037 1496.2573 1645.3269  1661.3854 1681.9865 1696.4318  1709.3965 1776.3535 3031.6569  3053.4431 3115.2110 3133.5302  3160.9795 3169.4706 3534.7974  3548.2581 3688.8516 3726.9481  3773.2782 3812.3599 3844.6824  3925.6529 3960.4761 3971.0234 |
| **P5**, CH3C(OH)CH2·(H2O)5  O -0.002421 0.679273 1.995030  H 0.699512 0.040204 1.837780  H -0.817338 0.158940 1.905737  C 2.043482 -1.619305 0.323343  C 1.962047 -0.423399 -0.261433  O 0.955231 -0.150360 -1.136921  C 2.939783 0.694984 -0.065403  H 1.292675 -2.378326 0.137800  H 2.879780 -1.866281 0.962928  H 2.426650 1.591826 0.293285  H 3.404348 0.949342 -1.021892  H 3.716397 0.421635 0.648630  O -0.126668 2.085964 -0.404095  H -1.058341 1.937244 -0.649988  H 0.627094 0.787585 -0.996114  H -0.093609 1.819871 0.533772  O -2.648888 0.999881 -0.858279  H -2.388217 0.197685 -1.326580  H -2.833925 0.661647 0.026615  O -2.251217 -0.817233 1.301527  H -2.765244 -1.418156 1.839458  H -1.943884 -1.312885 0.518944  O -1.312803 -1.555154 -1.122905  H -0.428882 -1.126204 -1.183106  H -1.294755 -2.316774 -1.701167  Frequencies  47.2793 58.6488 70.9944  77.9094 86.1108 110.0908  124.1502 136.2118 185.0378  191.0531 212.4202 223.1347  236.3456 254.4180 261.8796  271.6734 290.2139 303.2576  374.0229 398.7539 433.5280  456.4866 498.1277 512.7807  525.7724 546.7404 580.6189  595.2620 708.8419 743.3143  753.7058 772.6844 807.8863  852.7766 860.7753 874.8648  921.0295 996.1346 1036.2430  1068.0675 1081.9568 1326.1928  1416.4239 1435.5513 1477.9524  1494.0987 1557.5817 1656.2637  1674.9898 1691.4012 1717.0852  1745.2861 1759.0985 3043.5535  3051.1913 3118.0066 3154.5310  3168.7625 3265.6897 3420.8369  3598.7869 3624.0456 3641.6743  3715.7035 3808.9162 3859.9934  3873.2800 3970.3900 3973.6327 |
| **TS5**  O 1.707122 1.471142 1.197264  H 2.639454 1.495471 1.424401  H 1.342957 0.469017 1.327410  C 0.620391 -1.028466 1.355149  C 0.949504 -1.140912 0.023416  O 0.295260 -0.558457 -0.929759  C 2.198524 -1.876149 -0.405797  H -0.368545 -0.662141 1.626788  H 1.148626 -1.633381 2.084310  H 2.856707 -1.199639 -0.960175  H 1.914833 -2.673309 -1.097674  H 2.744783 -2.309517 0.432922  O 1.189733 1.899110 -1.118960  H 0.271626 2.239772 -1.088198  H 1.021503 0.949496 -1.358039  H 1.511030 1.747871 0.101382  O -1.383394 1.613857 -0.536964  H -2.176660 1.458751 -1.054788  H -0.954321 0.735209 -0.515313  O -2.614338 0.000416 1.614144  H -2.307262 0.856755 1.304716  H -2.667061 -0.507632 0.792085  O -2.381630 -1.119069 -1.042437  H -1.409219 -1.137540 -1.114338  H -2.680991 -2.012016 -1.208387  Frequencies  -697.4828 34.0930 58.8356  69.5737 84.3632 102.3268  120.6561 134.7412 141.9633  148.7912 159.6099 201.0831  211.7111 238.0609 243.8180  328.6209 346.0354 390.4713  444.4603 450.9147 457.4393  471.5250 498.7321 538.2455  555.4317 588.6384 606.6579  626.5804 652.7140 717.1667  745.1388 772.4652 820.8103  869.0879 880.4048 923.7360  1005.2029 1022.0099 1063.8746  1081.3406 1164.8635 1361.8641  1420.4017 1462.8478 1478.6261  1491.0553 1549.9714 1601.9385  1656.8424 1690.8107 1705.0719  1731.4117 1753.1977 1789.9450  2032.1046 3051.3712 3121.2586  3124.9671 3153.3115 3231.7892  3312.3412 3543.1700 3589.8244  3623.9568 3771.4198 3901.8088  3917.8042 3925.4816 3969.1528 |

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