Supporting Information

Dissociation Pathways of the CH₂CH₂ONO Radical:

NO₂ + Ethene, NO + Oxirane and a non-Intrinsic Reaction Coordinate HNO + Vinoxy Pathway

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Figure S1. Laser-independent background signal, and photofragment TOF data with and without subtraction of this background signal. We used the background-subtracted data (black) in our fitting, as the background signal interfered with analysis at these masses; in the main text we present the fits superimposed on the original data (blue). The background signal was determined by collecting a TOF spectrum without firing the photodissociation laser. The background signal is shown as red circles, which were interpolated by a moving average method to remove random

noise, giving the solid red line. (At m/e=29 no random noise correction was necessary.) At m/e=30, the photofragment data and background signal were accumulated for different lengths of time, so it was necessary to scale the background signal to match the shape of the photofragment data at long times; at m/e=29 and m/e=44 the two were collected simultaneously, so no such scaling was needed.



Figure S2 (previous page, 5 frames). TOF data and fits for m/e=30 (NO⁺, H₂CO⁺) at five synchrotron energies. A contribution from H₂CO⁺ is not observed at 9.845 and 10.50 eV, and appears weakly at 10.84 eV; this is to be expected, as its photoionization threshold is 10.89 eV (Dodson et al., JPCA 119 (2015), 1279-1291). The contribution from this source increases at higher synchrotron energies, as expected from its increasing photoionization cross section; the contributions from all other channels have been held at a constant ratio, because the different sources of NO are not expected to lead to NO with appreciably different photoionization cross sections. The relative contribution of stable CH₂CH₂ONO radicals has been adjusted in each figure to give the best total fit; this is physically reasonable because the relative photoionization cross section to observe CH₂CH₂ONO⁺ as NO⁺ need not be constant among the energies considered.

S1. Secondary dissociation of HNO to H + NO

Secondary dissociation of primary HNO photofragments is energetically accessible if the dissociation does not partition too much energy into rotations. Any HNO having $E_{vib} > 47.5$ kcal/mol will undergo secondary dissociation to H + NO (using energies from Active Thermochemical Tables). The contribution of dissociating HNO to the data at m/e=30 is represented by the solid green line in Fig. 6. The TOF distribution of the signal is fitted using the P(E_T) of Fig. 5 for photoelimination of HNO from BrCH₂CH₂ONO (the kinetic energy release of the secondary dissociation is safely neglected because, by conservation of momentum, the trajectory of the NO fragment is nearly indistinguishable from the trajectory of the dissociating HNO). NO⁺ signal from the dissociative ionization of HNO would have the same predicted TOF distribution, but the signal cannot arise from this source because photoionization at both 9.845 eV and 11.09 eV is below the 11.3 eV adiabatic appearance energy of NO⁺ from HNO. (We calculate this value by adding the 47.0 kcal/mol dissociation threshold of HNO to the 9.26 eV ionization threshold of NO.)

The primary photoelimination event produces HNO with a range of E_T , E_{rot} , and E_{vib} . In these experiments we were unable to determine how much of the HNO is formed with sufficient E_{vib} to undergo secondary dissociation. It is noteworthy that the entire HNO photoelimination $P(E_T)$ fits the HNO signal at m/e=31, the NO signal at m/e=30, and the signal due to dissociative ionization of BrCH₂CHO at m/e=29 and m/e=15; this agreement would not be expected if some E_T preferentially led to secondary dissociation of HNO. Nevertheless, it is possible that HNO formed with low E_T does preferentially dissociate, and that the HNO signal at long flight times (~60 µs) arises from secondary dissociation of CH₂CH₂ONO rather than from primary HNO. Further study is required to elucidate the internal energy partitioning of HNO.

S2. Photodissociation of BrCH₂CHO to produce CH₂Br + HCO

In Fig. S6 we show data acquired at m/e=29 (HCO⁺) with a synchrotron energy of 11.62 eV. The major contributions to the data are: dissociative ionization of primary BrCH₂CHO photofragments (solid green line) and of the BrCH₂CHO product of BrCH₂CH₂O (solid blue line); dissociative ionization of the oxirane product of CH₂CH₂ONO (dashed black line); and dissociative ionization of the H₂CO product of BrCH₂CH₂O (dashed red line). A small amount of signal, shown by the dashed green line peaking near 40 μ s, is not explained by these other channels. We have attempted to fit it as photodissociation of BrCH₂CHO leading to C-C bond photofission, producing the products CH₂Br + HCO. This follows a suggestion by Nelson et al. (Int. J. Chem. Kinet. 22 (1990), 577-590) that this photofission channel is accessed in the related molecule CCl₃CHO, as well as preliminary data of our own suggesting that it is accessed in ClCH₂CHO. The channel is fitted using an isotropic I(θ) and the P(E_T) shown in Fig. S7.

We include in the fit at m/e=93 no contribution from the CH₂Br product of this hypothesized photodissociation. We believe that the BrCH₂CHO channel is not competitive with the BrCH₂CH₂O channel, as it contributes little signal to the data at m/e=29, less indeed than is contributed by the energetically unfavorable oxirane channel or dissociative ionization of H₂CO. Also, whereas a significant fraction of BrCH₂CH₂O should dissociate by the lowest-barrier CH₂Br channel, C-C bond photofission in BrCH₂CHO requires an unlikely multiphoton event, which selectively cleaves the C-C bond rather than the C-Br bond; thus the BrCH₂CH₂O channel should dominate. Even so, we did attempt to fit the data at m/e=93 including fragments from photodissociation of BrCH₂CHO, but could not derive an acceptable fit with this channel present.

S3. Possible sources of HBr fragments

The TOF data of Fig. S3, collected at m/e=82 ($H^{81}Br^+$) with a photon energy of 14.59 eV, seem to evidence some HBr photofragments in this experiment. The source of this signal is not clear. We can fit it as a sum of two sources: secondary photodissociation of BrCH₂CHO to HBr + ketene, as a green line peaking near 80 µs; and a small contribution from secondary dissociation of BrCH₂CH₂O to HBr + vinoxy, as a blue line peaking near 55 µs. The photodissociation pathway from BrCH₂CHO is analogous to the 193 nm photodissociation of ClCH₂CHO leading to HCl + ketene; indeed, to fit this contribution we have used, without modification, the P(E_T) derived by Miller et al. for ClCH₂CHO (J. Chem. Phys. 121 (2004), 1830-1838), which gives a TOF prediction in remarkable agreement with the data.

Data at m/e=42 (ketene) would corroborate this assignment of the m/e=82 signal to photodissociation of BrCH₂CHO. We did not collect such data in this experiment; however, we can deduce by the following argument that this m/e=82 signal cannot represent primary photoelimination of HBr from the precursor. Primary photoelimination of HBr from BrCH₂CH₂ONO is conceivable, with vinyl nitrite, CH₂CHONO, as a cofragment. However, CH₂CHONO formed with any physically reasonable kinetic energy release (i.e., below ~90 kcal/mol) would be inconsistent with the other data: the neutral flight time of stable CH₂CHONO would be longer than the observed signal at any of its dissociative ionization products; and its most facile secondary dissociation channel, to vinoxy + NO, could not produce the sharp signal seen at m/e=43. We therefore exclude any possibility of primary HBr photoelimination. Therefore, we infer that the only source of HBr that can account for the data at long time is secondary photodissociation of BrCH₂CHO.

Some of the BrCH₂CH₂O radicals should have enough vibrational energy to surmount the 30 kcal/mol barrier to form HBr + vinoxy. The two other channels, having far lower barriers, are

expected to be strongly favored; nevertheless, we can ascribe a small part of the signal at m/e=82 to this channel, fitted as the blue line peaking near 55 μ s in Fig. S3. The fit was derived by requiring that it also fit the vinoxy data at m/e=43: by conservation of energy, the vinoxy cofragments to HBr must be stable to tertiary dissociation, so they can contribute a small amount to the observed vinoxy signal. We note, however, that the inclusion of this channel in the data at m/e=82 is essentially arbitrary: the other channel, photodissociation of BrCH₂CHO to HBr + ketene, can account for all of the HBr signal with only a small adjustment to its fitted P(E_T), and this photodissociation channel seems more physically reasonable based on the extremely high energetic barrier to dissociation of BrCH₂CH₂O to HBr + vinoxy (see the previous work of Wang et al.).

S4. Secondary dissociation of BrCH₂CH₂O to BrCH₂CHO + H

BrCH₂CH₂O radicals can undergo secondary dissociation via H loss, producing H + BrCH₂CHO. The mass of H is so small compared to BrCH₂CHO that, by conservation of momentum, the BrCH₂CHO fragments have virtually the same velocity as the original BrCH₂CH₂O fragments; thus the BrCH₂CHO from this channel can be treated using only the primary O-NO bond photofission P(E_T). Like the primary BrCH₂CHO fragments described in the main text, this channel also gives signal due to dissociative ionization at m/e=15, 29, and 79, represented by a dark blue line with a neutral flight time near 80 µs in each figure. This secondary source of BrCH₂CHO, however, also gives signal at the parent cation of m/e=122 with a synchrotron energy of 13.78 eV; the data and fit are shown in Fig. S8. Interestingly, the primary BrCH₂CHO co-fragment to HNO evidently does not photoionize to give the m/e=122 parent ion; it may be that only vibrationally cold fragments, produced through the secondary dissociation channel, lead to a bound cation at 13.78 eV. This BrCH₂CHO + H channel was also observed in the previous study by its dissociative ionization (under electron bombardment) to m/e=29 and m/e=79.

Many fragments observed in this study form from photodissociation of BrCH₂CHO. We have assumed throughout this report that photodissociation occurs exclusively in the primary BrCH₂CHO co-fragments to HNO, not in the secondary fragments of this channel. The primary fragments, being vibrationally hot, might be expected to have a higher photoabsorption cross section than the vibrationally cold BrCH₂CHO of this secondary channel. Nevertheless, it must be noted that the velocity distributions of the photoproducts of BrCH₂CHO are essentially identical from either source, as the velocity distributions of the BrCH₂CHO themselves are quite similar. It was therefore impossible in this experiment to discriminate between photodissociation of the BrCH₂CHO formed in these two channels.

S5. Statistical justification for photodissociation of BrCH₂CHO

In the text, we ascribe the vinoxy signal to photodissociation of BrCH₂CHO, not to secondary dissociation due to vibrational excitation; this point bears some justification. We calculate that the endoergicity of the transformation BrCH₂CHO \rightarrow Br + CH₂CHO is Δ H_{0K} = 60.3 kcal/mol with negligible barrier above the endoergicity. Any BrCH₂CHO with E_{vib} > 60.3 kcal/mol will therefore dissociate, and any excess E_{vib} will be distributed statistically among the 3N-6 = 15 vibrational degrees of freedom, one of which can be taken as the dissociation coordinate. The P(E_T) observed for this dissociation (Fig. 15) evidences a large partitioning of energy into the dissociation coordinate, $\langle E_T \rangle \sim 30$ kcal/mol; whereas the total energy available to the BrCH₂CHO fragments is less than 140 kcal/mol (see the discussion of photoelimination of HNO from the precursor), so the excess E_{vib} cannot exceed 140 – 60.3 = 80 kcal/mol. Thus, secondary dissociation of BrCH₂CHO to Br + CH₂CHO with the observed E_T would require the partitioning of a very large fraction of the available energy, 30 kcal/mol out of a maximum below 80 kcal/mol, into a single one of the 15 degrees of freedom. Such an event is statistically quite unlikely. Rather, the large kinetic energy release should be attributed to photofission of the C-Br bond when the BrCH₂CHO absorbs a 193 nm photon.



14.59 eV. The fits are somewhat arbitrary; for details see the preceding paragraphs of this

document.



Figure S4 (previous page, two frames). Predicted speed distributions for the ethene fragments of dissociation of CH_2CH_2ONO to NO_2 + ethene, and predicted angular distributions of the NO_2 fragment of this dissociation, where 0 degrees represents scattering in the direction of the

velocity of the dissociating CH₂CH₂ONO fragment. The different colors correspond to dissociation of CH₂CH₂ONO that was formed by photodissociation of each of the four precursor conformers, and from photodissociation of the *anti-trans* precursor conformer that isomerizes to *cis*-CH₂CH₂ONO before dissociation. These results were not used directly in our analysis: the speed distributions in particular show a spuriously large likelihood of low-velocity fragments, which is inconsistent with the data. The predictive model does not account for forces along the exit barrier of the reaction, which may explain this discrepancy.



Figure S5. $P(E_T)$ used for the photodissociation of NO₂ to NO + O. Reproduced from Butler et al., J. Chem. Phys. 79 (1983), 1708-1722.



Figure S6. Time-of-flight spectrum of the signal at m/e=29 (HCO⁺) at a synchrotron energy of 11.62 eV. Dissociative ionization of BrCH₂CHO to HCO⁺ is apparent (solid blue and solid green lines), as well as dissociative ionization of the oxirane product of CH₂CH₂ONO (dashed black line). Dissociative ionization of the H₂CO product of BrCH₂CH₂O is shown in red dashed line. The contribution of the green dashed line is tentatively assigned to photodissociation of

BrCH₂CHO, described above.



Figure S7. Photofragment recoil kinetic energy distribution of the secondary photodissociation BrCH₂CHO + $h\nu \rightarrow$ CH₂Br + HCO, derived by forward convolution fitting of the data of Fig.

S6.



Figure S8. Time-of-flight spectrum and fit of m/e = 122 (BrCH₂CHO⁺) signal at a photoionization energy of 13.78 eV. This fit is produced using the distribution of recoil kinetic energies, P(E_T), for primary photodissociation of BrCH₂CH₂ONO leading to NO + BrCH₂CH₂O to determine the velocity of dissociating BrCH₂CH₂O radicals; because the departing H atom has such a low mass, the BrCH₂CHO fragments have nearly the same TOF distribution as the

dissociating BrCH₂CH₂O.



Cartesian coordinates of the minima and transition states of CH₂CH₂ONO

MIN1

C -1.105570 0.551285 0.088111 C -2.130487 -0.511477 0.065184 H -1.857782 -1.530614 0.295767 H -3.166395 -0.274822 -0.123778 H -1.426412 1.434127 -0.467140 H -0.856997 0.872322 1.108571 O 0.122519 0.092519 -0.520480 N 1.183855 0.094873 0.419993 O 2.182098 -0.268015 -0.063663

MIN2

C 1.650461 0.629167 -0.294798 H 2.192879 0.342520 -1.184000 C 0.940943 -0.393854 0.495370 H 1.566806 1.677214 -0.053708 O -0.217511 -0.971273 -0.221831 H 0.585849 -0.008444 1.448838 H 1.546830 -1.283646 0.661203 N -1.355153 -0.189496 -0.293809 O -1.276828 0.869641 0.219443 C -0.793360 0.475479 -0.000002 C -2.198970 0.037533 0.000006 H -2.704064 -0.186858 0.927349 H -2.704101 -0.186777 -0.927336 H -0.531245 1.055905 -0.884946 H -0.531233 1.055899 0.884944 O 0.049369 -0.736628 -0.000009 N 1.420223 -0.530190 -0.000002 O 1.761014 0.598514 0.000006

MIN4

C 0.911358 0.319415 0.003662 C 2.224249 0.131612 0.016225 H 2.665190 -0.854055 -0.015755 H 2.879320 0.988078 0.046212 H 0.429326 1.286048 0.028205 H -1.839981 -1.214135 -0.208377 O 0.058321 -0.743237 -0.079928 N -1.337981 -0.404521 0.167576 O -1.756023 0.733180 -0.062902

MIN5

C -1.239213 0.201530 -0.000086 O -0.655413 -0.887345 -0.000110 C -2.654402 0.310335 0.000105 H -0.654413 1.133284 -0.000219 H 1.500666 -0.945330 0.000155 O 2.157617 0.758808 -0.000033 N 2.413466 -0.417411 0.000105 H -3.258740 -0.586373 0.000229 H -3.137723 1.277403 0.000126

TS1

C 2.236026 0.093419 -0.206720 C 0.913528 0.300742 0.411437 O -0.034683 -0.578550 -0.266165 N -1.399338 -0.395637 0.288056 O -1.965593 0.463884 -0.242024 H 0.571533 1.333160 0.276010 H 0.921334 0.063496 1.477825 H 3.006789 -0.468530 0.298090 H 2.400596 0.393690 -1.231105

TS2

C -1.818617 -0.656237 -0.047320 H -1.883380 -0.920846 -1.092233 C -0.999293 0.503095 0.374395 H -2.470461 -1.146887 0.661046 O 0.124817 0.752550 -0.475392 H -0.668178 0.402899 1.415965 H -1.567097 1.442274 0.323309 N 1.095112 -0.397531 -0.422493 O 1.854032 -0.262034 0.436255

TS3

C -2.013927 -0.280024 -0.364600 H -2.932399 0.267205 -0.216867 C -0.876520 -0.122474 0.559234 H -1.896819 -0.851846 -1.273677 O 0.092848 0.832273 -0.016695 H -0.350282 -1.059732 0.735131 H -1.165498 0.314696 1.512677 N 1.398234 0.400545 -0.268345 O 1.644658 -0.714666 0.010863

TS4

C 1.652709 0.625325 -0.289331 H 2.158570 0.470895 -1.231851 H 1.474372 1.640775 0.028440 C 1.161198 -0.454655 0.444107 H 1.583104 -1.434480 0.267390 H 0.832296 -0.274187 1.458592 O -0.461197 -1.011890 -0.217614 N -1.393109 -0.143201 -0.204118 O -1.186306 0.958812 0.214814

TS5

C 2.245164 -0.024549 -0.000004 C 0.996283 0.584874 0.000004 O -0.223844 -0.833558 0.000002 N -1.455133 -0.492618 -0.000001 O -1.776202 0.658164 -0.000002 H 2.730866 -0.304340 -0.923686 H 2.730876 -0.304343 0.923675 H 0.637937 1.049101 0.908617 H 0.637933 1.049112 -0.908601

TS6

C -2.059582 0.624037 -0.140423 C -1.569670 -0.537113 0.364667 O 0.371574 -0.488113 -0.500382 N 1.125724 0.232183 0.297551 0 2.289927 0.200189 0.007353 H -1.762578 -1.481964 -0.121222 H -1.164851 -0.581462 1.364436 H -1.926856 1.562283 0.380001 H -2.542285 0.657720 -1.107301

TS7

C 2.014883 -0.029468 0.363981 C 0.884527 0.627167 -0.291044 O 0.273370 -0.641950 -0.296699 N -1.523717 -0.580397 0.019722 O -1.884952 0.494397 0.196107 H 1.061953 1.021863 -1.292704 H 0.337395 1.356777 0.314890 H 1.989570 -0.197523 1.428660 H 2.773285 -0.524101 -0.221789

TS8

C 2.075725 -0.483652 0.173151 C 1.222234 0.687950 -0.033892 O 0.184655 -0.223846 -0.309239 N -1.467149 0.412261 0.195302 O -2.265645 -0.373320 -0.019278 H 1.476662 1.320085 -0.886701 H 1.029499 1.297823 0.851749 H 2.074130 -0.986177 1.127242 H 2.549913 -0.966020 -0.666824

TS9

C -0.877770 0.022377 0.433557 O -0.124625 1.006942 -0.041810 H -0.792205 -0.198367 1.509371 C -2.095133 -0.345295 -0.182568 H -0.100558 -0.977987 0.030241 N 1.142868 -0.284678 -0.454049 O 2.102785 -0.240130 0.168191 H -2.748233 -1.072156 0.280792 H -2.346946 0.044271 -1.159042

TS10

C 0.955946 -0.211475 0.130440 C 2.312050 -0.265354 -0.111971 H 2.856649 0.628696 -0.379416 H 2.851818 -1.192186 0.013648 H 0.417755 -1.137378 0.376726 H -1.843085 1.026114 0.577081 0 0.286314 0.864008 0.106950 N -1.622569 0.390075 -0.228817 O -1.852955 -0.763359 0.005908