## Supporting Information

## Dissociation Pathways of the $\mathbf{C H}_{\mathbf{2}} \mathbf{C H}_{\mathbf{2}} \mathbf{O N O}$ Radical:

$\mathrm{NO}_{2}+$ Ethene, $\mathrm{NO}+$ Oxirane and a non-Intrinsic Reaction Coordinate HNO + Vinoxy

## Pathway

Preston G. Scrape ${ }^{1}$, Trevor D. Roberts ${ }^{1}$, Shih-Huang Lee ${ }^{2}$, Laurie J. Butler ${ }^{1 *}$

1. The James Franck Institute and Department of Chemistry, The University of Chicago, Chicago, Illinois, 60637, USA
2. National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan, Republic of China

* Corresponding author: L. J. Butler: e-mail, L-Butler@uchicago.edu; phone, 773-702-

7206. 



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 $\mathrm{m} / \mathrm{e}=29$ no random noise correction was necessary.) At $\mathrm{m} / \mathrm{e}=30$, 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 $\mathrm{m} / \mathrm{e}=29$ and $\mathrm{m} / \mathrm{e}=44$ the two were collected simultaneously, so no such scaling was needed.


Figure S2 (previous page, 5 frames). TOF data and fits for $\mathrm{m} / \mathrm{e}=30\left(\mathrm{NO}^{+}, \mathrm{H}_{2} \mathrm{CO}^{+}\right)$at five synchrotron energies. A contribution from $\mathrm{H}_{2} \mathrm{CO}^{+}$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 $\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{ONO}$ 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 $\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{ONO}^{+}$as $\mathrm{NO}^{+}$need not be constant among the energies considered.

## S1. Secondary dissociation of HNO to $\mathbf{H}+\mathbf{N O}$

Secondary dissociation of primary HNO photofragments is energetically accessible if the dissociation does not partition too much energy into rotations. Any HNO having $\mathrm{E}_{\text {vib }}>47.5$ $\mathrm{kcal} / \mathrm{mol}$ will undergo secondary dissociation to $\mathrm{H}+\mathrm{NO}$ (using energies from Active Thermochemical Tables). The contribution of dissociating HNO to the data at $\mathrm{m} / \mathrm{e}=30$ is represented by the solid green line in Fig. 6. The TOF distribution of the signal is fitted using the $\mathrm{P}\left(\mathrm{E}_{\mathrm{T}}\right)$ of Fig. 5 for photoelimination of HNO from $\mathrm{BrCH}_{2} \mathrm{CH}_{2} \mathrm{ONO}$ (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 $\mathrm{HNO}) . \mathrm{NO}^{+}$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 $\mathrm{NO}^{+}$from HNO . (We calculate this value by adding the $47.0 \mathrm{kcal} / \mathrm{mol}$ dissociation threshold of HNO to the 9.26 eV ionization threshold of NO.)

The primary photoelimination event produces HNO with a range of $\mathrm{E}_{\mathrm{T}}, \mathrm{E}_{\text {rot }}$, and $\mathrm{E}_{\text {vib }}$. In these experiments we were unable to determine how much of the HNO is formed with sufficient $\mathrm{E}_{\text {vib }}$ to undergo secondary dissociation. It is noteworthy that the entire HNO photoelimination $\mathrm{P}\left(\mathrm{E}_{\mathrm{T}}\right)$ fits the HNO signal at $\mathrm{m} / \mathrm{e}=31$, the NO signal at $\mathrm{m} / \mathrm{e}=30$, and the signal due to dissociative ionization of $\mathrm{BrCH}_{2} \mathrm{CHO}$ at $\mathrm{m} / \mathrm{e}=29$ and $\mathrm{m} / \mathrm{e}=15$; this agreement would not be expected if some $\mathrm{E}_{\mathrm{T}}$ preferentially led to secondary dissociation of HNO. Nevertheless, it is possible that HNO formed with low $\mathrm{E}_{\mathrm{T}}$ does preferentially dissociate, and that the HNO signal at long flight times ( $\sim 60 \mu \mathrm{~s}$ ) arises from secondary dissociation of $\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{ONO}$ rather than from primary HNO . Further study is required to elucidate the internal energy partitioning of HNO.

## S2. Photodissociation of $\mathrm{BrCH}_{2} \mathbf{C H O}$ to produce $\mathrm{CH}_{2} \mathrm{Br}+\mathbf{H C O}$

In Fig. S6 we show data acquired at $\mathrm{m} / \mathrm{e}=29\left(\mathrm{HCO}^{+}\right)$with a synchrotron energy of 11.62 eV . The major contributions to the data are: dissociative ionization of primary $\mathrm{BrCH}_{2} \mathrm{CHO}$ photofragments (solid green line) and of the $\mathrm{BrCH}_{2} \mathrm{CHO}$ product of $\mathrm{BrCH}_{2} \mathrm{CH}_{2} \mathrm{O}$ (solid blue line); dissociative ionization of the oxirane product of $\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{ONO}$ (dashed black line); and dissociative ionization of the $\mathrm{H}_{2} \mathrm{CO}$ product of $\mathrm{BrCH}_{2} \mathrm{CH}_{2} \mathrm{O}$ (dashed red line). A small amount of signal, shown by the dashed green line peaking near $40 \mu \mathrm{~s}$, is not explained by these other channels. We have attempted to fit it as photodissociation of $\mathrm{BrCH}_{2} \mathrm{CHO}$ leading to $\mathrm{C}-\mathrm{C}$ bond photofission, producing the products $\mathrm{CH}_{2} \mathrm{Br}+\mathrm{HCO}$. 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 $\mathrm{CCl}_{3} \mathrm{CHO}$, as well as preliminary data of our own suggesting that it is accessed in $\mathrm{ClCH}_{2} \mathrm{CHO}$. The channel is fitted using an isotropic $\mathrm{I}(\theta)$ and the $\mathrm{P}\left(\mathrm{E}_{\mathrm{T}}\right)$ shown in Fig. S7.

We include in the fit at $\mathrm{m} / \mathrm{e}=93$ no contribution from the $\mathrm{CH}_{2} \mathrm{Br}$ product of this hypothesized photodissociation. We believe that the $\mathrm{BrCH}_{2} \mathrm{CHO}$ channel is not competitive with the $\mathrm{BrCH}_{2} \mathrm{CH}_{2} \mathrm{O}$ channel, as it contributes little signal to the data at $\mathrm{m} / \mathrm{e}=29$, less indeed than is contributed by the energetically unfavorable oxirane channel or dissociative ionization of $\mathrm{H}_{2} \mathrm{CO}$. Also, whereas a significant fraction of $\mathrm{BrCH}_{2} \mathrm{CH}_{2} \mathrm{O}$ should dissociate by the lowest-barrier $\mathrm{CH}_{2} \mathrm{Br}$ channel, $\mathrm{C}-\mathrm{C}$ bond photofission in $\mathrm{BrCH}_{2} \mathrm{CHO}$ requires an unlikely multiphoton event, which selectively cleaves the $\mathrm{C}-\mathrm{C}$ bond rather than the $\mathrm{C}-\mathrm{Br}$ bond; thus the $\mathrm{BrCH}_{2} \mathrm{CH}_{2} \mathrm{O}$ channel should dominate. Even so, we did attempt to fit the data at $\mathrm{m} / \mathrm{e}=93$ including fragments from photodissociation of $\mathrm{BrCH}_{2} \mathrm{CHO}$, 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 $\mathrm{m} / \mathrm{e}=82\left(\mathrm{H}^{81} \mathrm{Br}^{+}\right)$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 $\mathrm{BrCH}_{2} \mathrm{CHO}$ to HBr + ketene, as a green line peaking near $80 \mu \mathrm{~s}$; and a small contribution from secondary dissociation of $\mathrm{BrCH}_{2} \mathrm{CH}_{2} \mathrm{O}$ to $\mathrm{HBr}+$ vinoxy, as a blue line peaking near $55 \mu \mathrm{~s}$. The photodissociation pathway from $\mathrm{BrCH}_{2} \mathrm{CHO}$ is analogous to the 193 nm photodissociation of $\mathrm{ClCH}_{2} \mathrm{CHO}$ leading to $\mathrm{HCl}+$ ketene; indeed, to fit this contribution we have used, without modification, the $\mathrm{P}\left(\mathrm{E}_{\mathrm{T}}\right)$ derived by Miller et al. for $\mathrm{ClCH}_{2} \mathrm{CHO}$ (J. Chem. Phys. 121 (2004), 1830-1838), which gives a TOF prediction in remarkable agreement with the data.

Data at $\mathrm{m} / \mathrm{e}=42$ (ketene) would corroborate this assignment of the $\mathrm{m} / \mathrm{e}=82$ signal to photodissociation of $\mathrm{BrCH}_{2} \mathrm{CHO}$. We did not collect such data in this experiment; however, we can deduce by the following argument that this $\mathrm{m} / \mathrm{e}=82$ signal cannot represent primary photoelimination of HBr from the precursor. Primary photoelimination of HBr from $\mathrm{BrCH}_{2} \mathrm{CH}_{2} \mathrm{ONO}$ is conceivable, with vinyl nitrite, $\mathrm{CH}_{2} \mathrm{CHONO}$, as a cofragment. However, $\mathrm{CH}_{2} \mathrm{CHONO}$ formed with any physically reasonable kinetic energy release (i.e., below $\sim 90$ $\mathrm{kcal} / \mathrm{mol}$ ) would be inconsistent with the other data: the neutral flight time of stable $\mathrm{CH}_{2} \mathrm{CHONO}$ 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 $\mathrm{m} / \mathrm{e}=43$. 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 $\mathrm{BrCH}_{2} \mathrm{CHO}$.

Some of the $\mathrm{BrCH}_{2} \mathrm{CH}_{2} \mathrm{O}$ radicals should have enough vibrational energy to surmount the $30 \mathrm{kcal} / \mathrm{mol}$ barrier to form $\mathrm{HBr}+$ 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 $\mathrm{m} / \mathrm{e}=82$ to this channel, fitted as the blue line peaking near $55 \mu \mathrm{~s}$ in Fig. S3. The fit was derived by requiring that it also fit the vinoxy data at $\mathrm{m} / \mathrm{e}=43$ : 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 $\mathrm{m} / \mathrm{e}=82$ is essentially arbitrary: the other channel, photodissociation of $\mathrm{BrCH}_{2} \mathrm{CHO}$ to $\mathrm{HBr}+$ ketene, can account for all of the HBr signal with only a small adjustment to its fitted $\mathrm{P}\left(\mathrm{E}_{\mathrm{T}}\right)$, and this photodissociation channel seems more physically reasonable based on the extremely high energetic barrier to dissociation of $\mathrm{BrCH}_{2} \mathrm{CH}_{2} \mathrm{O}$ to $\mathrm{HBr}+$ vinoxy (see the previous work of Wang et al.).

## S4. Secondary dissociation of $\mathrm{BrCH}_{2} \mathrm{CH}_{2} \mathrm{O}$ to $\mathrm{BrCH}_{2} \mathrm{CHO}+\mathrm{H}$

$\mathrm{BrCH}_{2} \mathrm{CH}_{2} \mathrm{O}$ radicals can undergo secondary dissociation via H loss, producing $\mathrm{H}+$ $\mathrm{BrCH}_{2} \mathrm{CHO}$. The mass of H is so small compared to $\mathrm{BrCH}_{2} \mathrm{CHO}$ that, by conservation of momentum, the $\mathrm{BrCH}_{2} \mathrm{CHO}$ fragments have virtually the same velocity as the original $\mathrm{BrCH}_{2} \mathrm{CH}_{2} \mathrm{O}$ fragments; thus the $\mathrm{BrCH}_{2} \mathrm{CHO}$ from this channel can be treated using only the primary O-NO bond photofission $\mathrm{P}\left(\mathrm{E}_{\mathrm{T}}\right)$. Like the primary $\mathrm{BrCH}_{2} \mathrm{CHO}$ fragments described in the main text, this channel also gives signal due to dissociative ionization at $\mathrm{m} / \mathrm{e}=15,29$, and 79 , represented by a dark blue line with a neutral flight time near $80 \mu$ s in each figure. This secondary source of $\mathrm{BrCH}_{2} \mathrm{CHO}$, however, also gives signal at the parent cation of $\mathrm{m} / \mathrm{e}=122$ with a synchrotron energy of 13.78 eV ; the data and fit are shown in Fig. S8. Interestingly, the primary $\mathrm{BrCH}_{2} \mathrm{CHO}$ co-fragment to HNO evidently does not photoionize to give the $\mathrm{m} / \mathrm{e}=122$ 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 $\mathrm{BrCH}_{2} \mathrm{CHO}+\mathrm{H}$ channel was also
observed in the previous study by its dissociative ionization (under electron bombardment) to $\mathrm{m} / \mathrm{e}=29$ and $\mathrm{m} / \mathrm{e}=79$.

Many fragments observed in this study form from photodissociation of $\mathrm{BrCH}_{2} \mathrm{CHO}$. We have assumed throughout this report that photodissociation occurs exclusively in the primary $\mathrm{BrCH}_{2} \mathrm{CHO}$ 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 $\mathrm{BrCH}_{2} \mathrm{CHO}$ of this secondary channel. Nevertheless, it must be noted that the velocity distributions of the photoproducts of $\mathrm{BrCH}_{2} \mathrm{CHO}$ are essentially identical from either source, as the velocity distributions of the $\mathrm{BrCH}_{2} \mathrm{CHO}$ themselves are quite similar. It was therefore impossible in this experiment to discriminate between photodissociation of the $\mathrm{BrCH}_{2} \mathrm{CHO}$ formed in these two channels.

## S5. Statistical justification for photodissociation of $\mathrm{BrCH}_{2} \mathbf{C H O}$

In the text, we ascribe the vinoxy signal to photodissociation of $\mathrm{BrCH}_{2} \mathrm{CHO}$, not to secondary dissociation due to vibrational excitation; this point bears some justification. We calculate that the endoergicity of the transformation $\mathrm{BrCH}_{2} \mathrm{CHO} \rightarrow \mathrm{Br}+\mathrm{CH}_{2} \mathrm{CHO}$ is $\Delta \mathrm{H}_{0 \mathrm{~K}}=$ $60.3 \mathrm{kcal} / \mathrm{mol}$ with negligible barrier above the endoergicity. Any $\mathrm{BrCH}_{2} \mathrm{CHO}$ with $\mathrm{E}_{\text {vib }}>60.3$ $\mathrm{kcal} / \mathrm{mol}$ will therefore dissociate, and any excess $\mathrm{E}_{\mathrm{vib}}$ will be distributed statistically among the $3 N-6=15$ vibrational degrees of freedom, one of which can be taken as the dissociation coordinate. The $\mathrm{P}\left(\mathrm{E}_{\mathrm{T}}\right)$ observed for this dissociation (Fig. 15) evidences a large partitioning of energy into the dissociation coordinate, $<\mathrm{E}_{\mathrm{T}}>\sim 30 \mathrm{kcal} / \mathrm{mol}$; whereas the total energy available to the $\mathrm{BrCH}_{2} \mathrm{CHO}$ fragments is less than $140 \mathrm{kcal} / \mathrm{mol}$ (see the discussion of photoelimination of HNO from the precursor), so the excess $\mathrm{E}_{\mathrm{vib}}$ cannot exceed $140-60.3=80 \mathrm{kcal} / \mathrm{mol}$. Thus, secondary dissociation of $\mathrm{BrCH}_{2} \mathrm{CHO}$ to $\mathrm{Br}+\mathrm{CH}_{2} \mathrm{CHO}$ with the observed $\mathrm{E}_{\mathrm{T}}$ would require the
partitioning of a very large fraction of the available energy, $30 \mathrm{kcal} / \mathrm{mol}$ out of a maximum below $80 \mathrm{kcal} / \mathrm{mol}$, 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 $\mathrm{BrCH}_{2} \mathrm{CHO}$ absorbs a 193 nm photon.


Figure S3. Time-of-flight spectrum of $m / e=82\left(\mathrm{H}^{81} \mathrm{Br}^{+}\right)$signal at a photoionization energy of 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 $\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{ONO}$ to $\mathrm{NO}_{2}+$ ethene, and predicted angular distributions of the $\mathrm{NO}_{2}$ fragment of this dissociation, where 0 degrees represents scattering in the direction of the velocity of the dissociating $\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{ONO}$ fragment. The different colors correspond to dissociation of $\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{ONO}$ 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 $-\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{ONO}$ 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 $\mathrm{S} 5 . \mathrm{P}\left(\mathrm{E}_{\mathrm{T}}\right)$ used for the photodissociation of $\mathrm{NO}_{2}$ to $\mathrm{NO}+\mathrm{O}$. Reproduced from Butler et al., J. Chem. Phys. 79 (1983), 1708-1722.


Figure S6. Time-of-flight spectrum of the signal at $\mathrm{m} / \mathrm{e}=29\left(\mathrm{HCO}^{+}\right)$at a synchrotron energy of 11.62 eV . Dissociative ionization of $\mathrm{BrCH}_{2} \mathrm{CHO}$ to $\mathrm{HCO}^{+}$is apparent (solid blue and solid green lines), as well as dissociative ionization of the oxirane product of $\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{ONO}$ (dashed black line). Dissociative ionization of the $\mathrm{H}_{2} \mathrm{CO}$ product of $\mathrm{BrCH}_{2} \mathrm{CH}_{2} \mathrm{O}$ is shown in red dashed line. The contribution of the green dashed line is tentatively assigned to photodissociation of $\mathrm{BrCH}_{2} \mathrm{CHO}$, described above.


Figure S7. Photofragment recoil kinetic energy distribution of the secondary photodissociation $\mathrm{BrCH}_{2} \mathrm{CHO}+h \nu \rightarrow \mathrm{CH}_{2} \mathrm{Br}+\mathrm{HCO}$, derived by forward convolution fitting of the data of Fig.

S6.


Figure S8. Time-of-flight spectrum and fit of m/e $=122\left(\mathrm{BrCH}_{2} \mathrm{CHO}^{+}\right)$signal at a
photoionization energy of 13.78 eV . This fit is produced using the distribution of recoil kinetic energies, $\mathrm{P}\left(\mathrm{E}_{\mathrm{T}}\right)$, for primary photodissociation of $\mathrm{BrCH}_{2} \mathrm{CH}_{2} \mathrm{ONO}$ leading to $\mathrm{NO}+\mathrm{BrCH}_{2} \mathrm{CH}_{2} \mathrm{O}$ to determine the velocity of dissociating $\mathrm{BrCH}_{2} \mathrm{CH}_{2} \mathrm{O}$ radicals; because the departing H atom has such a low mass, the $\mathrm{BrCH}_{2} \mathrm{CHO}$ fragments have nearly the same TOF distribution as the dissociating $\mathrm{BrCH}_{2} \mathrm{CH}_{2} \mathrm{O}$.

## Cartesian coordinates of the minima and transition states of $\mathbf{C H}_{\mathbf{2}} \mathbf{C H}_{\mathbf{2}} \mathbf{O N O}$



MIN1
C - 1.1055700 .5512850 .088111
C - $2.130487-0.5114770 .065184$
H - 1.857782 -1.530614 0.295767
H -3.166395-0.274822-0.123778
H-1.426412 1.434127-0.467140
H -0.856997 0.8723221 .108571
O $0.1225190 .092519-0.520480$
N 1.1838550 .0948730 .419993
O 2.182098 -0.268015-0.063663
MIN2
C $1.6504610 .629167-0.294798$
H $2.1928790 .342520-1.184000$
C $0.940943-0.3938540 .495370$
H $1.5668061 .677214-0.053708$
O-0.217511-0.971273-0.221831
H $0.585849-0.0084441 .448838$
H 1.546830 -1.283646 0.661203
N -1.355153-0.189496-0.293809
O-1.276828 0.8696410 .219443
MIN3

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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 0.5985140.000006
MIN4
C 0.911358 0.3194150.003662
C 2.224249 0.1316120.016225
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
0 -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
0-1.965593 0.463884-0.242024
H 0.571533 1.333160 0.276010
H 0.9213340.063496 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
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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
0 -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
0-1.776202 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
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TS6
C -2.059582 0.624037-0.140423
C - $1.569670-0.5371130 .364667$
O $0.371574-0.488113-0.500382$
N 1.1257240 .2321830 .297551

O 2.2899270 .2001890 .007353
H -1.762578-1.481964-0.121222
H-1.164851-0.581462 1.364436
H -1.926856 1.5622830 .380001
H-2.542285 0.657720-1.107301
TS7
C 2.014883 -0.029468 0.363981
C 0.884527 0.627167-0.291044
O $0.273370-0.641950-0.296699$
$\mathrm{N}-1.523717-0.5803970 .019722$
O-1.884952 0.4943970 .196107
H 1.061953 1.021863-1.292704
H 0.3373951 .3567770 .314890
H $1.989570-0.1975231 .428660$
H $2.773285-0.524101-0.221789$
TS8
C $2.075725-0.4836520 .173151$
C $1.2222340 .687950-0.033892$
O $0.184655-0.223846-0.309239$
N -1.467149 0.4122610 .195302
0-2.265645-0.373320-0.019278
H $1.4766621 .320085-0.886701$
H 1.0294991 .2978230 .851749
H $2.074130-0.9861771 .127242$
H $2.549913-0.966020-0.666824$
TS9
C - 0.8777700 .0223770 .433557
0-0.124625 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 $2.102785-0.2401300 .168191$
H-2.748233-1.072156 0.280792
H-2.346946 0.044271-1.159042
TS10
C $0.955946-0.2114750 .130440$
C 2.312050-0.265354-0.111971
H $2.8566490 .628696-0.379416$
H 2.851818 -1.192186 0.013648
H $0.417755-1.1373780 .376726$
H-1.843085 1.0261140 .577081

O 0.2863140 .8640080 .106950
N -1.622569 0.390075-0.228817
0-1.852955-0.763359 0.005908

