

**Supporting Information for:**

**Direct Kinetics Study of CH<sub>2</sub>OO + Methyl Vinyl Ketone and CH<sub>2</sub>OO +  
Methacrolein Reactions and an Upper Limit Determination for CH<sub>2</sub>OO + CO  
Reaction**

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**Table S1:** Ionization energies of the reference species in eV.

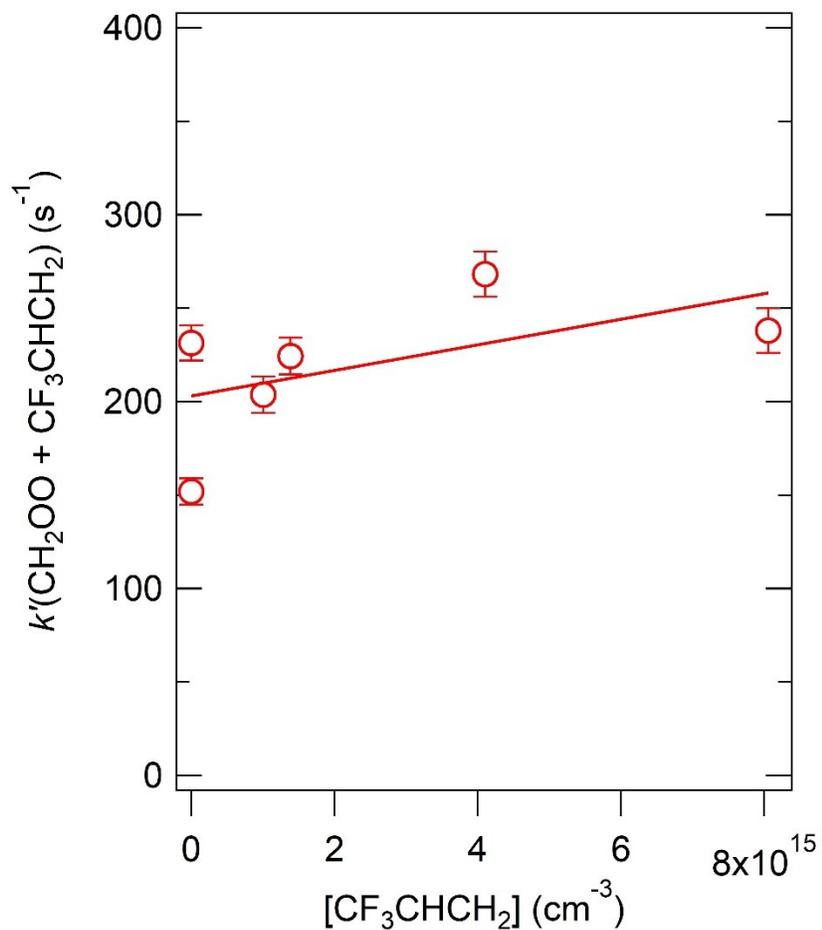
Species	Literature (reference)	XTB	HF	B3LYP	CC <sup>a</sup>	CBS*	Combined
Acetone	9.70 (1)	15.76	8.20	9.39	9.78	9.55	9.69
2-Butanone	9.52 (2)	15.16	8.08	9.19	9.62	9.36	9.53
Acetaldehyde	10.22 (3)	16.33	8.74	9.96	10.29	10.06	10.21
Propanal	9.96 (3)	15.72	8.58	9.67	10.08	9.82	9.99
2-Methyl-Propanal	9.72 (4)	15.31	8.45	9.39	9.84	9.51	9.73
2-Methyl-1-Propene	9.19 (5)	14.76	7.63	8.81	9.23	9.23	9.21
Cyclopentane	10.35 (5)	15.05	9.92	9.94	10.52	10.39	10.45
Tetrahydrofuran	9.54 (6)	14.91	8.10	9.01	9.52	9.30	9.43

<sup>a</sup>DLPNO-CCSD(T)/CBS(TZ,QZ)**Table S2:** Ionization energies of the reference species in eV.

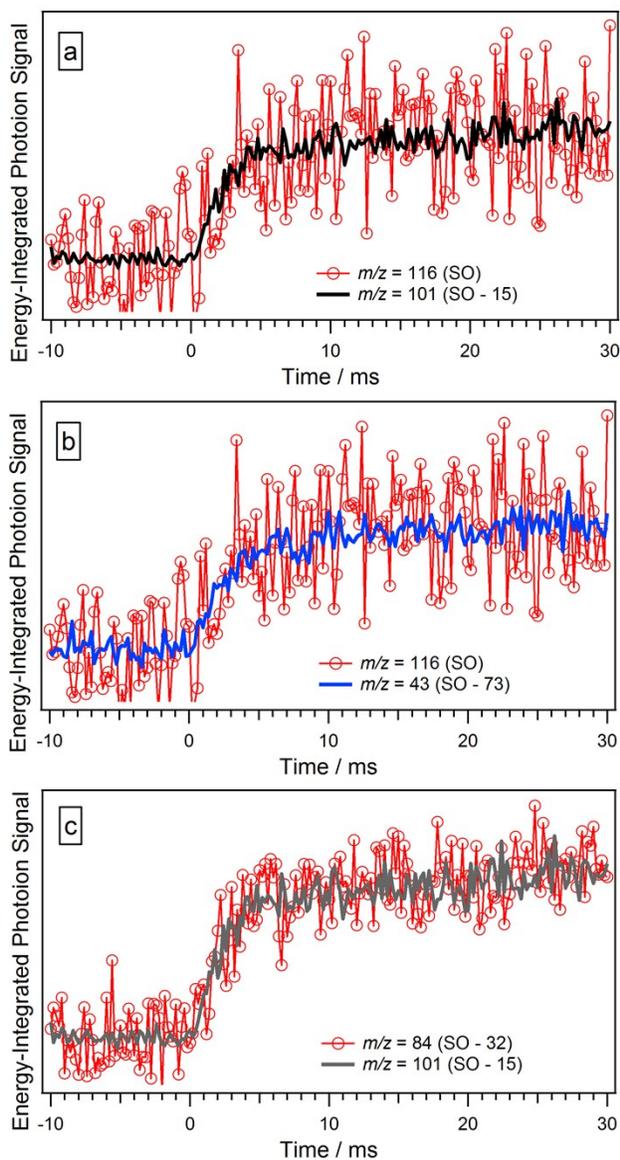
Species	Literature (reference)	HF	B3LYP	CC <sup>a</sup>	CBS*	Combined
2-Pentanone	9.37 (7)	8.02	9.09	9.55	9.28	9.45
3-Pentanone	9.31 (2)	7.98	9.00	9.46	9.18	9.36
Butanal	9.83 (4)	8.51	9.51	9.99	9.71	9.89
MVK	9.66 (8)	8.01	9.29	8.73	9.51	9.65
Ethene	10.50 (9)	8.75	10.22	10.51	10.53	10.50
Methoxyethene	8.93 (6)	7.42	8.63	8.96	8.81	8.90
Cyclopentene	9.02 (10)	7.58	8.55	9.04	9.04	9.02
2,5-Dihydrofuran	9.16 (11)	8.69	8.64	9.37	9.25	9.30

<sup>a</sup>DLPNO-CCSD(T)/CBS(TZ,QZ)**Table S3.** Lennard-Jones parameters from group additivity theory <sup>12</sup>:

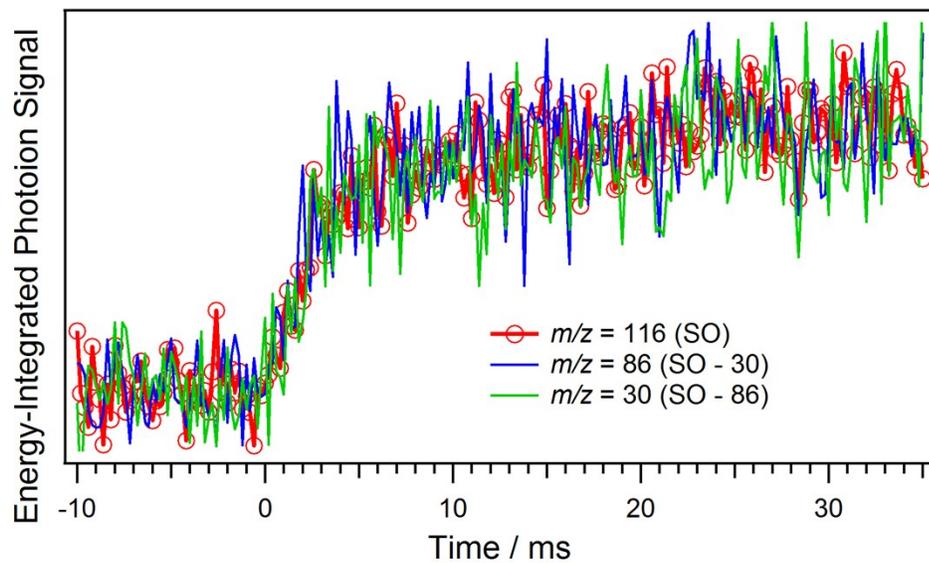
Species	A	B	C	E	F	G
$\sigma$	6.03 Å	6.03 Å	5.82 Å	5.86 Å	5.86 Å	5.92 Å
$\epsilon$	396.2 K	396.2 K	404.0 K	398.7 K	398.7 K	396.7 K



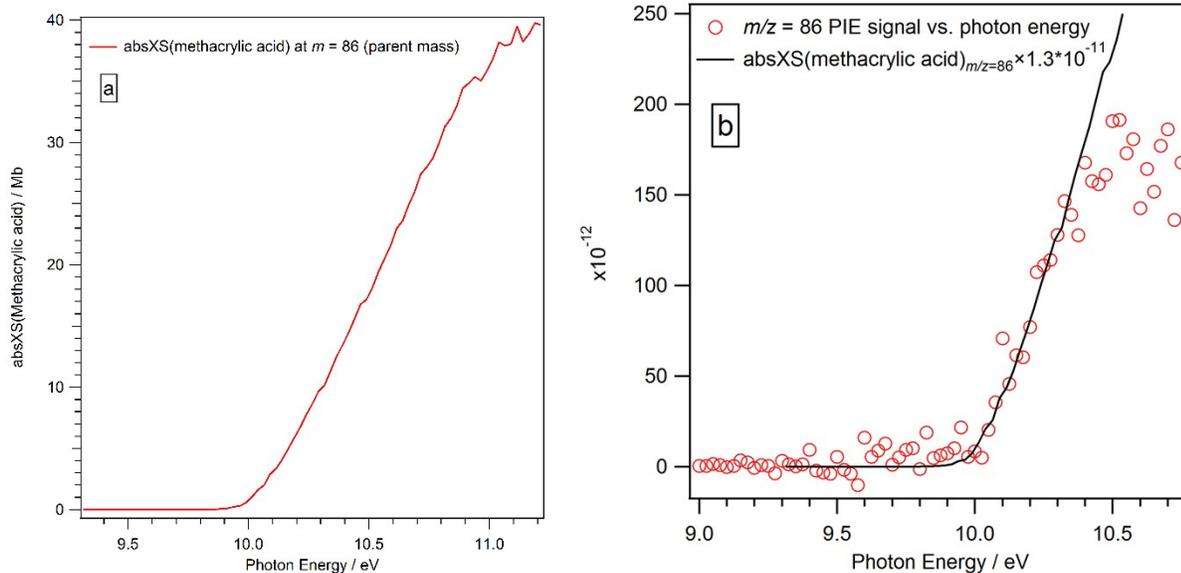
**Figure S1.** Bimolecular plot of CH<sub>2</sub>OO decay rate at 4 Torr and 300 K temperature *versus* CF<sub>3</sub>CHCH<sub>2</sub> concentration. A linear fit (red line in figure) to the data returns  $k(\text{CH}_2\text{OO} + \text{CF}_3\text{CHCH}_2) = (6.85 \pm 10.44) \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$  ( $\pm 2\sigma$  uncertainty) from which an upper limit  $k(\text{CH}_2\text{OO} + \text{CF}_3\text{CHCH}_2) < 1.75 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$  is obtained.



**Figure S2.** a) Comparison of time behavior of  $m/z = 101$  signal, probably originating from a dissociative ionization of  $\text{CH}_2\text{OO-MVK}$  adduct, with the parent signal of the  $\text{CH}_2\text{OO-MVK}$  adduct at  $m/z = 116$ . b) Comparison of time behavior of  $m/z = 43$  signal, may be originating from a dissociative ionization of the  $\text{CH}_2\text{OO-MVK}$  adduct, with the parent signal of the  $\text{CH}_2\text{OO-MVK}$  adduct at  $m/z = 116$ . c) Comparison of time behavior of  $m/z = 84$  signal with  $m/z = 101$  signal. All signals are obtained by integration over photon energies from 9.0 – 10.75 eV.



**Figure S3.** Comparison of time behaviors of  $m/z = 86$  and  $m/z = 30$  signals with the parent ( $\text{CH}_2\text{OO}$ -MACR adduct) signal at  $m/z = 116$ . All signals are obtained by integration over photon energies from 9.0 – 10.75 eV.



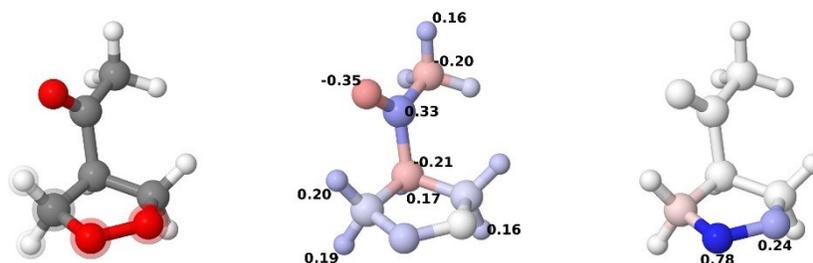
**Figure S4.** a) Absolute photoionization spectrum of methacrylic acid at parent  $m/z = 86$  measured in this work. b) Comparison of experimental product spectrum at  $m/z = 86$  from  $\text{CH}_2\text{OO} + \text{MACR}$  reaction (as shown with blue line in figure 2b) with the absolute photoionization spectrum of methacrylic acid at  $m/z = 86$ .

## Cationic molecular properties of CH<sub>2</sub>OO + MVK/MACR adducts

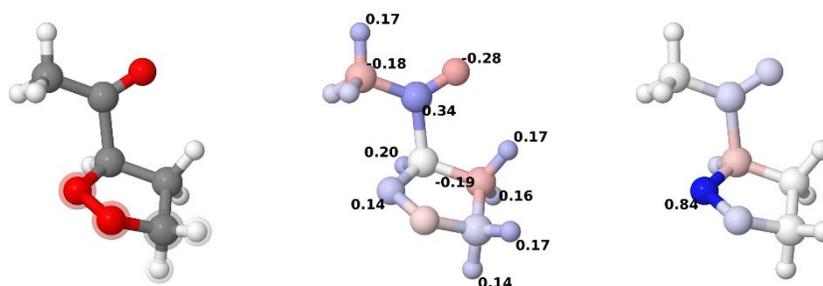
Schemes S1 and S2 show the cation minimum energy conformers of the CH<sub>2</sub>OO + MVK/MACR adduct structures, respectively, and show their partial charges, spin densities, and AIEs. Note that partial charges and spin densities with absolute values below 0.15 are not shown. The five-membered rings of the cationic adduct structures are less puckered compared to the neutral structures, as can be observed by comparing Scheme S1 *versus* Scheme 2 and Scheme S2 *versus* Scheme 3, respectively. Within these rings one can observe the most significant change in partial charge distribution: The peroxide bridge has a combined partial charge of about -0.5 *e* in the neutral case, but is practically neutral in the cationic case. In addition, the partial charges of the hydrogen atoms attached to the ring are roughly 0.06 *e* larger in the cationic case compared to the neutral case, summing up to a total change of charge of about 0.36 *e* (MVK) and 0.30 *e* (MACR). The remaining 0.14 – 0.20 *e* are mostly covered by the increase of the partial charge of the keto-group oxygen when ionizing the adduct structures.

Except for compounds A and E, it is observed that the doublet spin is predominantly located at the "terminal" oxygen of the peroxide bridge, *i.e.* the terminal oxygen of the former Criegee intermediate. For compound A, the doublet spin is predominantly located at the "central" oxygen of the former Criegee intermediate and for compound E, the doublet spin is distributed among both oxygens of the peroxide bridge. This peroxide bridge-focused spin density distribution coincides with the neutralization of the peroxide bridge upon ionization.

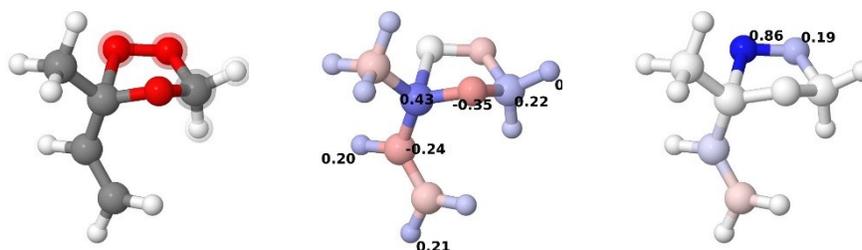
(a) Compound A [1-(1,2-dioxolan-4-yl)ethan-1-one]:  $IE = 9.12$  eV



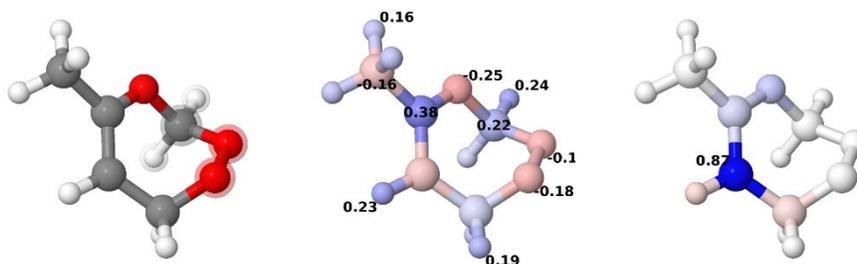
(b) Compound B [1-(1,2-dioxolan-3-yl)ethan-1-one]:  $IE = 9.04$  eV



(c) Compound C [(*S*)-3-methyl-3-vinyl-1,2,4-trioxolane]:  $IE = 9.21$  eV

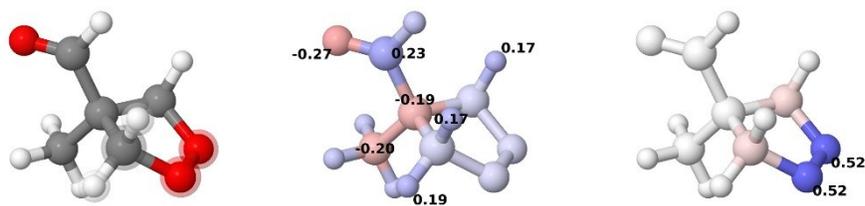


(d) Compound D [5-methyl-7*H*-1,2,4-trioxepine]:  $IE = 8.61$  eV

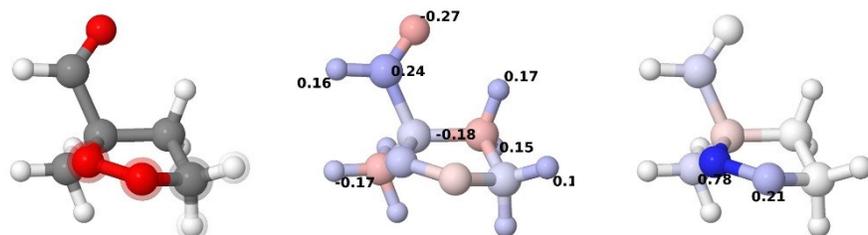


Scheme S1: Cation molecular structures, partial charges, and spin densities of the  $\text{CH}_2\text{OO-MVK}$  adducts and their calculated adiabatic ionization energies. The atoms which previously belonged to the Criegee intermediate are highlighted. Partial charges and spin densities with absolute values below 0.15 are not shown.

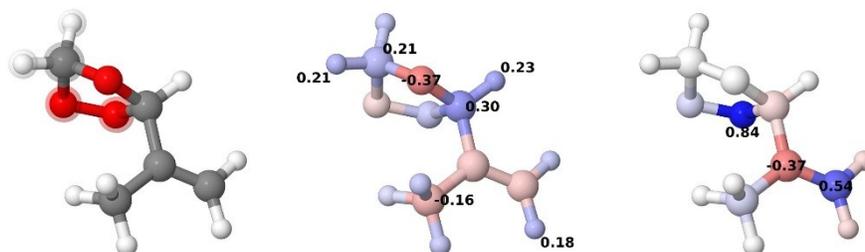
(e) Compound E [4-methyl-1,2-dioxolane-4-carbaldehyde]:  $IE = 9.25$  eV



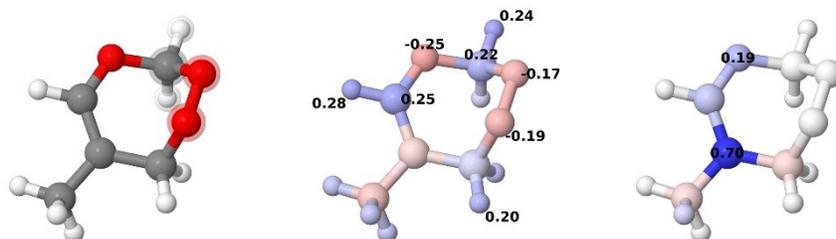
(f) Compound F [(*R*)-3-methyl-1,2-dioxolane-3-carbaldehyde]:  $IE = 9.29$  eV



(g) Compound G [3-(prop-1-en-2-yl)-1,2,4-trioxolane]:  $IE = 9.45$  eV



(h) Compound H [6-methyl-7H-1,2,4-trioxepine]:  $IE = 8.59$  eV



Scheme S2: Cation molecular structures, partial charges, and spin densities of the CH<sub>2</sub>OO-MACR adducts and their calculated adiabatic ionization energies. The atoms which previously belonged to the Criegee intermediate are highlighted. Partial charges and spin densities with absolute values below 0.15 are not shown.

## References

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