Supplementary File 1. Supplementary materials and methods to this study.

1 Computational parameters

Adsorption of EME* on the Cu(111) surface is the initial and key step in its decomposition process. Thus, computational parameters were evaluated based on the convergence of the adsorption energy of EME.

1.1 Test of energy cutoff

Adsorption energies of EME(I)* on the Cu(111) surface were calculated, using energy cutoffs of 400, 450, 500 and 550 eV. The corresponding results are listed in Table S1.

Table S1 The adsorption energies (E_{ads}) of EME(I)* with different energy cutoffs.

Cutoff (eV)	400	450	500	550
E_{ads} (eV)	−0.71	−0.72	−0.72	−0.72

It can be seen that adsorption energies remain unchanged for cutoff values equal to or greater than 450 eV. Thus, an energy cutoff of 450 eV was adopted in this work to balance computational accuracy and efficiency.

1.2 Test of *k*-points

Adsorption energies of EME(I)* were calculated using *k*-point meshes of 2 × 2 × 1, 3 × 3 × 1, 4 × 4 × 1 and 5 × 5 × 1. The corresponding results are listed in Table S2.

Table S2. Adsorption energies of EME(I)* on the Cu(111) surface with different *k*-point meshes.

k-point meshes	2 × 2 × 1	3 × 3 × 1	4 × 4 × 1	5 × 5 × 1
E_{ads} (eV)	−0.69	−0.72	−0.72	−0.73

It can be seen that the adsorption energy differences are less than 0.01 eV for *k*-point meshes greater than 3 × 3 × 1. Thus, the *k*-point mesh of 3 × 3 × 1 was selected in this work.

1.3 Test of electronic convergence threshold

Adsorption energies of EME(I)* were calculated using electronic convergence thresholds of 10^{-4}, 10^{-5}, and 10^{-6} eV. The results are summarized in Table S3.

Table S3 Adsorption energies of EME(I)* on the Cu(111) surface with different electronic convergence thresholds.

Electronic convergence criteria (eV)	10^{-4}	10^{-5}	10^{-6}
E_{ads} (eV)	−0.72	−0.72	−0.72

As shown in Table S3, the adsorption energy of EME(I)* remains unchanged across the tested convergence criteria, indicating that the effect of electronic convergence threshold on the calculated adsorption energy is negligible. Thus, a commonly adopted value of 10^{-5} eV was adopted in this work to balance computational accuracy and efficiency.

1.4 Summary of computational parameters for the VASP package

Table S4 Summary of computational parameters.

Package	VASP
Pseudopotential	Projector-augmented wave (PAW)
Exchange-correlation potential	Perdew-Burke-Ernzerhof (PBE) functional
Van der Waals correction	DFT-D3
Transition states searching methods	Climbing image nudged elastic band (CI-NEB) and improved dimer (IDM)
Electronic convergence criteria	10^{-5} eV
Ionic convergence criteria	0.03 eV/Å
Energy cutoff	450 eV
k-point meshes	3 × 3 × 1

2 Calculation method for Gibbs free energy of activation

The ZPE-corrected energy (E) was calculated as:

$$E = E_{\mathrm{DFT}} + E_{\mathrm{ZPE}} \quad (1)$$

where E_{DFT} is the energy obtained from the density functional theory calculations, and E_{ZEP} is the zero-point energy correction.

E_{ZEP} was calculated as:

$$E_{\mathrm{ZPE}} = \sum_i \frac{h\nu_i}{2} \quad (2)$$

where h is the Planck constant, and ν_i is the vibrational frequency.

The standard Gibbs free energy (G°) for each adsorbed species was calculated as:

$$G^\circ = E + U_{\text{vib}}{}^\circ - TS_{\text{vib}}{}^\circ \quad (3)$$

where $U_{\text{vib}}{}^\circ$ is the standard vibrational internal energy and $S_{\text{vib}}{}^\circ$ is the vibrational entropy.

$$U_{\text{vib}}{}^\circ = RT\sum_i \frac{h\nu_i/k_{\text{B}}T}{e^{h\nu_i/k_{\text{B}}T}-1} \quad (4)$$

$$S_{\text{vib}}{}^\circ = R\sum_i \left[-\ln\left(1-e^{-h\nu_i/k_{\text{B}}T}\right) + \frac{h\nu_i/k_{\text{B}}T}{e^{h\nu_i/k_{\text{B}}T}-1}\right] \quad (5)$$

where R is the gas constant; T is temperature; k_{B} is the Boltzmann constant.

The Gibbs free energy of activation (ΔG) was calculated using the following equation: $\Delta G = G_{\text{TS}} - G_{\text{IS}}$ (6)

where G_{TS} is the Gibbs free energy of transition state, and G_{IS} is the Gibbs free energy of the initial state.

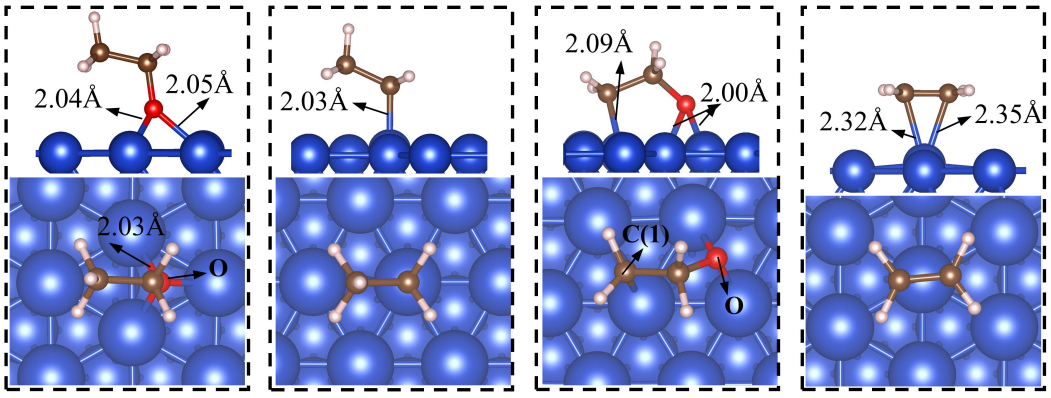
3 Adsorption of decomposition products of EME(I)* and EME(II)*

The adsorption structures of CH_3CH_2O*, CH_3CH_2*, CH_2CH_2O* and C_2H_4* are presented in Fig. S1. CH_3CH_2O* forms an interaction with the surface through its O atom, with three O–Cu bond lengths of 2.03 Å, 2.04 Å, and 2.05 Å, respectively. The methyl group in CH_3CH_2O* tilts slightly toward the vacuum.

CH_3CH_2* adsorbs at the top site through one of its C atoms. The C–Cu bond is nearly perpendicular to the surface, with a bond length of 2.03 Å, while the C–C bond tilts slightly, positioning the methyl group toward the vacuum.

CH_2CH_2O* forms interactions with the surface through the C(1) and O atoms. The C(1)–Cu bond length is 2.09 Å, while both O–Cu bonds are 2.00 Å. This adsorption structure suggests that the O atom in CH_2CH_2O* adopts an sp^3 hybridization.

C_2H_4* interacts with the surface through its π bond. Both C atoms coordinate with a top-Cu atom, with C–Cu bond lengths of 2.32 Å and 2.35 Å, respectively.



(a) CH_3CH_2O* (b) CH_3CH_2* (c) CH_2CH_2O* (d) C_2H_4*

Fig. S1. The adsorption structure of (a) CH_3CH_2O*, (b) CH_3CH_2*, (c)CH_2CH_2O*, (d) C_2H_4*

4 Bader charge calculations

The results of Bader charge calculations for CH_3CHOCH_3(I)* and CH_3CHOCH_3(II)* are shown in Table S5 and Table S6, respectively.

For reaction R4 (EME(I)* → CH_3* + CH_2OCH_3*), the Bader calculations for transition state TS4 are presented in Table S7.

Table S5 Bader charges of CH_3CHOCH_3(I)*

Atom	Total charge	Obtained electrons
Cu	11.000614	0.000614
Cu	10.988395	-0.011605
Cu	11.039917	0.039917
Cu	11.01995	0.01995
Cu	10.971281	-0.028719
Cu	11.015239	0.015239
Cu	11.011278	0.011278
Cu	10.961084	-0.038916
Cu	11.046016	0.046016
Cu	11.034428	0.034428
Cu	10.955803	-0.044197
Cu	11.019586	0.019586
Cu	11.025778	0.025778
Cu	10.964428	-0.035572
Cu	11.017587	0.017587
Cu	10.991437	-0.008563
Cu	10.962291	-0.037709
Cu	11.038473	0.038473
Cu	11.031569	0.031569
Cu	10.96956	-0.03044
Cu	11.017296	0.017296
Cu	11.036267	0.036267
Cu	10.963116	-0.036884
Cu	10.986251	-0.013749
Cu	11.014986	0.014986
Cu	10.949703	-0.050297
Cu	11.000945	0.000945
Cu	11.01464	0.01464
Cu	10.94264	-0.05736
Cu	11.051306	0.051306
Cu	10.989919	-0.010081
Cu	10.96356	-0.03644
Cu	11.020116	0.020116
Cu	11.032272	0.032272

Cu	10.977442	-0.022558
Cu	11.021654	0.021654
Cu	11.005352	0.005352
Cu	10.942149	-0.057851
Cu	10.991498	-0.008502
Cu	11.021756	0.021756
Cu	10.957616	-0.042384
Cu	11.010593	0.010593
Cu	11.049597	0.049597
Cu	10.934949	-0.065051
Cu	11.03903	0.03903
Cu	10.982016	-0.017984
Cu	10.969235	-0.030765
Cu	11.017275	0.017275
Cu	11.036938	0.036938
Cu	10.977432	-0.022568
Cu	11.015467	0.015467
Cu	10.932485	-0.067515
Cu	10.942772	-0.057228
Cu	11.012209	0.012209
Cu[a]	**10.853205**	**-0.146795**
Cu	10.9518	-0.0482
Cu	11.016587	0.016587
Cu	11.043682	0.043682
Cu	10.969397	-0.030603
Cu	11.014789	0.014789
Cu	10.99089	-0.00911
Cu	11.00458	0.00458
Cu	11.05051	0.05051
Cu	11.013379	0.013379
Cu	10.993391	-0.006609
Cu	10.998964	-0.001036
Cu	11.001861	0.001861
Cu	10.985361	-0.014639
Cu	10.996185	-0.003815
Cu	10.995629	-0.004371
Cu	10.99104	-0.00896
Cu	10.992562	-0.007438
Cu	11.0371	0.0371
Cu	10.961853	-0.038147
Cu	11.017305	0.017305
O	**7.010403**	**1.010403**
C	3.636846	-0.363154
C	3.800357	-0.199643
C	4.090796	0.090796

H	0.924103	-0.075897
H	0.967444	-0.032556
H	0.956209	-0.043791
H	0.957689	-0.042311
H	0.980131	-0.019869
H	0.940419	-0.059581
H	0.970348	-0.029652

[a] Cu atom bonded to the O atom

Table S6 Bader charges of CH_3CHOCH_3(II)*

Atom	Total charge	Obtained electrons
Cu	10.999409	-0.000591
Cu	10.963189	-0.036811
Cu	11.038259	0.038259
Cu	10.987673	-0.012327
Cu	10.975562	-0.024438
Cu	11.013734	0.013734
Cu	11.018648	0.018648
Cu	10.966125	-0.033875
Cu	11.046055	0.046055
Cu	11.033911	0.033911
Cu	10.953095	-0.046905
Cu	11.022041	0.022041
Cu	11.029262	0.029262
Cu	10.945300	-0.0547
Cu	11.018100	0.0181
Cu	10.993883	-0.006117
Cu	10.988576	-0.011424
Cu	11.039282	0.039282
Cu	11.028173	0.028173
Cu	10.965524	-0.034476
Cu	11.015234	0.015234
Cu	11.025991	0.025991
Cu	10.964222	-0.035778
Cu	11.010609	0.010609
Cu	11.014432	0.014432
Cu	10.952763	-0.047237
Cu	10.995879	-0.004121
Cu	11.023024	0.023024
Cu	10.938426	-0.061574
Cu	11.051245	0.051245
Cu	10.989526	-0.010474
Cu	10.961687	-0.038313

Cu	10.998742	-0.001258
Cu	11.025275	0.025275
Cu	10.969710	-0.03029
Cu	11.021938	0.021938
Cu	10.994083	-0.005917
Cu	10.950326	-0.049674
Cu	10.995250	-0.00475
Cu	11.025545	0.025545
Cu	10.956208	-0.043792
Cu	10.986641	-0.013359
Cu	11.016958	0.016958
Cu	10.933211	-0.066789
Cu	11.037746	0.037746
Cu	11.011227	0.011227
Cu	10.975249	-0.024751
Cu	11.016568	0.016568
Cu	11.040535	0.040535
Cu	10.976284	-0.023716
Cu	11.039756	0.039756
Cu	10.921333	-0.078667
Cu	10.941833	-0.058167
Cu	10.994146	-0.005854
Cu[a]	**10.846802**	**-0.153198**
Cu	10.953849	-0.046151
Cu	11.015056	0.015056
Cu	11.034950	0.03495
Cu	10.965920	-0.03408
Cu	11.016187	0.016187
Cu	11.019783	0.019783
Cu	11.005054	0.005054
Cu	11.048385	0.048385
Cu	11.021183	0.021183
Cu	10.988547	-0.011453
Cu	11.001321	0.001321
Cu	11.005476	0.005476
Cu	10.987715	-0.012285
Cu	10.993888	-0.006112
Cu	10.993428	-0.006572
Cu	10.987685	-0.012315
Cu	11.010906	0.010906
Cu	11.033069	0.033069
Cu	10.989568	-0.010432
Cu	11.020180	0.02018
O	**7.020860**	**1.02086**
C	3.601110	-0.39889

C	3.836219	-0.163781
C	4.074307	0.074307
H	0.944360	-0.05564
H	0.918838	-0.081162
H	1.011433	0.011433
H	0.969762	-0.030238
H	0.974895	-0.025105
H	0.951565	-0.048435
H	0.960308	-0.039692

[a] Cu atom bonded to the O atom

Table S7 Bader charges of TS4 (CH_3*--CH_2OCH_3*)

Atom	Total charge	Obtained electrons
Cu	11.022833	0.022833
Cu	11.000625	0.000625
Cu	11.039747	0.039747
Cu	11.021351	0.021351
Cu	10.96527	-0.03473
Cu	11.018396	0.018396
Cu	11.02323	0.02323
Cu	10.963125	-0.036875
Cu	11.0207	0.0207
Cu	11.038262	0.038262
Cu	10.961431	-0.038569
Cu	11.041389	0.041389
Cu	11.035831	0.035831
Cu	10.939113	-0.060887
Cu	11.033627	0.033627
Cu	11.003205	0.003205
Cu	10.966029	-0.033971
Cu	11.018396	0.018396
Cu	11.012938	0.012938
Cu	10.950348	-0.049652
Cu	11.001451	0.001451
Cu	11.005911	0.005911
Cu	10.959255	-0.040745
Cu	10.990805	-0.009195
Cu	11.01885	0.01885
Cu	10.967947	-0.032053
Cu	10.991745	-0.008255
Cu	11.001321	0.001321
Cu	10.966981	-0.033019
Cu	11.012831	0.012831
Cu	11.037261	0.037261

Cu	10.990189	-0.009811
Cu	11.012718	0.012718
Cu	11.060591	0.060591
Cu	10.989596	-0.010404
Cu	11.021476	0.021476
Cu	11.038801	0.038801
Cu	10.984795	-0.015205
Cu	11.025552	0.025552
Cu	11.039429	0.039429
Cu	10.963269	-0.036731
Cu	11.023222	0.023222
Cu	11.021953	0.021953
Cu	10.932309	-0.067691
Cu	11.04919	0.04919
Cu	11.02763	0.02763
Cu	10.960226	-0.039774
Cu	11.021991	0.021991
Cu	11.035205	0.035205
Cu	10.948988	-0.051012
Cu	10.993248	-0.006752
Cu[a]	**10.746876**	**-0.253124**
Cu	10.956867	-0.043133
Cu	11.008037	0.008037
Cu	10.920215	-0.079785
Cu	10.927883	-0.072117
Cu	11.013337	0.013337
Cu	11.050205	0.050205
Cu	10.965857	-0.034143
Cu	11.009423	0.009423
Cu	11.020105	0.020105
Cu	11.005443	0.005443
Cu	11.043965	0.043965
Cu	11.03212	0.03212
Cu	10.973735	-0.026265
Cu	11.00524	0.00524
Cu	11.02372	0.02372
Cu	10.976593	-0.023407
Cu	11.022083	0.022083
Cu	11.03516	0.03516
Cu	10.975383	-0.024617
Cu	11.002983	0.002983
Cu	11.027145	0.027145
Cu	10.966573	-0.033427
Cu	11.003445	0.003445
O	7.102722	1.102722

C	3.665197	-0.334803
C(2)	**3.686834**	**-0.313166**
C(1)	**4.323988**	**0.323988**
H	0.919549	-0.080451
H	0.960736	-0.039264
H	0.91796	-0.08204
H	0.891895	-0.108105
H	0.914399	-0.085601
H	0.887757	-0.112243
H	0.893928	-0.106072
H	0.952021	-0.047979

[a] Cu atom bonded to both C(1) and C(2) atoms

5 Imaginary frequencies for transition states

The single imaginary for each transition state along the reaction coordinate is listed in Table S8.

Table S8. Single imaginary frequency for each transition state.

No.	Reactions	Imaginary frequency (cm^{-1})
R1	EME(I)* → $CH_2CH_2OCH_3$(I)* + H*	891.2
R2	EME(I)* → CH_3CHOCH_3(I)* + H*	676.8
R3	EME(I)* → $CH_3CH_2OCH_2$(I)* + H*	892.2
R4	EME(I)* → CH_3* + CH_2OCH_3*	511.1
R5	EME(I)* → CH_3CH_2* + CH_3O*	240.3
R6	EME(I)* → CH_3CH_2O* + CH_3*	363.2
R7	EME(II)* → $CH_2CH_2OCH_3$(II)* + H*	965.9
R8	EME(II)* → CH_3CHOCH_3(II)* + H*	629.2
R9	EME(II)* → $CH_2CH_2OCH_2$(II)* + H*	836.1
R10	EME(II)* → CH_3* + CH_2OCH_3*	372.6
R11	EME(II)* → CH_3CH_2* + CH_3O*	263.4
R12	EME(II)* → CH_3CH_2O* + CH_3*	337.0
R13	$CH_2CH_2OCH_3$(I)* → $CHCH_2OCH_3$* + H*	609.1
R14	$CH_2CH_2OCH_3$(I)* →CH_2CHOCH_3* + H*	907.3
R15	$CH_2CH_2OCH_3$(I)* →$CH_2CH_2OCH_2$* + H*	758.1
R16	$CH_2CH_2OCH_3$(I)* →CH_2* + CH_2OCH_3*	211.2
R17	$CH_2CH_2OCH_3$(I)* →C_2H_4* + CH_3O*	311.9
R18	$CH_2CH_2OCH_3$(I)* → CH_2CH_2O* + CH_3*	302.6