O$_2$-Oxidation of Cyanomethylene Radical: Infrared Identification of Criegee Intermediates $\text{syn}$- and $\text{anti}$-NCC(H)OO$^\dagger$

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Cyanomethylene radical (HCCN) is an important intermediate in the nitrile chemistry in both the earth’s and the Titan’s atmosphere. Despite that the mechanism for the oxidation of HCCN has been already computationally explored, the key Criegee intermediate, NCC(H)OO, remains unobserved yet. By photolyzing mixtures (1:50:1000) of either HC(N$_2$)CN/O$_2$/N$_2$ (266 nm) or HCCNCO/O$_2$/N$_2$ (193 nm) at 15.0 K, the elusive carbonyl oxides NCC(H)OO, in $\text{syn}$- and $\text{anti}$-conformations, have been generated and characterized with IR spectroscopy. The spectroscopic identification is supported by $^{13}$O-labeling experiments and the quantum chemical calculations at the BP86/6-311+G(3df,3pd) level. Upon subsequent UV-light irradiation, both conformers of NCC(H)OO further react with O$_2$ and yield NCC(O)H and O$_3$, whereas, the dioxirane isomer HC(O$_2$)CN, which is lower than $\text{syn}$-NCC(H)OO by 23.7 kcal/mol at the CCSD(T)-F12a/aug-cc-pVTZ//BP86/6-311+G(3df,3pd) level, was not observed experimentally.

**Key words:** Methylene radicals, Criegee intermediates, Oxidation, Photochemistry, IR spectroscopy

I. INTRODUCTION

Nitriles, R-CN, are well known as one of the most abundant prebiotic organic molecules in the star-forming regions in the interstellar medium [1–3]. For instance, the simplest acetonitrile (CH$_3$CN) is a major product of the vacuum ultraviolet (VUV) photochemistry of interstellar ice analogs [4]. CH$_3$CN and its deuterated isotopologue CDH$_2$CN have been detected in the Sgr B and Sgr A molecular clouds [5, 6]. Very recently, CH$_3$CN and its diverse fragmentation species CH$_2$CN, HCN/HNC, and CCN, and CN have been observed in the nearby Galactic diffuse molecular clouds by Jansky Very Large Array [7]. Moreover, its isomer methyl cyanide (CH$_3$NC) [8, 9] and ketenimine (CH$_2$=C=NH) [10] are also interstellar species that have been detected in Orion Kleinmann-Low (Orion-KL) region [11] and the hot cores of Sagittarius B2(N) [10], respectively. In addition to the important role in interstellar medium, CH$_3$CN is also involved in the combustion and thermal decomposition of nitrogen-containing compounds in the earth’s atmosphere [12].

As one of the most important properties of CH$_3$CN, its decomposition under different conditions keeps attracting enormous interest [13–18]. Similar to the degradation of most volatile organic compounds (VOCs) in the atmosphere [19], the X-ray irradiation-induced decomposition of CH$_3$CN in solid noble gas matrices at 5 K yields dehydrogenation products CH$_2$CN/CH$_2$NC, HCCN/HCNC, and CCN/CNC, together with minor amounts of fragmentation species CH$_3$, CN, HCN, and HNC [20]. Among these species, the cyanomethylene radical (HCCN) features as the parent molecule for the synthetically useful cyanocarbenes [21–23]. In addition to the synthetic applications of HCCN as a versatile nitrile transfer reagent [24], the fundamentally important properties of this triplet species including the spectroscopy and molecular structure have been the focus of numerous experimental and computational studies [25–33]. Due to the involvement in the combustion chemistry of CH$_3$CN, the mechanism for the oxidation of HCCN has also been computationally explored [34]. Similar to the O$_2$-oxidation of many other carbenes [35–37], the theoretical results suggest that the oxidation of triplet HCCN is initiated by forming carbonyl oxide NCC(H)OO in either $\text{syn}$- or $\text{anti}$-conformations (Scheme 1) with concomitant energy release of about 48 kcal/mol at the CCSD(T)/CCSD/6-311G(d,p) level [34]. However, NCC(H)OO is highly unstable since its isomerization to either NCC(O)HO or HC(O)NCO is exothermic by releasing energies of about 40 and 115 kcal/mol, respectively [34]. Alter-
natively, the O$_2$-oxidation of HCCN might also yield the cyclic peroxide isomer (Scheme 1), which has been computationally predicted to be lower in energy than the zwiterionic structure (syn and anti) for the intensively studied parent molecule CH$_2$OO [38].

Experimentally, the attempt to generate NCC(H)OO by reacting HCCN, formed through the decomposition of the highly explosive azide precursor HCCN$_3$ (→HCCN+N$_2$), with O$_2$ gas at room temperature failed, only formyl cyanide NCC(O)H and O$_3$ were identified by gas-phase IR spectroscopy [39]. The absence of NCC(H)OO in the oxidation products can be reasonably explained by its quick reaction with another O$_2$ molecule once it was formed in the first step of oxidation. Structurally, NCC(H)OO can also be viewed as a CN-substituted derivative, the parent Criegee intermediate (C) CH$_2$OO. Similar to the alkyl-substituted Criegee intermediates RC(H)OO (e.g., R=CH$_3$ [40] and Et [41]), NCC(H)OO can also adopt two conformations (Scheme 1). Importantly, it was found that the reactivity of asymmetrically substituted Cls strongly depends on the conformation [42–47]. For instance, the recent study on the reactions of CH$_3$C(H)OO with NO/NO$_2$ reveals that the anti-conformer displays dramatically higher reactivity than the syn-conformer, and the former also decays much faster in the absence of the nitrogen oxides [40].

Continuing our interest in the spectroscopy and reactivity of peroxides (e.g., OSOO [48] and FP(O)OO [49]), herein, we report the first-time observation of the syn- and anti-conformers of NCC(H)OO in the O$_2$-oxidation of HCCN in cryogenic matrices.

II. METHODS

A. Sample preparation

Caution! Solvent-free diazoacetanitrite is highly explosive. Although we have not experienced any incident during this work, safety precautions (face shields, leather gloves, and protective leather clothing) are recommended.

Diazoacetanitrite, HC(N$_2$)CN, was prepared and purified according to the published protocol [50]. Briefly, aminoacetanitrite hydrochloride (0.23 g, 2.5 mmol) was dissolved in CH$_2$Cl$_2$ (0.2 mL), and then the solution was cooled to 0 °C. The solution of NaNO$_2$ (0.17 g, 2.5 mmol) in water (0.5 mL) was added by drops. Then the mixture was stirred at 0 °C for 30 min. The aqueous phase was washed by CH$_2$Cl$_2$ (0.5 mL) twice and the combined organic layers were dried over Na$_2$SO$_4$ (5.0 g). The volatile products were separated by passing through three successive cold U-traps at −45, −80, and −196 °C. Pure HC(N$_2$)CN, was retained in the first trap. Alkyny isocynate, HC≡CN=O, was prepared from the thermal decomposition of HC≡CC(O)N$_3$ according to the published protocol [51]. N$_2$ (≥99.999%, Messer) and O$_2$ (≥99.999%, Messer) gases were used without further purification. For the isotope labeling experiments, $^{18}$O$_2$ (97 atom%, Aldrich) was used.

B. Matrix-isolation IR spectroscopy

Matrix IR spectra were recorded on a FT-IR spectrometer (Bruker 70 V) in a reflection mode using a transfer optic. A KBr beam splitter and wide band MCT detector were used in the mid-IR region (4000–400 cm$^{-1}$). Typically, 200 scans at a resolution of 0.5 cm$^{-1}$ were co-added for each spectrum. The gaseous samples of HC(N$_2$)CN and HC≡CC(O)N$_3$ were mixed by passing a flow of N$_2$ gas through a U-trap (HC(N$_2$)CN: −48 °C, HC≡CC(O)N$_3$: −58 °C) containing ca. 20 mg of the precursors. Then the mixture (ca. 1:50:1000, sample: O$_2$:N$_2$, estimated) passed through an aluminum oxide furnace (o.d. 2.0 mm, i.d. 1.0 mm), was deposited (2 mmol/h) in a high vacuum (~10$^{-6}$ Pa) onto the Rh-plated Cu block matrix support (15 K) using a closed-cycle helium cryostat (Sumitomo Heavy Industries, SRDK-408D2-F50H) inside the vacuum chamber. Temperatures at the second stage of the cold head were controlled and monitored using a LakeShore 335 digital cryogenic temperature controller a Silicon Diode (DT-670). The voltage and current used in the pyrolysis experiments were 4.0 V and 2.66 A, respectively. Photolysis experiments were performed using an ArF excimer laser (Gamlaser EX5/250, 3 Hz, 193 nm), Nd$^{3+}$:YAG laser (MPL-F-266, 266 nm, 10 mW), UV lamp (365 nm, 24 mW), and flashlight (Boyu T648, 30 W).

C. Quantum chemical calculations

Structures and IR frequencies for stationary points and transition states were calculated using the DFT-BP86 method [52, 53] with the 6-311+G(3df,3pd) [54] basis sets. Local minima were confirmed by vibrational frequency analysis, and transition states were further confirmed by intrinsic reaction coordinate (IRC) calculations [55, 56]. Time-dependent (TD) DFT (BP86/6-311+G(3df,3pd)) was performed for the prediction of UV-Vis transitions energies. These computations were carried out with the Gaussian 09 program [57].

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and 665.6 cm$^{-2}$ the UV-light photolysis of O active oxygen atoms, which can be produced during the oxidation of HCN by the highly reactive oxygen atoms, can be produced during the irradiation conditions. Traces of HNCO might be formed from the oxidation of HCCN (+O$^2$-matrix (ca. 1:50:1000) at 15.0 K upon 365 nm LED irradiation (15 min). The IR bands of a: HC(N$_2$)CN, b: HCCN, c: NCC(O)H, d: O$_3$, e: CO$_2$, f: HCN, g: N$_2$O, h: H$_2$O, i: HNCO, and "*": unknown species are marked.

were performed using the Gaussian 09 software package [57]. Ab initio CCSD(T)-F12a [58] methods with aug-cc-pVTZ [59, 60] basis sets were also used for the single point energy computation. These computations were performed using the MOLPRO 2012 program [61, 62]. The NRT analysis was performed using the NBO 7.0 program [63].

III. RESULTS AND DISCUSSION

A. Generation and characterization of NCC(H)OO

The generation of HCCN (b, 3243.7, 1750.4, and 1189.2 cm$^{-1}$) [39, 50, 64] was carried out by the purple light (400±20 nm) photolysis of HC(N$_2$)CN (a) in N$_2$-matrix at 15.0 K (FIG. 1(A)). When the photolysis of HC(N$_2$)CN was performed in the O$_2$-doped N$_2$-matrix (ca. 1:50:1000) using UV-light (365 nm), the oxidation products NCC(O)H (c) together with O$_3$ (d, 1042.0 and 705.2 cm$^{-1}$) [65], CO$_2$ (e, 2346.4 and 665.6 cm$^{-1}$) [66], HCN (f, 3289.9 and 740.7 cm$^{-1}$) [67], N$_2$O (g, 2237.3) [68], HNCO (i, 2265.3 cm$^{-1}$) [69], and unknown species with IR bands (j and j$'$) mainly in the range of 1400−700 cm$^{-1}$ were obtained (FIG. 1(B)). The presence of CO$_2$ and HCN suggests that complete oxidation of HCCN (+O$_2$→CO$_2$+HCN) occurs under the irradiation conditions. Traces of HNCO might be formed from the oxidation of HCN by the highly reactive oxygen atoms, which can be produced during the UV-light photolysis of O$_2$/O$_3$, whereas, the association of N$_2$ with mobile oxygen atoms yields N$_2$O.

The absence of NCC(H)OO among the photooxidation products indicates that this photolabile intermediate might be immediately destroyed by the applied UV-light (365 nm), since most carbonyl oxides are known to have strong absorptions at around 350 nm (e.g., CH$_2$OO: $\lambda_{max}$=335 nm [70], CH$_3$C(H)OO: 328 nm [71], and PhC(H)OO: 398 nm [37]). When changing the irradiation source from 365 nm UV-LED to a 266 nm laser, the formation of new species with IR bands (j and j$'$) mainly in the range of 1400−700 cm$^{-1}$ can be clearly observed after 1 min of irradiation (FIG. 2(A)). Concomitantly, only very weak IR bands for the final oxidation product NCC(O)H (c) appear. Considering the TD-BP86/6-311++G(3df,3pd) calculated intense absorptions at 307 and 303 nm for the syn- and anti-conformers of NCC(H)OO (Table S1 in supplementary materials), the matrix containing the laser photolysis products was briefly subjected to the 365 nm LED irradiation (1 min). The corresponding IR difference spectrum (FIG. 2(B)) demonstrates complete depletion of the aforementioned new IR bands. As the result, NCC(O)H (c) and O$_3$ (d) form as the main oxidation products. By analogy with the well-established photochemistry of CH$_2$OO (→CH$_2$O+O) [70, 72], the formation of NCC(O)H and O$_3$ is likely due to the initial photodecomposition of NCC(H)OO (→NCC(O)H+O), followed by association of the oxygen atoms with the neighbor-
ing O₂ molecules in the O₂-doped N₂-matrix. Consistent with the existence of absorption at 350 nm for the precursor HCC(N₂)CN (a) [64], the intensities for its IR bands also decrease upon the 365 nm irradiation. Attempts to increase the amounts of the new species by increasing the laser irradiation time cause complete depletion of the accompanied IR bands.

Among the IR bands (j and j′) for the extremely photolabile species, the two weak ones at 3127.1 and 3105.2 cm⁻¹ are very close to the C–H stretching vibration (ν(CH) in HCC(N₂)CN at 3135.3 cm⁻¹ (FIG. 2(B), N₂-matrix). It should be noted that the ν(CH) modes in the two Criegee intermediates CH₂OO [38] and CH₃C(H)OO [40] were not experimentally observed in the previous IR spectroscopy studies. And they are in good agreement with the calculated IR frequencies for the ν(CH) modes in the expected intermediates syn-NCC(H)OO (j, 3149 cm⁻¹), anti-NCC(H)OO (j′, 3111 cm⁻¹) at the BP86/6-311+G(3df,3pd) level (Table I). According to the observed and calculated intensities for the two well-separated bands at 3127.1 and 3105.2 cm⁻¹, a ratio of 1:0.4 can be estimated for the relative abundance of the syn- and anti-conformers.

Consistent with the two calculated IR frequencies at 1400 and 1376 cm⁻¹ for the syn- and anti-conformers of NCC(H)OO, two weak but distinguishable bands at 1395.6 and 1368.6 cm⁻¹ appear after the 266 nm laser irradiation (FIG. 2(A)), whereas they disappear after the subsequent 365 nm irradiation (FIG. 2(B)). Similar to the IR band at 1435 cm⁻¹ for CH₂OO, [38] these two bands correspond to the in-plane C–H deformation modes (δᵡ(CH)), which are strongly mixed with the C–O stretching vibration (ν(CO)). The assignment is supported by the ¹⁸O-labeling experiments using ¹⁸O₂ in the oxidation reaction (FIG. 2(C)). As expected, the bands shift to 1387.3 and 1363.2 cm⁻¹ in syn- and anti-HC(¹⁸O)O CN, corresponding to ¹⁶/¹⁸O-isotopic shifts of 8.3 (calc. 10.5 cm⁻¹) and 5.4 cm⁻¹ (calc. 7.7 cm⁻¹), respectively. The ν(CO) modes, which are mixed with the δᵡ(CH) modes, locate at 1236.8 (calc. 1262 cm⁻¹) and 1227.6 cm⁻¹ (calc. 1250 cm⁻¹) with much larger ¹⁶/¹⁸O-isotopic shifts of 30.7 (calc. 28.8 cm⁻¹) and 34.4 cm⁻¹ (calc. 27.0 cm⁻¹), respectively. Similar mixed vibration mode in CH₂OO occurs at 1286 cm⁻¹ [38].

According to the calculated vibration displacement vectors for the syn-conformer of NCC(H)OO (Table I), the characteristic O–O stretching vibration (ν(OO)) appears at 949.3 cm⁻¹ (calc. 970 cm⁻¹) with an ¹⁶/¹⁸O-isotopic shift of 38.3 cm⁻¹ (calc. 33.3 cm⁻¹). It is higher than that in CH₂OO (908 cm⁻¹) [38], since it couples with the C–H rocking mode (ρ(CH)) at 1000.8 cm⁻¹ as evidenced by the large ¹⁶/¹⁸O-isotopic shift of 12.1 cm⁻¹ (calc. 17.2 cm⁻¹). In sharp contrast to the syn-conformer, the ν(OO) mode in anti-NCC(H)OO at 1027.5 cm⁻¹ (calc. 1069 cm⁻¹) is higher by 78.2 cm⁻¹, and the ¹⁶/¹⁸O-isotopic shift is 60.3 cm⁻¹ (calc. 59.7 cm⁻¹).

### Table I. The calculated and observed IR data of syn- and anti-NCC(H)OO and cyclic-HC(O₂)CN.

<table>
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<tr>
<th>νᵢₑₘₙ a</th>
<th>νᵢₑₘₙ b</th>
<th>Δν(¹⁸O/¹⁹O) a</th>
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<td>3105.2(3)</td>
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<td>1368.6(8)</td>
<td>7.7 5.4</td>
<td>δᵡ(CH)/ν(CO)</td>
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<tr>
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<td>1227.6(27)</td>
<td>27.0 34.4</td>
<td>ν(CO)/δᵡ(CH)</td>
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<td>1069(135)</td>
<td>1027.5(100)</td>
<td>59.7 60.3</td>
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* Harmonic IR frequencies (>400 cm⁻¹) and intensities (km/mol, in parentheses) at BP86/6-311+++G(3df,3pd).
* Observed band position and intensities (km/mol, in parentheses) for the most intense matrix site.
* Calculated isotope shifts at BP86/6-311+++G(3df,3pd).
* Observed isotope shifts in N₂-matrix.
* Assignment based on the calculated vibrational displacement vectors at the BP86/6-311+++G(3df,3pd) level.

Similar frequencies with large ¹⁶/¹⁸O-isotopic shifts have been frequently found for the ν(OO) modes in peroxyl radicals such as CF₂OO (ν(OO)=1093.0 cm⁻¹, Δν(¹⁸O/¹⁹O)=52.2 cm⁻¹) [73] and CH₃S(O)OO (ν(OO)=1081.3 cm⁻¹, Δν(¹⁸O/¹⁹O)=58.3 cm⁻¹) [74]. The C–H rocking mode (ρ(CH)) in anti-NCC(H)OO.
is fully reproducible. Interestingly, the ratio for the syn:

\text{rates (Table II), the two conformers of NCC(H)OO have

a 1:0.4 mixture of HC(O)N}_2\text{C} \rightarrow \text{HCCN+O}_2\text{. The subsequent O}_2\text{-}

oxidation of HCCN to NCC(H)OO (FIG. 3(A)) followed by further photolysis to NCC(O)H and O}_3\text{ (FIG. 3(B)) is fully reproducible. Interestingly, the ratio for the syn-}

\text{and anti-conformers of NCC(H)OO (1:0.2) observed in

the 193 nm laser photolysis of HCCNCO is slightly different. The identification of the two conformers for

NCC(H)OO in the photochemistry of HCCNCO is also

supported by the independent 18\text{O}-labeling experiments (FIG. 3(C)). Additionally, the photosomerization of the precursor HCCNCO (i) to NCC(H)CO (m) via 1,3-CO migration has also been observed upon the UV-light ir-

radiation (365 nm, FIG. 3(B)).

FIG. 3 (A) IR difference spectrum showing the change of the matrix containing the flash vacuum pyrolysis products of a mixture of HC≡\text{CC(O)N}_2\text{O}_2\text{ and N}_2\text{ (ca. 1:50:1000) at 15.0 K upon 193 nm laser irradiation (22 min). (B) IR difference spectrum showing the depletion of syn- and anti-NCC(H)OO upon 365 nm LED irradiation (20 min). (C) IR difference spectrum showing the depletion of syn- and anti-NCC(H)OO}^{18\text{O}}\text{O}_2\text{ upon 365 nm LED irradiation (10 min). The IR bands of b: HCCN, c: NCC(O)H, c′: NCC(18\text{O})H, d: O}_3\text{, d′: }^{18}\text{O}_2\text{, e: CO}_2\text{, e′: C(18)O}_2\text{, g: N}_2\text{O, g′: N}_2^{18}\text{O}_2\text{, j: syn-NCC(H)OO, j′: anti-NCC(H)OO, l: HC≡\text{CNCO, m: NCC(H)CO, n: CO, and } ^{**}\text{: unknown species are marked.}

B. Stability and structure of NCC(H)OO

The molecular structures and energies for the syn- and anti-conformers of NCC(H)OO and its iso-

mers including isocyanide CNC(H)OO and dioxirane HC(O)CN have been calculated at the CCSD(T)-

F12a/aug-cc-pVTZ//BP86/6-311++G(3df,3pd) level (FIG. 4).

In agreement with the experimental observation of a 1:0.4 mixture of syn- and anti-NCC(H)OO in the

O}_2\text{-oxidation of HCCN, NCC(H)OO favors a syn-}

conformation by 0.5 kcal/mol. The carbonyl oxide stabilization energies (COSE), estimated by means of

isodesmic reaction with CH}_4\text{ (Eq.(1)), can be used to
gauge the stability of other Criegee intermediates rel-

tive to the parent molecule CH}_2\text{OO [75]. Based on its

definition, the COSE is stabilizing when the cor-

responding value is positive. Apparently, the alkyl

substituents increase the stability of the carbonyl ox-
ides, whereas, the strong electron-withdrawing effect of the CN ligand reduces the stability due to nega-

tive COSE values of −2.4 and −2.8 kcal/mol for the syn-}

\text{and anti-conformers of NCC(H)OO. Similar nega-
tive COSE value (−7.1 kcal/mol) has been previously

reported for CF}_2\text{C(H)OO [75]. Similar to the closed-

shell singlet ground state for most Criegee intermedi-

ates (Table II), the two conformers of NCC(H)OO have

large energy gaps between the singlet and triplet (syn: −36.8 kcal/mol; anti: −22.1 kcal/mol).

The barrier (TS1) for the syn→anti conformational

conversion in NCC(H)OO via the out-of-plane rotation of the O–O bond is ca. 40.2 kcal/mol, ruling

out its occurrence under the matrix-isolation conditions (∼35 K). CNC(H)OO is higher in energy than

NCC(H)OO by 17.5 kcal/mol, and the activation barrier (TS3) for the isomerization from syn-NCC(H)OO

is 49.3 kcal/mol, rendering the formation of CNC(H)OO unlikely, although similar rearrangement reactions have

been observed for other RCN compounds such as OSCN

(→OSNC) [76] and CH}_2\text{CN (→CH}_2\text{NC) [77] upon UV-

light irradiations. Energetically, the dioxirane isomer

cyclic-HC(O)CN is more stable than the two conform-
ers of NCC(H)OO by ca. 24 kcal/mol. The preference of a cyclic peroxide structure over the carbonyl oxide

structure has also been found for the parent molecule

CH}_2\text{OO, for which the Criegee intermediate structure is

24.0 kcal/mol higher in energy [78]. In fact, the fluorine-substituted dioxirane cyclic-CF}_2\text{O}_2\text{ is isobole compou}
d at room temperature [79–81], in contrast, the higher-energy carbonyl oxide isomer remains elu-

sive yet. The barrier (TS2) for the formation of cyclic-

HC(O)CN from anti-NCC(H)OO via ring-closure is

18.5 kcal/mol. The formation of NCC(O)H and O}_3

instead of cyclic-HC(O)CN from NCC(H)OO in O}_2-
doped N}_2\text{-matrix is probably due to immediate oxida-
tion of O}_2 by the highly oxidative Criegee intermediate

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FIG. 4 The potential energy profile (kcal/mol) for the isomerization of NCC(H)OO calculated at the CCSD(T)-F12a/aug-cc-pVTZ//BP86/6-311++G(3df,3pd) level (with zero-point vibrational energy corrections). Selected structural parameters (bond lengths in Å and angles in degree) are also depicted.

TABLE II The calculated carbonyl oxide stabilization energies (COSE $\Delta H$) and singlet-triplet energy splittings ($\Delta E_{S-T}$) for different Criegee intermediates.

<table>
<thead>
<tr>
<th>Intermediates</th>
<th>$\Delta H^*$ (kcal/mol)</th>
<th>$\Delta E_{S-T}^*$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$COO</td>
<td>0.0</td>
<td>-29.1</td>
</tr>
<tr>
<td>(CH$_3$)$_2$COO</td>
<td>22.2</td>
<td>-34.5</td>
</tr>
<tr>
<td>syn-H(CH$_3$)COO</td>
<td>14.1</td>
<td>-33.5</td>
</tr>
<tr>
<td>anti-H(CH$_3$)COO</td>
<td>9.6</td>
<td>-28.7</td>
</tr>
<tr>
<td>syn-H(CN)COO</td>
<td>-2.4</td>
<td>-36.8</td>
</tr>
<tr>
<td>anti-H(CN)COO</td>
<td>-2.8</td>
<td>-22.1</td>
</tr>
</tbody>
</table>

*Calculated at CBS-QB3 level.

NCC(H)OO in the presence of excessive O$_2$ molecules. According to the TD-BP86/6-311++G(3df,3pd) calculation (Table S1 in supplementary materials), cyclic-HC(O$_2$)CN has intense absorptions at 258 and 303 nm, which means that, the cyclic species, once formed in the photooxidation of HCCN, would be immediately depleted by the applied irradiations (266 and 365 nm).

It is known that most Criegee intermediates are stabilized by the zwitterionic (I and III, Scheme 2) and diradical resonance structures (II, Scheme 2). Due to partial conjugation with the C≡N group, an additional resonance structure bearing heterocumulenic N=C=C moiety (IV) might also contribute to the stability of NCC(H)OO. According to the calculated molecular structures for NCC(H)OO (FIG. 4), the C=O bond lengths in syn-NCC(H)OO (1.271 Å) and anti-NCC(H)OO (1.270 Å) are comparable with that in CH$_2$OO (calc.: 1.268 Å, exp.: 1.2689(2) Å) [82, 83]. And, the O=O bond lengths (syn: 1.326 Å, anti: 1.327 Å) are shorter than that in CH$_2$OO (calc.: 1.341 Å, exp.: 1.3405(1) Å), coinciding with the experimentally observed higher frequencies for $\nu$(OO) in the syn (949.3 cm$^{-1}$) and anti-conformers (1027.5 cm$^{-1}$) than that in CH$_2$OO (908 cm$^{-1}$) [38]. This is consistent with the contribution of structures III (syn: 11.72%, anti: 8.22%) and IV (syn: 12.99%, anti: 15.01%) in NCC(H)OO (Table III) for which the terminal O=O bond has partial double bond character, which can also be inferred by the calculated Wiberg bond indexes (WBI) of 1.1628 and 1.1631 in the syn- and anti-conformers of NCC(H)OO. The WBI for the C=O bond is 1.4023 and 1.4031, suggesting predominant contribution from the zwitterionic structure I (syn: 23.78%, anti: 29.09%). In sharp contrast, the zwitterionic structure I plays the key role in other Criegee intermediates CH$_2$OO (40.50%), CH$_3$C(H)OO (syn: 42.98%, anti: 40.04%), and (CH$_3$)$_2$COO (42.20%).

The natural bond orbital (NBO) analysis of the two conformers of NCC(H)OO (FIG. 5) reveals negligible negative charges (syn: -0.05, anti: -0.05) at the oxygen atom (C=O), whereas, the terminal oxygen atoms carry significant negative charges (syn: -0.34, anti: -0.34). Due to large electronegativity, the nitrogen atoms also carry negative charges (syn: -0.20, anti:
Scheme 2 Lewis resonance structures of NCC(H)OO.

TABLE III Resonance contributions to the equilibrium stationary points for the different Criegee intermediates, calculated at the BP86/6-311++G(3df,3pd) level.

<table>
<thead>
<tr>
<th>Resonance contribution/%</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1=H, R2=H</td>
<td>40.50</td>
<td>33.50</td>
<td>18.92</td>
<td></td>
</tr>
<tr>
<td>R1=CH₃, R2=CH₃</td>
<td>42.20</td>
<td>26.94</td>
<td>18.45</td>
<td></td>
</tr>
<tr>
<td>R1=H, R2=CH₃</td>
<td>42.98</td>
<td>27.19</td>
<td>18.61</td>
<td></td>
</tr>
<tr>
<td>R1=H, R2=CH₃</td>
<td>40.04</td>
<td>30.26</td>
<td>18.37</td>
<td></td>
</tr>
<tr>
<td>R1=H, R2=CN</td>
<td>23.78</td>
<td>24.12</td>
<td>11.72</td>
<td>12.99</td>
</tr>
<tr>
<td>R1=H, R2=CN</td>
<td>29.09</td>
<td>28.01</td>
<td>8.22</td>
<td>15.01</td>
</tr>
</tbody>
</table>

a For the syn-conformer.
b For the anti-conformer.

0.4 kcal/mol. The disclosed mechanism for the oxidation of HCCN will aid further studies on its atmospheric and interstellar chemistry.

Supplementary materials: The calculated vertical transition, atomic coordinates, and energies are included.

V. ACKNOWLEDGMENTS

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