

pubs.acs.org/JPCA

Article

# Aminohydroxymethylene (H<sub>2</sub>N–C–OH), the Simplest Aminooxycarbene

Published as part of The Journal of Physical Chemistry virtual special issue "10 Years of the ACS PHYS Astrochemistry Subdivision".

Bastian Bernhardt,<sup>#</sup> Marcel Ruth,<sup>#</sup> Hans Peter Reisenauer, and Peter R. Schreiner\*



**ABSTRACT:** We generated and isolated hitherto unreported aminohydroxymethylene (1, aminohydroxycarbene) in solid Ar via pyrolysis of oxalic acid monoamide (2). Astrochemically relevant carbene 1 is persistent under cryogenic conditions and only decomposes to HNCO +  $H_2$  and  $NH_3$  + CO upon irradiation of the matrix at 254 nm. This photoreactivity is contrary to other hydroxycarbenes and aminomethylene, which undergo [1,2]H shifts to the corresponding carbonyls or imine. The experimental data are well supported by the results of CCSD(T)/cc-pVTZ and B3LYP/6-311++G(3df,3pd) computations.

#### INTRODUCTION

Aminohydroxymethylene (1, aminohydroxycarbene) is a prototypical electron donor stabilized carbene,<sup>1-3</sup> which has, however, never been spectroscopically identified. While diaminocarbenes and especially *N*,*N*-heterocyclic carbenes are ubiquitously used as ligands and catalysts,<sup>4-6</sup> amino-oxycarbenes are far less popular.<sup>7,8</sup> This is surprising considering the very large isodesmic stabilization enthalpy of the corresponding parent species (Scheme 1)<sup>9,10</sup> but can be explained by their suspected high reactivity. The first



<sup>*a*</sup>Left: Aminohydroxymethylene (1) and structural analogues. Dihydroxycarbene is a known and surprisingly stable  $CH_2O_2$  isomer (*cf.* Criegee intermediate);<sup>18,19</sup> diaminocarbene is unknown. Isodesmic stabilizations in kcal mol<sup>-1</sup> relative to methylene (0.0 kcal mol<sup>-1</sup>) obtained from ref 10 are given in parentheses. Right: Experimentally reported persistent aminooxycarbenes bearing bulky O-substituents.<sup>13</sup>



generation of N,O-heterocyclic carbenes (oxazolidin-2-ylidenes) was achieved 1996 by pyrolysis of 2-alkoxy-2-amino- $\Delta^3$ -1,3,4-oxadiazolines.<sup>11,12</sup> Only two years later Alder et al. reported several persistent aminooxycarbenes (Scheme 1), enabled by steric blocking of the carbene center by the O-substituent,<sup>13</sup> which is absent in cyclic systems. Since then, only a few examples of aminooxycarbenes appeared in the literature; they have mostly been used as metal ligands.<sup>14–17</sup> Here we report on the generation, characterization, and reactivity of the simplest aminooxycarbene 1.

Carbene 1 is an isomer of formamide (9) and formimidic acid (10; Scheme 2). H<sub>2</sub>NCOH species have been discussed in the context of interstellar and prebiotic chemistry as they may form in the reactions of HCN with H<sub>2</sub>O.<sup>20</sup> Indeed, 1 has been implied in the on-surface isomerization of formamide.<sup>21,22</sup> The radical cation of 1 has been identified in mass spectrometric studies,<sup>23</sup> and it readily adds to alkenes.<sup>24,25</sup> A deprotonated derivative of 1, namely, lithium *N*,*N*-dicyclohexylmethyleneolate (Cy<sub>2</sub>NCOLi), has recently been proposed as an intermediate in transition-metal-free Fischer–Tropsch chemistry.<sup>26</sup> 1-Aminoethenol<sup>27</sup> may be considered the dimerization product of 1 and methylene.

 Received:
 July 9, 2021

 Revised:
 July 30, 2021

 Published:
 August 10, 2021



Scheme 2. Reaction Products of Hydroxymethylene (3) and Aminomethylene (4) and the Absence of These Products in Their "Hybrid" Aminohydroxymethylene  $(1)^{a}$ 



<sup>a</sup>Carbene 1 instead decomposes to HNCO + H<sub>2</sub> and NH<sub>3</sub> + CO.

Structurally, 1 combines the functionalities of hydroxymethylene  $(3)^{28}$  and aminomethylene (4),<sup>10</sup> both of which have been studied under matrix isolation conditions (Scheme 2). As most hydroxycarbenes,  $^{29-31}$  3 undergoes a [1,2]H shift to yield formaldehyde (5) via quantum mechanical tunneling (QMT) or photochemical excitation.<sup>28</sup> Carbene 4 reacts in a similar fashion to methanimine 6 but only when the matrix is irradiated with UV light.<sup>10</sup> Herein we demonstrate that 1 does not follow either of these reaction paths but instead decomposes photochemically to  $NH_3 + CO$  and  $HNCO + H_2$ . Earlier studies demonstrated that the irradiation of thiazole-

2-carboxylic acid  $(7a)^{32}$  and imidazole-2-carboxylic acid  $(7b)^{33}$  in an Ar matrix at 10 K yields the corresponding carbenes 8a and 8b complexed with CO<sub>2</sub> (Scheme 3). In

Scheme 3. Examples of Strategies To Generate and Isolate **Carbenes from Various Precursors under Matrix Conditions** 



contrast, 1 cannot be detected directly upon photolysis of oxalic acid monoamide (2) but presumably is an intermediate during photodecomposition of 2 into HNCO + H<sub>2</sub> and NH<sub>3</sub> + CO.<sup>34</sup> As we have demonstrated in multiple cases (Scheme 3), $^{29-31}$  decarboxylation via flash vacuum pyrolysis (FVP) of  $\alpha$ -keto carboxylic acids is the method of choice for the generation, matrix isolation, and structural elucidation of hydroxycarbenes. Accordingly, we generated 1 via pyrolysis of oxalic acid monoamide (2).

A gas phase study by Terlouw et al.<sup>35</sup> hints toward the possibility to isolate 1 under matrix isolation conditions but also toward its facile isomerization to formamide (9) and/or formimidic acid (10), because all three species were detected after one-electron reduction of their cations in collision induced dissociation mass spectra. The relationship between 1, 9, and 10 has been the subject of several computational studies.<sup>36-38</sup> The spectroscopic properties of 10 were elucidated in an investigation on the photoreactivity of 9 in an Ar matrix.<sup>39</sup> According to this study, irradiation with a KrF excimer laser ( $\lambda = 248$  nm) induces a [1,3]H shift of 9 to yield 10.<sup>39</sup> In contrast, irradiation of 9 at 193 nm vields the photodecomposition products NH<sub>3</sub> + CO as well as HNCO +  $H_2$ .<sup>40</sup> These findings are also in fair agreement with a study by Duvernay et al., which shows that irradiation of formamide at 240 nm leads to 10 while broad-band UV irradiation  $(\lambda > 160 \text{ nm})$  results in dehydrogenation and dehydration of **10**.<sup>41</sup>

#### **EXPERIMENTAL SECTION**

Details of the compound syntheses and characterizations are described in the Supporting Information. A Sumitomo cryostat system consisting of an RDK 408D2 closed-cycle refrigerator cold head and an F-70 compressor unit was used for matrix isolation experiments. A polished CsI window was mounted in the cold head's sample holder. The sample holder, connected with silicon diodes for temperature measurements, was covered by the vacuum shroud, which was equipped with KBr windows to allow for IR measurements. In some experiments BaF<sub>2</sub> windows were used due to their higher transparency when measuring UV/vis spectra. The sample and the host gas (Ar, purity of 99.999%) were co-deposited at 15 K. All spectral data were collected at 3 K except for two kinetic experiments, which were performed at 20 K. The pyrolysis zone was equipped with a heatable 90 mm long quartz tube (inner diameter 7 mm), controlled by a Ni/CrNi thermocouple. The travel distance of the sample from the pyrolysis zone to the matrix was  $\sim$ 45 mm. Ar was stored in a 2 L gas balloon, which was evacuated and filled three times before every experiment. The sample was evaporated from a Schlenk tube at 55 °C (water) and reduced pressure ( $\sim 3 \times 10^{-6}$  mbar) and co-deposited with a high excess of argon on both sides of the matrix window in the dark (preventing unwanted photochemistry) at a rate of  $\sim 1$  mbar min<sup>-1</sup>, based on the pressure inside the Ar balloon. Pyrolyses were carried out at 700 °C. IR spectra were recorded between 7000 and 350 cm<sup>-1</sup> with a resolution of 0.7 cm<sup>-1</sup> with a Bruker Vertex 70 FTIR spectrometer. A spectrum of the cold matrix window before deposition was used as background spectrum for the subsequent IR measurements. UV/vis spectra were recorded between 200 and 800 nm with a resolution of 1 nm with a Jasco V-760 spectrophotometer. A high-pressuremercury lamp equipped with a monochromator (LOT Quantum Design) or a low-pressure-mercury lamp (Gräntzel) fitted with a Vycor filter were used for irradiation of the matrix during photochemical experiments. Computational details are provided in the Supporting Information.

#### RESULTS AND DISCUSSION

Experimental Results. We pyrolyzed 2 at 700 °C in high vacuum prior to trapping the resulting products in an Ar matrix. Under the applied conditions the thermal fragmentation of 2 was not complete and complex IR spectra resulted (Figures S12–S15). The main components formed in such experiments are  $CO_2^{42}$  formamide (9),<sup>43,44</sup> the two most stable conformers of formimidic acid (10),<sup>39</sup> HCN,<sup>45</sup> H<sub>2</sub>O,<sup>46</sup> CO,<sup>47</sup> NH<sub>3</sub>,<sup>48</sup> and HNCO,<sup>49</sup> whose bands agree with published reference data as well as with our own reference spectra of the respective matrix-isolated pure compounds. In addition, hitherto unreported bands at 3661.8, 3654.3, 3537.0, 3529.9, 1608.0, 1605.4, 1250.6, 1247.7, 602.5, 598.2, 551.5, and 545.0 cm<sup>-1</sup> (only the strongest bands are listed; for an exhaustive list see Table S1) can be assigned to transaminohydroxymethylene (1t). Upon short-time irradiation (1-15 min) at 254 nm these IR bands vanish and the signals of CO, NH<sub>3</sub>, and HNCO increase in intensity. Due to the interaction with the co-product  $H_2$ , the band of the latter is shifted to significantly higher frequencies than that of the undisturbed molecule present after pyrolysis (2264 vs 2259 cm<sup>-1</sup>).<sup>40</sup> Besides a small decrease of IR absorptions of unreacted 2t and the corresponding growth of those of the cisrotamer 2c due to photochemical isomerization (see the Supporting Information for details),<sup>34</sup> the IR bands of all other pyrolysis products remain unchanged. Hence, subtraction of spectra measured before and after photolysis provides an excellent tool for monitoring the photolytical reactions and evaluating the IR absorption bands of 1t (Figure 1). Due to



**Figure 1.** Black: Experimental matrix IR difference spectrum of spectra measured before and after irradiation of the pyrolysate at 254 nm for 15 min. Blue: Anharmonic B3LYP/6-311++G(3df,3pd) spectrum of 1t, which reacts to HNCO + H<sub>2</sub> and CO + NH<sub>3</sub> upon photolysis. Note that the rotamerization  $2c \rightarrow 2t$  occurs under the same conditions.<sup>34</sup>

matrix effects, all bands are split in mainly two components separated by a few wavenumbers. The excellent agreement between the experimental and computed IR absorption bands provides convincing evidence for the successful preparation of **1t** and allows for band assignments. Nine of the twelve fundamental vibrations of **1t** can be assigned in the experimental difference spectrum. For example, a strong band of the OH stretching vibration appears at 3661.8/ 3654.3 cm<sup>-1</sup> and that of the asymmetric stretching of the NH<sub>2</sub> group at 3537.0/3529.9 cm<sup>-1</sup>. A very intense band (1608.0/ 1605.4 cm<sup>-1</sup>) is assigned to the NH<sub>2</sub> scissoring vibration, while a couple of CO stretching and NH<sub>2</sub> rocking vibrations give rise to another very strong band at 1250.6/1247.7 cm<sup>-1</sup>. Further

band assignments are provided in Table S1. Spectra of the pyrolysis products of  $d_3$ -2 support our assignments through excellent matching of the experimentally observed and computed shifts in vibrational frequencies upon deuteration (see Tables S2, S3 and Figure S18).

Scheme 4 summarizes the reaction network also including the results of earlier photolysis experiments with  $2.^{34}$  The





observed photobehavior of 1 is different from that of hydroxymethylene<sup>28</sup> and aminomethylene,<sup>10</sup> which undergo [1,2]H shifts to form the corresponding aldehyde (here 9) and imine (here 10; Scheme 2), respectively. Keeping a matrix containing 1t for one day in the dark did not lead to any changes in the recorded IR spectra. In agreement with other heteroatom-stabilized hydroxycarbenes (HO– $\ddot{C}$ –OH and MeO– $\ddot{C}$ –OH)<sup>18</sup> and aminomethylene,<sup>10</sup> 1t is persistent under cryogenic conditions and does not undergo QMT.

UV/vis measurements provide additional evidence for the successful isolation of 1t (Figure 2). The recorded very weak absorption with a maximum at 248 nm is in good agreement with the EOM-CCSD/aug-cc-pVTZ//CCSD(T)/cc-pVTZ



**Figure 2.** Experimental matrix UV/vis difference spectrum of spectra measured before and after irradiation of the pyrolysate at 254 nm for 15 min. Natural bond orbitals (NBOs) of **1t** corresponding to the HOMO  $\rightarrow$  LUMO transition were computed at the B3LYP/6-311++G(3df,3pd) level of theory (see the Supporting Information for details).

computed HOMO  $\rightarrow$  LUMO transition at 235.8 nm with a low oscillator strength of f = 0.0236. Furthermore, the measured UV absorption maximum fairs well with those of dimethoxycarbene (257 nm)<sup>50</sup> and dihydroxycarbene (256 nm).<sup>18</sup> Apparently, a second donor substituent attached to the carbene center causes a remarkable large hypsochromic band shift (*cf*. H $-\ddot{C}-OH$ :  $\lambda_{max} = 428$  nm). This means that the S<sub>0</sub>-S<sub>1</sub> energy gap in **1t** of roughly 100 kcal mol<sup>-1</sup> is nearly twice as large as in parent hydroxymethylene. This high value not only exceeds all bond dissociation energies in **1t** (*cf*. **Scheme S13**) but makes an internal conversion process from S<sub>1</sub> to S<sub>0</sub> preceding a reaction from S<sub>1</sub> highly improbable. This may account for the differences in the photochemical reactivity of **1t**.

**Computational Results.** Carbene 1 possesses a singlet ground state with an adiabatic singlet/triplet energy separation of 66.9 kcal mol<sup>-1</sup> at B3LYP/6-311++G(3df,3pd). This value clearly indicates a strong stabilizing effect of the heteroatom substituents (OH and NH<sub>2</sub>) on the carbene center, which is further demonstrated when comparing bond lengths in 1t with those in aminohydroxymethane (11; Figure 3). Interactions of



**Figure 3.** Top: Computed B3LYP/6-311++G(3df,3pd) distances (in Å) and angles in 1t and aminohydroxymethane (11). The HOMO-2 of 1t resembles a  $\pi$  bonding interaction between the nitrogen lone pair and the carbene center. Bottom: This interaction is also apparent in the NRT analysis and Wiberg bond indices of 1t.

the empty p-orbital at the carbene center with the heteroatom lone pairs result in a shortage of the CN bond (by 0.127 Å) and the CO bond (by 0.066 Å). This stabilization manifests in two resonance structures provided by natural resonance theory (NRT). According to these, the stabilizing effect of N is larger than of O, in line with their atomic properties.<sup>51</sup> Our natural bond orbital (NBO) analysis even suggests a CN  $\pi$ -bond in **1t**. A similar NBO resembling a CO  $\pi$ -bond is absent. The concentration of negative charge on the carbene carbon indicates that **1t** is expected to be highly nucleophilic. Additional information about the NBO and NRT analyses can be found in the Supporting Information.

The PES around 1 is depicted in Figure 4. Its global minimum is 9, which is among the main products after pyrolysis of 2. The computed activation barrier of only 35.4 kcal mol<sup>-1</sup> of the [1,2]H shift connecting 1 and 9 is the lowest of all conceivable reaction paths of 1. Other pathways lead to the second rearrangement product 10 or to fragmentation into NH<sub>3</sub> + CO, HNCO + H<sub>2</sub>, or HCN (via HNC) +  $H_2O$ . The computed enthalpies of the respective transition states (TS1–TS7) are considerably higher in energy. Nevertheless, all these products could be detected in low concentrations by their characteristic absorption bands in the IR spectrum of the pyrolysate, thus providing additional strong chemical evidence for the generation of 1. Note that HCN can form by rearrangement of HNC under the pyrolysis conditions as this process is associated with a barrier of 30.0 kcal  $mol^{-1}$ and an exothermicity of 14.7 kcal mol<sup>-1</sup> (cf. Scheme S11).

It should be noted that the thermal  $H_2$  elimination leading to HCNO as well as the fragmentation into  $NH_3 + CO$ requires the intermediacy of the *cis*-conformer 1c, which could not be detected directly by spectroscopy neither as pyrolysis product nor after photolysis. This is in contrast to other stabilized hydroxycarbenes (R = OH,<sup>18</sup> OMe,<sup>18</sup> CN,<sup>52</sup> and CCH<sup>53</sup>) for which the *trans*- and the *cis*-conformers have been spectroscopically detected. *cis*-Aminohydroxymethylene (1c) is computed to be 5.2 kcal mol<sup>-1</sup> higher in energy than 1t, separated from the latter by an activation barrier of only 9.2 kcal mol<sup>-1</sup>. The reason for the nonobservability of 1c is



Figure 4. PES around 1 computed at the CCSD(T)/cc-pVTZ level of theory including zero-point vibrational energies (ZPVEs) at the same level. Note that only conformers of 10 directly linked to 1 are depicted. We refer to Scheme S10 for details of the PES around 10.

#### The Journal of Physical Chemistry A

provided by canonical variational theory (CVT) in conjunction with small curvature tunneling (SCT)<sup>54</sup> at B3LYP/6-311+ +G(3df,3pd), which predicts that **1c** would undergo QMT with a half-life of only 2.7 s to **1t**. An analogous QMT reaction with an experimental half-life of 15 min (in a much more stabilizing N<sub>2</sub> matrix) has recently been reported for *cis-cis*dihydroxycarbene.<sup>19</sup> Note that we cannot detect  $d_3$ -**1c** in the corresponding experiments even though its QMT half-life is expected to be much longer (*cf.* Table S14). The computed QMT half-life of **1t**  $\rightarrow$  **9** amounts to 170 d at CVT/SCT// B3LYP/6-311++G(3df,3pd) in agreement with the persistence of **1t** at cryogenic temperatures, because it is stabilized through the OH and the NH<sub>2</sub> substituents (*vide supra*).

### CONCLUSIONS

We prepared, isolated, and characterized aminohydroxymethylene (1), the simplest aminooxycarbene, in an Ar matrix via pyrolysis of oxalic acid monoamide (2). Irradiation of its observed trans-conformer 1t at 254 nm leads to the formation of HNCO +  $H_2$  and  $NH_3$  + CO. This result is in contrast to other hydroxycarbenes and aminomethylene, which undergo [1,2]H shifts to the corresponding carbonyls or imine. Due to very significant heteroatom stabilization, QMT from 1t to formamide (9) or formimidic acid (10) does not take place on laboratory time-scales but may be relevant in astrochemical processes. The above-mentioned products together with HCN +  $H_2O$ , 9, and 10 are also present after pyrolysis of 2 and, hence, provide chemical evidence for the generation of 1 and hint toward the intermediate presence of the higher energy cisconformer 1c. This species is not persistent even at 3 K due to its fast QMT reaction to 1t.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.1c06151.

Synthetic details, matrix IR and UV/vis spectra, matrix IR band assignments, details on the kinetic analyses, and computational details (PDF)

#### AUTHOR INFORMATION

#### **Corresponding Author**

Peter R. Schreiner – Institute of Organic Chemistry, Justus Liebig University, 35392 Giessen, Germany; orcid.org/ 0000-0002-3608-5515; Email: prs@uni-giessen.de

#### Authors

Bastian Bernhardt – Institute of Organic Chemistry, Justus Liebig University, 35392 Giessen, Germany

- Marcel Ruth Institute of Organic Chemistry, Justus Liebig University, 35392 Giessen, Germany
- Hans Peter Reisenauer Institute of Organic Chemistry, Justus Liebig University, 35392 Giessen, Germany

Complete contact information is available at:

## https://pubs.acs.org/10.1021/acs.jpca.1c06151

#### Author Contributions

<sup>#</sup>B.B. and M.R. contributed equally. The manuscript was written and the research conducted through contributions of all authors. All authors have given approval to the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

B.B. thanks the Fonds der Chemischen Industrie for a doctoral scholarship. We thank our colleagues Dr. Dennis Gerbig, Henrik Quanz, Markus Schauermann, and Dr. Ephrath Solel for fruitful discussions.

#### REFERENCES

(1) Moss, R. A.; Zdrojewski, T.; Ho, G.-J. Push–Pull Carbenes: Methoxytrifluoromethylcarbene. J. Chem. Soc., Chem. Commun. 1991, 946–947.

(2) Moss, R. A.; Zdrojewski, T.; Krogh-Jespersen, K.; Włostowski, M.; Matro, A. Push-Pull Carbenes: Alkoxycyanocarbenes. *Tetrahedron Lett.* **1991**, *32*, 1925–1928.

(3) Buron, C.; Gornitzka, H.; Romanenko, V.; Bertrand, G. Stable Versions of Transient Push-Pull Carbenes: Extending Lifetimes from Nanoseconds to Weeks. *Science* **2000**, *288*, 834–836.

(4) Yang, L.; Wang, H. Recent Advances in Carbon Dioxide Capture, Fixation, and Activation by using N-Heterocyclic Carbenes. *ChemSusChem* **2014**, *7*, 962–998.

(5) Flanigan, D. M.; Romanov-Michailidis, F.; White, N. A.; Rovis, T. Organocatalytic Reactions Enabled by N-Heterocyclic Carbenes. *Chem. Rev.* **2015**, *115*, 9307–9387.

(6) Peris, E. Smart N-Heterocyclic Carbene Ligands in Catalysis. *Chem. Rev.* 2018, 118, 9988-10031.

(7) Melaimi, M.; Soleilhavoup, M.; Bertrand, G. Stable Cyclic Carbenes and Related Species beyond Diaminocarbenes. *Angew. Chem., Int. Ed.* **2010**, *49*, 8810–8849.

(8) Slaughter, L. M. Acyclic Aminocarbenes in Catalysis. ACS Catal. 2012, 2, 1802–1816.

(9) Kelemen, Z.; Hollóczki, O.; Oláh, J.; Nyulászi, L. Oxazol-2ylidenes. A New Class of Stable Carbenes? *RSC Adv.* **2013**, *3*, 7970– 7978.

(10) Eckhardt, A. K.; Schreiner, P. R. Spectroscopic Evidence for Aminomethylene (H–C–NH<sub>2</sub>)—The Simplest Amino Carbene. *Angew. Chem., Int. Ed.* **2018**, *57*, 5248–5252.

(11) Couture, P.; Terlouw, J. K.; Warkentin, J. 2-Alkoxy-2-amino- $\Delta$ 3-1,3,4-oxadiazolines as Novel Sources of Alkoxyaminocarbenes. *J. Am. Chem. Soc.* **1996**, *118*, 4214–4215.

(12) Couture, P.; Warkentin, J. Spiro-fused 2-alkoxy-2-amino- $\Delta$ 3-1,3,4-oxadiazolines. Synthesis and thermolysis to corresponding aminooxycarbenes. *Can. J. Chem.* **1997**, *75*, 1264–1280.

(13) Alder, R. W.; Butts, C. P.; Orpen, A. G. Stable Aminooxy- and Aminothiocarbenes. J. Am. Chem. Soc. 1998, 120, 11526–11527.

(14) Klementyeva, S. V.; Abramov, P. A.; Somov, N. V.; Dudkina, Y. B.; Budnikova, Y. H.; Poddel'sky, A. I. Deprotonation of Benzoxazolium Salt: Trapping of a Radical-Cation Intermediate. *Org. Lett.* **2019**, *21*, 946–950.

(15) Hahn, F. E.; Hein, P.; Lügger, T. Synthesis of Heterobimetallic Metal Derivatives: a Carbene Complex as Chelate Ligand. Z. Anorg. Allg. Chem. 2003, 629, 1316–1321.

(16) Ruiz, J.; Perandones, B. F.; García, G.; Mosquera, M. E. G. Synthesis of N-Heterocyclic Carbene Complexes of Manganese(I) by Coupling Isocyanide Ligands with Propargylamines and Propargylic Alcohols. *Organometallics* **2007**, *26*, 5687–5695.

(17) Seo, H.; Snead, D. R.; Abboud, K. A.; Hong, S. Bulky Acyclic Aminooxycarbene Ligands. *Organometallics* **2011**, *30*, 5725–5730.

(18) Schreiner, P. R.; Reisenauer, H. P. Spectroscopic Identification of Dihydroxycarbene. *Angew. Chem., Int. Ed.* **2008**, *47*, 7071–7074.

(19) Quanz, H.; Bernhardt, B.; Erb, F. R.; Bartlett, M. A.; Allen, W. D.; Schreiner, P. R. Identification and Reactivity of s-cis,s-cis-Dihydroxycarbene, a New  $[CH_2O_2]$  Intermediate. *J. Am. Chem. Soc.* **2020**, *142*, 19457–19461.

(20) Heikkilä, A.; Pettersson, M.; Lundell, J.; Khriachtchev, L.; Räsänen, M. Matrix Isolation and ab Initio Studies of 1:1 Hydrogen-

#### The Journal of Physical Chemistry A

pubs.acs.org/JPCA

Bonded Complexes HCN-H<sub>2</sub>O and HNC-H<sub>2</sub>O Produced by Photolysis of Formaldoxime. J. Phys. Chem. A **1999**, 103, 2945–2951.

(21) Nguyen, H. T.; Nguyen, M. T. Effects of Water Molecules on Rearrangements of Formamide on the Kaolinite Basal (001) Surface. *J. Phys. Chem. A* **2014**, *118*, 7017–7023.

(22) Nguyen, H. T.; Nguyen, M. T. Effects of Sulfur-Deficient Defect and Water on Rearrangements of Formamide on Pyrite (100) Surface. *J. Phys. Chem. A* **2014**, *118*, 4079–4086.

(23) Ruttink, P. J. A.; Burgers, P. C.; Terlouw, J. K. The decarbonylation of ionized formamide,  $H-C(=O)-NH_2^+$ , and aminohydroxycarbene,  $HO-C-NH_2^+$ : decay via an excited state. A quantum chemical investigation. *Int. J. Mass Spectrom. Ion Processes* **1995**, 145, 35–43.

(24) Bouchoux, G.; Espagne, A. Ionized Aminohydroxycarbene and its Isomers: Relative Stability and Unimolecular Reactivity. *Chem. Phys. Lett.* **2001**, *348*, 329–336.

(25) Bouchoux, G.; Chamot-Rooke, J. Electrophilic and Radical Reactivity of Ionized Aminohydroxycarbene Toward Alkenes. *Int. J. Mass Spectrom.* **2002**, *219*, 625–641.

(26) Xu, M.; Qu, Z.-w.; Grimme, S.; Stephan, D. W. Lithium Dicyclohexylamide in Transition-Metal-Free Fischer–Tropsch Chemistry. J. Am. Chem. Soc. **2021**, 143, 634–638.

(27) Mardyukov, A.; Keul, F.; Schreiner, P. R. Preparation and Characterization of the Enol of Acetamide: 1-Aminoethenol, a High-Energy Prebiotic Molecule. *Chem. Sci.* **2020**, *11*, 12358–12363.

(28) Schreiner, P. R.; Reisenauer, H. P.; Pickard IV, F. C.; Simmonett, A. C.; Allen, W. D.; Mátyus, E.; Császár, A. G. Capture of Hydroxymethylene and its Fast Disappearance Through Tunnelling. *Nature* **2008**, *453*, 906–909.

(29) Ley, D.; Gerbig, D.; Schreiner, P. R. Tunnelling Control of Chemical Reactions – the Organic Chemist's Perspective. *Org. Biomol. Chem.* **2012**, *10*, 3781–3790.

(30) Schreiner, P. R. Tunneling Control of Chemical Reactions: The Third Reactivity Paradigm. *J. Am. Chem. Soc.* 2017, 139, 15276–15283.

(31) Schreiner, P. R. Quantum Mechanical Tunneling Is Essential to Understanding Chemical Reactivity. *Trends Chem.* **2020**, *2*, 980–989. (32) Maier, G.; Endres, J.; Reisenauer, H. P. 2,3-Dihydrothiazol-2-

ylidene. Angew. Chem., Int. Ed. Engl. 1997, 36, 1709-1712.

(33) Maier, G.; Endres, J. 2,3-Dihydroimidazol-2-ylidene. *Eur. J. Org. Chem.* **1998**, 1998, 1517–1520.

(34) Maier, G.; Endres, J.; Reisenauer, H. P. Interconversions Between Oxalic Acid Monoamide Rotamers: Photochemical Process Versus Tunneling. J. Mol. Struct. **2012**, 1025, 2–5.

(35) McGibbon, G. A.; Burgers, P. C.; Terlouw, J. K. The Imidic Acids H-N=C(H)-OH and  $CH_3-N=C(H)-OH$  and Their Tautomeric Carbenes  $H_2N-\ddot{C}-OH$  and  $CH_3-N(H)-\ddot{C}-OH$ : Stable Species in the Gas Phase Formed by One-Electron Reduction of Their Cations. *Int. J. Mass Spectrom. Ion Processes* **1994**, *136*, 191– 208.

(36) Nguyen, V. S.; Abbott, H. L.; Dawley, M. M.; Orlando, T. M.; Leszczynski, J.; Nguyen, M. T. Theoretical Study of Formamide Decomposition Pathways. J. Phys. Chem. A **2011**, 115, 841–851.

(37) Gahlaut, A.; Paranjothy, M. Unimolecular Decomposition of Formamide via Direct Chemical Dynamics Simulations. *Phys. Chem. Chem. Phys.* **2018**, *20*, 8498–8505.

(38) Vichietti, R. M.; da Silva, A. B. F.; Haiduke, R. L. A. Providing Theoretical Data for Detection of Four Formamidic Acid Isomers in Astrophysical Media. *Mol. Astrophys.* **2018**, *10*, 1–10.

(39) Maier, G.; Endres, J. Isomerization of Matrix-Isolated Formamide: IR-Spectroscopic Detection of Formimidic Acid. *Eur. J. Org. Chem.* **2000**, 2000, 1061–1063.

(40) Lundell, J.; Krajewska, M.; Räsänen, M. Matrix Isolation Fourier Transform Infrared and Ab Initio Studies of the 193-nm-Induced Photodecomposition of Formamide. *J. Phys. Chem. A* **1998**, *102*, 6643–6650.

(41) Duvernay, F.; Trivella, A.; Borget, F.; Coussan, S.; Aycard, J.-P.; Chiavassa, T. Matrix Isolation Fourier Transform Infrared Study of Photodecomposition of Formimidic Acid. J. Phys. Chem. A 2005, 109, 11155–11162.

(42) Schriver, A.; Schriver-Mazzuoli, L.; Vigasin, A. A. Matrix Isolation Spectra of the Carbon Dioxide Monomer and Dimer Revisited. *Vib. Spectrosc.* **2000**, *23*, 83–94.

(43) King, S.-T. Infrared Study of the NH<sub>2</sub> 'Inversion' Vibration for Formamide in the Vapor Phase and in an Argon Matrix. *J. Phys. Chem.* **1971**, *75*, 405–410.

(44) Räsänen, M. A Matrix Infrared Study of Monomeric Formamide. J. Mol. Struct. 1983, 101, 275–286.

(45) Pacansky, J.; Calder, G. V. The Infrared Spectra of HCN Isotopes in Argon Matrices: An Examination of the Assumptions of Matrix Isolation Spectroscopy. J. Mol. Struct. **1972**, *14*, 363–383.

(46) Ayers, G. P.; Pullin, A. D. E. The i.r. Spectra of Matrix Isolated Water Species—I. Assignment of Bands to  $(H_2O)_{2^{j}}$   $(D_2O)_{2}$  and HDO Dimer Species in Argon Matrices. Spectrochim. Acta, Pt. A: Mol. Spectrosc. **1976**, 32, 1629–1639.

(47) Leroi, G. E.; Ewing, G. E.; Pimentel, G. C. Infrared Spectra of Carbon Monoxide in an Argon Matrix. J. Chem. Phys. **1964**, 40, 2298–2303.

(48) Cugley, J. A.; Pullin, A. D. E. The Infrared Spectrum of Ammonia Isolated in Argon and Nitrogen Matrices. *Spectrochim. Acta, Pt. A: Mol. Spectrosc.* **1973**, *29*, 1665–1672.

(49) Teles, J. H.; Maier, G.; Andes Hess, B., Jr; Schaad, L. J.; Winnewisser, M.; Winnewisser, B. P. The CHNO Isomers. *Chem. Ber.* **1989**, *122*, 753–766.

(50) Reisenauer, H. P.; Romański, J.; Mlostoń, G.; Schreiner, P. R. Dimethoxycarbene: Conformational Analysis of a Reactive Intermediate. *Eur. J. Org. Chem.* **2006**, 2006, 4813–4818.

(51) Kapp, J.; Schade, C.; El-Nahasa, A. M.; von Ragué Schleyer, P. Heavy Element  $\pi$  Donation is not Less Effective. *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 2236–2238.

(52) Eckhardt, A. K.; Erb, F. R.; Schreiner, P. R. Conformer-Specific [1,2]H-Tunnelling in Captodatively-Stabilized Cyanohydroxycarbene (NC-C-OH). *Chem. Sci.* **2019**, *10*, 802–808.

(53) Bernhardt, B.; Ruth, M.; Eckhardt, A. K.; Schreiner, P. R. Ethynylhydroxycarbene (H $-C\equiv C-\ddot{C}-OH$ ). J. Am. Chem. Soc. 2021, 143, 3741–3746.

(54) Bao, J. L.; Truhlar, D. G. Variational Transition State Theory: Theoretical Framework and Recent Developments. *Chem. Soc. Rev.* 2017, 46, 7548–7596.