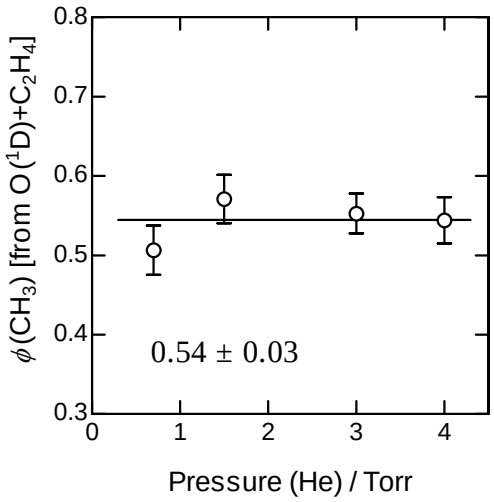


Figure 1S. The yield of CH_3, $\phi(CH_3)$, from the reaction of $O(^1D) + C_2H_4$. The yield was determined by comparing CH_3 radical signal with the reference reaction, $O(^1D) + CH_4 \rightarrow OH + CH_3$ ($\phi = 0.71 \pm 0.05$).

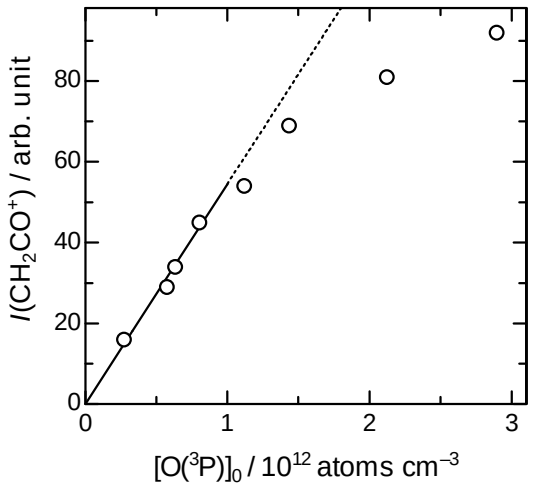


Figure 2S. Initial O-atom concentration dependence of the signal intensity of CH_2CO.

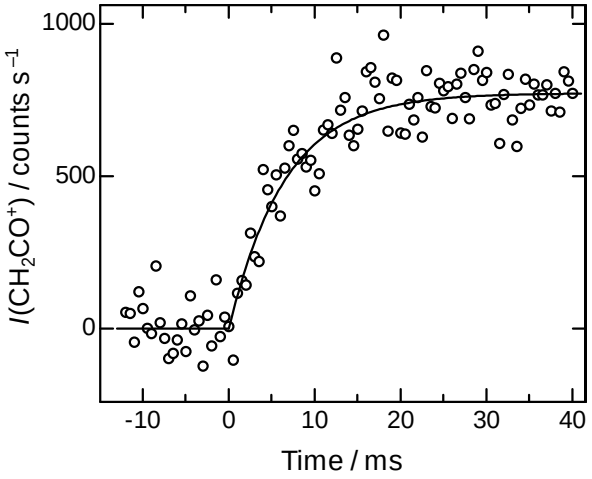


Figure 3S. Example of the observed time profile of CH_2CO.

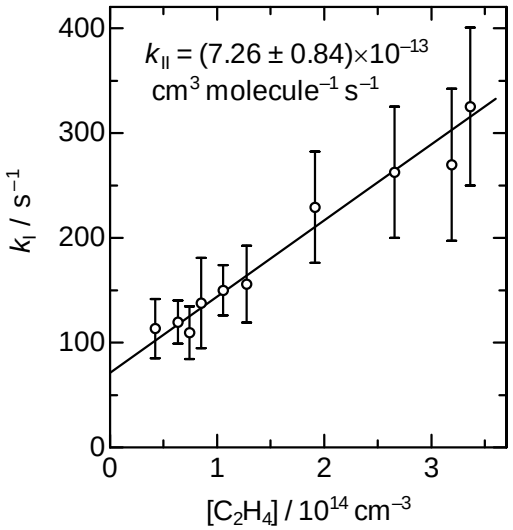
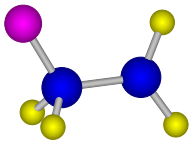


Figure 4S. First-order plot of the rise rate of CH_2CO against $[C_2H_4]$.

TABLE 1S. Geometry of biradicals and transition states optimized at MP2(Full)/6-31G(d). Geometric parameters are given in the Z-matrix forms.

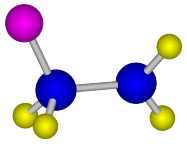
[singlet biradical] [a)]



```
C
C,1,R(CC)
O,1,R(CO),2,A(CO)
H,1,R(H4),2,A(H4),3,D(H4),0
H,1,R(H5),2,A(H5),3,D(H5),0
H,2,R(H6),1,A(H6),3,D(H6),0
H,2,R(H7),1,A(H7),3,D(H7),0

R(CC)=1.4884
R(CO)=1.3859
R(H4)=1.1064
R(H5)=1.1028
R(H6)=1.0807
R(H7)=1.0819
A(CO)=115.5971
A(H4)=111.5443
A(H5)=111.9921
A(H6)=119.6857
A(H7)=120.4502
D(H4)=119.2528
D(H5)=-124.2389
D(H6)=-11.2059
D(H7)=176.7643
```

[triplet biradical]

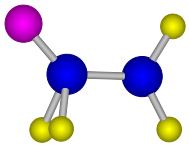


```
C
C,1,R(CC)
O,1,R(CO),2,A(CO)
H,1,R(H4),2,A(H4),3,D(H4),0
H,1,R(H5),2,A(H5),3,D(H5),0
H,2,R(H6),1,A(H6),3,D(H6),0
H,2,R(H7),1,A(H7),3,D(H7),0

R(CC)=1.4849
R(CO)=1.3901
R(H4)=1.0997
R(H5)=1.1126
R(H6)=1.0810
R(H7)=1.0812
A(CO)=112.6670
A(H4)=112.2469
A(H5)=111.7906
A(H6)=119.2267
A(H7)=121.1206
D(H4)=126.7641
D(H5)=-114.882
D(H6)=36.9634
D(H7)=-148.9017
```

a) No stationary point was found for the $^{1}\sigma\sigma$ form [25] of the single biradical in MP2(Full)/6-31G(d) calculation.

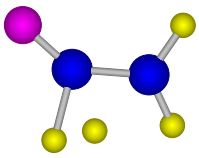
[SP_1]



```
C
C,1,R(CC)
O,1,R(CO),2,A(CO)
H,1,R(H4),2,A(H4),3,D(H4),0
H,1,R(H5),2,A(H5),3,D(H5),0
H,2,R(H6),1,A(H6),3,D(H6),0
H,2,R(H7),1,A(H7),3,D(H7),0

R(CC)=1.4248
R(CO)=1.2267
R(H4)=1.2132
R(H5)=1.2132
R(H6)=1.0814
R(H7)=1.0821
A(CO)=133.4492
A(H4)=102.5829
A(H5)=102.5829
A(H6)=121.0514
A(H7)=119.5345
D(H4)=148.1434
D(H5)=-148.1434
D(H6)=0.
D(H7)=180.
```

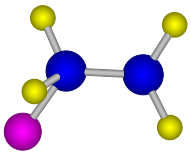
[SP_2]



```
C
C,1,R(CC)
O,1,R(CO),2,A(CO)
H,1,R(H4),2,A(H4),3,D(H4),0
H,1,R(H5),2,A(H5),3,D(H5),0
H,2,R(H6),1,A(H6),3,D(H6),0
H,2,R(H7),1,A(H7),3,D(H7),0

R(CC)=1.4005
R(CO)=1.2048
R(H4)=1.3423
R(H5)=1.4723
R(H6)=1.0880
R(H7)=1.0851
A(CO)=141.3931
A(H4)=99.6164
A(H5)=69.1314
A(H6)=120.2192
A(H7)=115.8096
D(H4)=200.8122
D(H5)=-130.0458
D(H6)=-14.7751
D(H7)=192.9782
```

[SP_3]



```
C
C,1,R(CC)
O,1,R(CO),2,A(CO)
H,1,R(H4),2,A(H4),3,D(H4),0
H,1,R(H5),2,A(H5),3,D(H5),0
H,2,R(H6),1,A(H6),3,D(H6),0
H,2,R(H7),1,A(H7),3,D(H7),0

R(CC)=1.4152
R(CO)=1.3691
R(H5)=1.0964
R(H6)=1.0819
R(H7)=1.0814
A(CO)=123.4110
A(H5)=117.5758
A(H6)=120.1835
A(H7)=120.1917
D(H5)=-160.5688
D(H6)=-8.8553
D(H7)=179.0406
R(H4)=1.1930
A(H4)=110.1920
D(H4)=74.0774
```

TABLE 2S. Calculated energies of the stationary points.

	G3(MP2) potential energy / hartree	G3(MP2) E(0K) / hartree	relative E(0K) / kJ mol–1
$O(^3P) + C_2H_4$	–153.473446	–153.424541	0.0
OCH_2CH_2 (3) [a]	–153.510941	–153.461466	–96.9
OCH_2CH_2 (1) [b]	–153.511232	–153.462270	–99.1
SP-a [c]	–153.515615	–153.468687	–115.9
CH_3CHO	–153.653201	–153.599687	–459.8
$CH_3 + HCO$	–153.510791	–153.470298	–120.1
SP_1	–153.503737	–153.459500	–91.8
SP_2	–153.516635	–153.471534	–123.4
$H_2 + CH_2CO$	–153.600742	–153.560749	–357.6
SP_3	–153.506714	–153.460532	–94.5
CH_2CHOH	–153.638451	–153.583920	–418.4
SP-b [d]	–153.479545	–153.436734	–32.0
$H + CH_2CHO$	–153.489788	–153.449520	–65.6

a) Triplet biradical. *b*) Singlet biradical. *c*) Hydrogen-shift saddle point between singlet biradical and CH_3CHO. *d*) H-elimination saddle point between triplet biradical and $H + CH_2CHO$.