

Supplementary Materials for

**Gas Phase Detection of Oxirene**

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**Fig. S1.**

FTIR spectra of CH3OH–CH3CHO ices at 5 K before (black line) and after (red line) irradiation at 20 nA for 15 minutes. Detailed assignments are listed in table S1.

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**Fig. S2.**

FTIR spectra of CH3OH–CH3CHO ice at 5 K before (black line) and after (red line) irradiation at 20 nA for 60 minutes. Detailed assignments are listed in table S2.

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**Fig. S3.**

Simulated ultraviolet-visible (UV-Vis) spectra of ketene and oxirene calculated at the TD-PBE0/cc-pVTZ level of theory. The spectra were convoluted using a Gaussian line shape function with a full width at half maximum (FWHM) of 4 nm.

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**Fig. S4.**

Formation schemes of ketene and oxirene. Reaction schemes showing pathways from acetaldehyde (**A**), acetaldehyde-*d*3 (**B**), acetaldehyde-*d*4 (**C**), and acetaldehyde-13C2 (**D**) to ketene and oxirene.The atoms are color-coded in white (hydrogen), light blue (deuterium), gray (carbon), and red (oxygen).

D:\Dropbox\Astrochemistry\5 C2H2O-oxirene\Figure\Figure S4.tif**Fig. S5.**

PI-ReTOF-MS data recorded at 9.20 eV during the temperature-TPD phase of irradiated (20 nA, 15 minutes) CH3CHO ice.TPD desorption profile of ion signal for *m/z* = 42 shows no evidence for the formation of oxirene.

Table S1.

Absorption peaks observed in CH3OH−CH3CHO ice before and after electron irradiation (20 nA, 15 minutes) at 5 K.

|  |  |
| --- | --- |
| Pristine ice, before irradiation (cm−1) |  |
| **CH3OH** | Assignmenta |
| 3402, 3261, 3048 | ν1 |
| 2991 | ν2 |
| 2955 | ν9 |
| 2914 | 2ν4 / 2ν5 / 2ν10 |
| 2825 | ν3 |
| 2594 | ν4 + ν11 |
| 2517 | ν6 + ν11 |
| 2233 | 2ν11/2ν7 |
| 2038 | 2ν8 |
| 1475 | ν4 |
| 1455 | ν5 |
| 1420 | ν6 |
| 1033 | ν8 |
| **CH3CHO** | Assignmentb |
| 2866 | 2ν6 |
| 2760 | ν3 |
| 1767 | 2ν9 |
| 1718 | ν4 |
| 1430 | ν12 / ν5 |
| 1392 | ν6 |
| 1345 | ν7 |
| 1122 | ν8 |
| 887 | ν14 + ν15 |
| 777 | ν14 |
| New absorption after irradiation (cm−1) | Assignmentb |
| 2130 | ν(CO) |
| 1842 | CH3CȮ ν(CO) |

a Assignments based on references (*27, 67*).

b Assignments based on reference (*28*).

**Table S2.**

Absorption peaks observed in CH3OH−CH3CHO ice before and after electron irradiation (20 nA, 60 minutes) at 5 K.

|  |  |
| --- | --- |
| Pristine ice, before irradiation (cm−1) |  |
| **CH3OH** | Assignmenta |
| 3402, 3261, 3048 | ν1 |
| 2993 | ν2 |
| 2955 | ν9 |
| 2920 | 2ν4 / 2ν5 / 2ν10 |
| 2824 | ν3 |
| 2598 | ν4 + ν11 |
| 2521 | ν6 + ν11 |
| 2237 | 2ν11/2ν7 |
| 2038 | 2ν8 |
| 1475 | ν4 |
| 1455 | ν5 |
| 1420 | ν6 |
| 1029 | ν8 |
| **CH3CHO** | Assignmentb |
| 2866 | 2ν6 |
| 2760 | ν3 |
| 1767 | 2ν9 |
| 1718 | ν4 |
| 1431 | ν12 / ν5 |
| 1392 | ν6 |
| 1345 | ν7 |
| 1122 | ν8 |
| 887 | ν14 + ν15 |
| 773 | ν14 |
| New absorption after irradiation (cm−1) | Assignmentc |
| 2129 | ν(CO) |
| 1840 | CH3CȮ ν(CO) |
| 1306 | ν4 (CH4) |
| 1199 | ν4 (ĊH2OH) |

a Assignments based on references (*27, 67*).

b Assignments based on reference (*28*).

c Assignments based on references (*27, 28*).

**Table S3.**

Absorption positions of methanol (CH3OH), acetaldehyde (CH3CHO), and oxirene (*c*-C2H2O). The numbers in brackets show the widths of the peaks observed in pure methanol or acetaldehyde ice (*48, 68*).

|  |  |
| --- | --- |
| Absorptions of methanol (cm−1) | Assignmenta |
| 3402 (419), 3261 (602), 3048 (874) | ν1 |
| 2993 (63) | ν2 |
| 2956 (116) | ν9 |
| 2920 (195) | 2ν4 / 2ν5 / 2ν10 |
| 2828 (53) | ν3 |
| 2600 (166) | ν4 + ν11 |
| 2525 (120) | ν6 + ν11 |
| 2237 (87) | 2ν11/2ν7 |
| 2042 (83) | 2ν8 |
| 1478 (21) | ν4 |
| 1455 (84) | ν5 |
| 1420 (129) | ν6 |
| 1130 (40) | ν7 |
| 1040 (37) | ν11 |
| 1030 (61) | ν8 |
| Absorptions of acetaldehyde (cm−1) | Assignmentb |
| 3416 (58) | 2ν4 |
| 3001 (51) | ν1 |
| 2916 (35) | ν2 |
| 2865 (97) | 2ν6 |
| 2759 (85) | ν3 |
| 1769 (55) | 2ν9 |
| 1718 (46) | ν4 |
| 1430 (50) | ν12 / ν5 |
| 1392 (27) | ν6 |
| 1347 (39) | ν7 |
| 1123 (45) | ν8 |
| 886 (38) | ν14 + ν15 |
| 772 (43) | ν14 |
| Calculated absorptions of oxirene (cm−1)c | Assignmentc |
| 3419 | ν1+ ν9 |
| 3402 | 2ν2 |
| 3338 | ν7+ ν9 |
| 3282 | ν1 |
| 3201 | ν7 |
| 2740 | ν2 + ν3 |
| 2625 | ν2 + ν8 |
| 2549 | ν2 + ν4 |
| 2244 | ν2 + ν5 |
| 1772 | ν4 + ν8 |
| 1701 | ν2 |
| 1696 | 2ν4 |
| 1467 | ν5 + ν8 |
| 1401 | ν6 + ν8 |
| 1391 | ν4 + ν5 |
| 1325 | ν4 + ν6 |
| 1061 | ν8 + ν9 |
| 1039 | ν3 |
| 1020 | ν5 + ν6 |
| 924 | ν8 |
| 848 | ν4 |
| 543 | ν5 |
| 477 | ν6 |
| 137 | ν9 |

a Assignments based on references (*27, 67*).

b Assignments based on reference (*28*).

c Calculated frequencies obtained from CCCBDB Vibrational Listing Page (nist.gov), computed at the CCSD(T)=FULL/cc-pVTZ level. The frequency error of oxirene is estimated to be 25 cm–1.

**Table S4.**

Error analysis of adiabatic ionization energies (IEs) and relative energies (Δ*E*) of distinct C2H2O isomers; IEs and Δ*E* were computed at the CCSD(T)/CBS(aug-T,Q)//CCSD(T)/aug-cc-pVTZ level of theory including the zero-point vibrational energy corrections. An offset of 0.03 eV was subtracted to correct for the electric field effect (*69*). The computed Cartesian coordinates and vibrational frequencies are shown in table S6.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Isomer | Structure | Δ*E*  (kJ mol-1) | Experimental IE (eV) | Computed IE (eV) | IE difference to lower bound (eV) | | IE difference to upper bound (eV) | IE range after error analysis (eV) | Corrected IE with electric field effect (eV) |
| **1**  Oxirene |  | 314 |  | 8.66 |  |  | | 8.66 – 8.67 | 8.63 – 8.64 |
| **2**  Ketene | D:\Dropbox\Astrochemistry\5 C2H2O-oxirene\Theory-FC\C2H2O\ketene-ppt.png | 0 | 9.617 ± 0.003 (*25*) | 9.61 | 0.004 | 0.010 | | 9.61 – 9.62 | 9.58 – 9.59 |
| **3**  Oxiranylidene |  | 256 |  | 9.85 |  |  | | 9.85 – 9.86 | 9.82 – 9.83 |
| **4**  Ethynol |  | 139 |  | 10.03 |  |  | | 10.03 – 10.04 | 10.00 – 10.01 |
| **5**  Formylcarbene (triplet) | D:\Dropbox\Astrochemistry\5 C2H2O-oxirene\Figure\oxirene\carbene-triplet.png | 311 |  | 6.38 |  |  | | 6.38 – 6.39 | 6.35 – 6.36 |
|  |  |  |  |  | Combined error limits  +0.004 – +0.010 | | |  |  |

# Table S5.

# Parameters for the generation of vacuum ultraviolet (VUV) light used in this work. The uncertainty for VUV photon energies is less than 0.005 eV.

|  |  |  |  |
| --- | --- | --- | --- |
| VUV energy (eV) | 9.70  (2ω1 - ω2) | 9.20  (2ω1 - ω2) | 8.25  (2ω1 - ω2) |
| VUV wavelength (nm) | 127.819 | 134. 765 | 150.284 |
| Nonlinear medium | Krypton | Xenon | Xenon |
| ω1 wavelength (nm) | 202.316 | 222.566 | 249.628 |
| Nd:YAG output (nm) | 532 | 355 | 355 |
| Dye laser output (nm) | 606.948 | 445.132 | 499.256 |
| Dye | Rhodamine 610/640  (0.17/0.04 g L−1 ethanol) | Coumarin 450  (0.2 g L−1 ethanol) | Coumarin 503  (0.4 g L−1 ethanol) |
| ω2 wavelength (nm) | 484.982 | 638.667 | 736.448 |
| Nd:YAG output (nm) | 355 | 532 | 532 |
| Dye laser output (nm) | 484.982 | 638.667 | 736.448 |
| Dye | Coumarin 480  (0.4 g L−1 ethanol) | DCM  (0.3 g L−1 DMSO) | LDS 722  (0.25 g L−1 ethanol) |

**Table S6.**

Cartesian Coordinates for C2H2O structures. CCSD(T)/aug-cc-pVTZ optimized geometry (distances in Angstrom), vibrational frequencies (cm−1) of neutral molecules, electronic energies E and E(CBS) (in hartree), zero-point vibrational energies (kcal/mol) as well as Anh. corr. (kcal/mol).

|  |
| --- |
| **ethynol**  H -1.539319641 0.829856603 0.000000000  O -1.175065699 -0.063647434 0.000000000  C 0.142513804 0.011189067 0.000000000  C 1.350437908 0.003324672 0.000000000  H 2.412144728 0.007461759 0.000000000  E = -152.3039861  E(CBS) = -152.3776612  ZPVE = 19.7228  Anh. corr. = 0.238  **Frequency Intensity**  355.1584 9.2506  378.5624 5.3712  527.2053 52.8696  610.2357 45.2486  1061.9691 78.9352  1270.1902 86.8722  2231.0818 128.804  3474.4798 84.2645  3799.153 114.2566  **ethynol radical cation**  H -2.424138646 0.011228422 0.000000000  C -1.349420840 -0.007434067 0.000000000  C -0.102007022 0.037916682 0.000000000  O 1.139287507 -0.072916693 0.000000000  H 1.624721991 0.783061062 0.000000000  E = -151.9477262  E(CBS) = -152.0081104  ZPVE = 19.1948 |
| **formylcarbene singlet**  H -1.460937182 0.841630612 0.705032184  C -1.034814858 0.243311122 -0.090299065  C -0.000958848 -0.619432138 0.038600369  O 0.856471853 0.335413094 -0.006169080  H 0.200887458 -1.686471298 0.008443092  E = -152.2342135  E(CBS) = -152.3072744  ZPVE = 18.5247  Anh. corr. = 0.251  **Frequency Intensity**  296.6473 36.4084  451.6903 229.0214  690.0529 76.5703  972.971 7.3336  1157.7451 34.0687  1399.239 39.9735  1518.6785 15.1998  3165.2661 6.7598  3228.3475 9.1788 |
| **formylcarbene triplet**  H -2.276127960 0.152328439 0.000000000  C -1.271623243 -0.252112350 0.000000000  C 0.011203868 0.381832802 0.000000000  O 1.090966506 -0.200741892 0.000000000  H -0.030704594 1.489031800 0.000000000  E = -152.2396046  E(CBS) = -152.3100130  ZPVE = 18.5967  Anh. corr. = 0.240  **Frequency Intensity**  466.9951 11.4264  468.6682 1.1648  873.7371 11.0643  949.0429 0.2516  1115.5953 48.1644  1387.0736 5.6099  1585.4944 74.991  2910.3849 51.1827  3216.4299 0.0856  **formylcarbene radical cation (quartet state)**  H -2.273621608 0.072144698 0.000000000  C -1.240042633 -0.254296397 0.000000000  C -0.003032170 0.414026168 0.000000000  O 1.069253697 -0.220096767 0.000000000  H 0.104868198 1.519075716 0.000000000  E = -151.8641170  E(CBS) = -151.9202896  ZPVE = 18.1417 |
| **ketene**  O 0.000000000 0.000000000 -1.188203868  C 0.000000000 0.000000000 -0.020833195  C 0.000000000 0.000000000 1.298512327  H 0.942940379 0.000000000 1.822275579  H -0.942940379 0.000000000 1.822275579  E = -152.3691021  E(CBS) = -152.4307654  ZPVE = 19.6581  Anh. corr. = 0.216  **Frequency Intensity**  434.5529 2.6533  506.8637 60.6434  587.6051 46.3401  989.9896 2.0512  1148.6591 4.4311  1411.5277 13.1207  2181.6866 597.6073  3192.6388 25.5261  3297.527 6.9494  **ketene radical cation**  O 0.000000000 0.000000000 -1.188535282  C 0.000000000 0.000000000 -0.060392428  C 0.000000000 0.000000000 1.334842625  H 0.959012275 0.000000000 1.844128657  H -0.959012275 0.000000000 1.844128657  E = -152.0180054  E(CBS) = -152.0772688  ZPVE = 19.5556 |
| **oxiranylidene**  O -0.501388802 0.544504297 0.000000000  C -0.442094417 -0.747807189 0.000000000  C 0.875395211 -0.004714980 0.000000000  H 1.399082891 0.159237102 0.931289547  H 1.399082891 0.159237102 -0.931289547  E = -152.2626507  E(CBS) = -152.3334567  ZPVE = 20.2229  Anh. corr. = 0.251  **Frequency Intensity**  817.9362 30.7101  838.855 41.6549  885.0955 1.845  1101.4491 13.5458  1116.652 1.7738  1399.8045 32.5565  1519.1688 22.043  3146.0007 2.1293  3260.5395 3.7728  **oxiranylidene radical cation**  O -0.742156619 0.387278417 0.000000000  C -0.234199870 -0.706492660 0.000000000  C 0.989752801 0.117266964 0.000000000  H 1.391162394 0.434709955 0.957824939  H 1.391162394 0.434709955 -0.957824939  E = -151.9113247  E(CBS) = -151.9703272  ZPVE = 19.5899 |
| **oxirene**  H 0.000000000 1.655416097 0.833013394  C 0.000000000 0.637527386 0.502199978  O 0.000000000 0.000000000 -0.858514308  C 0.000000000 -0.637527386 0.502199978  H 0.000000000 -1.655416097 0.833013394  E = -152.2322559  E(CBS) = -152.3079364  ZPVE = 18.0425  Anh. corr. = 0.245  E(CBS, vertical triplet energy) = -152.2041980  **Frequency Intensity**  187.6211 0.978  505.2871 77.4479  589.646 0  871.9501 56.0558  959.4067 6.8418  1063.3295 8.6286  1757.1488 3.622  3322.1987 47.295  3395.0532 2.7118  **oxirene radical cation**  H 0.000000000 1.695689729 0.753383961  C 0.000000000 0.654300945 0.460958687  O 0.000000000 0.000000000 -0.786597940  C 0.000000000 -0.654300945 0.460958687  H 0.000000000 -1.695689729 0.753383961  E = -151.9319836  E(CBS) = -151.9917672  ZPVE = 19.2440 |
| **TS1**  H -1.543948397 1.082500300 0.283804056  C -0.884778804 0.307549366 -0.041573996  O 0.816440171 0.337399837 0.000968929  C -0.079728204 -0.699803198 0.014627189  H 0.070670087 -1.766781391 0.021669290  E = -152.2317062  E(CBS) = -152.3064973  ZPVE = 17.8351  Anh. corr. = 0.244  *v*i = 268.0464 |
| **TS2**  H -1.726214663 0.366910914 0.903209042  C -1.293409365 0.200293197 -0.097767460  C 0.012518619 -0.394621461 0.015949355  O 1.072548598 0.217917731 0.003060475  H -0.044563270 -1.511590102 0.022413133  E = -152.2255527  E(CBS) = -152.2981266  ZPVE = 17.3561  Anh. corr. = 0.240  *v*i = 402.5632 |

**Table S7.** Calculated CASPT2(16,14) single-point relative energies of various stationary structures along the oxirene → formylcarbene → ketene isomerization pathway with different basis sets and extrapolated to the CBS limit.a

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | oxirene | singlet formylcarbene | triplet formylcarbene | ketene | TS1 | TS2 |
| CASPT2/cc-pVTZ | 0.0 | 0.6 | -14.4 | -318.0 | 12.0 | 34.8 |
| CASPT2/cc-pVQZ | 0.0 | 19.2 | -7.8 | -314.6 | 12.6 | 38.6 |
| CASPT2/cc-pV5Z | 0.0 | 21.3 | 0.3 | -307.2 | 13.5 | 44.1 |
| CASPT2/CBS(T,Q)b | 0.0 | 32.1 | -3.2 | -312.2 | 13.1 | 41.2 |
| CASPT2/CBS(Q,5)c | 0.0 | 23.3 | 7.8 | -300.3 | 14.2 | 49.3 |
| CASPT2/CBS(T,Q,5)d | 0.0 | 17.3 | 9.3 | -298.3 | 14.5 | 50.8 |
| CASPT2/aug-cc-pVTZ | 0.0 | 19.2 | -4.1 | -305.4 | 17.6 | 42.8 |
| CASPT2/aug-cc-pVQZ | 0.0 | 20.2 | -0.9 | -306.2 | 17.9 | 44.9 |
| CASPT2/aug-cc-pV5Z | 0.0 |  |  | -306.1 |  |  |
| **CASPT2/CBS(aug-T,Q)**b | **0.0** | **20.8** | **1.2** | **-306.8** | **18.1** | **46.3** |
| CASPT2/CBS(aug-Q,5)c | 0.0 |  |  | -305.9 |  |  |
| CASPT2/CBS(aug-T,Q,5)d | 0.0 |  |  | -305.6 |  |  |

aGeometries of all structures were optimized at the CCSD(T)/aug-cc-pVTZ level of theory, harmonic ZPE were computed using the same method and anharmonic corrections were evaluated at the PBE0/aug-cc-pVTZ level. ZPE with anharmonic corrections are included in the calculations of relative energies.

bThe CBS(T,Q) energy is extrapolated as E(VQZ) + 0.69377\*{E(VQZ) – E(VTZ)}.

cThe CBS(Q,5) energy is extrapolated as E(V5Z) + 0.931445\*{E(V5Z) – E(VQZ)}.

dThe CBS(T,Q,5) energy is extrapolated using the exponential decay function in terms of the basis set cardinal number x = 3, 4, and 5.