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Thermally Persistent Carbonyl Nitrene: FC(O)N

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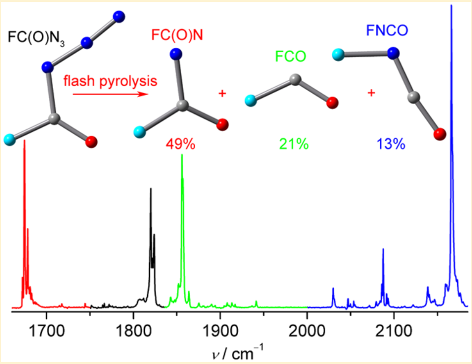
S Supporting Information

ABSTRACT: Transient carbonyl nitrenes RC(O)N, formed during thermal- or photoinduced decomposition of carbonyl azides $RC(O)N_3$, are highly liable to the Curtius rearrangement, producing isocyanates RNCO in almost quantitative yield. Contrary to common belief, we found a thermally persistent triplet carbonyl nitrene, FC(O)N, that can be produced by flash pyrolysis of $FC(O)N_3$ in 49% yield. The computed CBS-QB3 activation barrier for the thermal decomposition of $FC(O)N_3$ to FC(O)N is 29 kJ mol^{-1} lower than that for a concerted pathway producing FNCO.



Upon either photolysis or pyrolysis, carbonyl azides may eliminate molecular nitrogen and form isocyanates, RNCO. This is well-known as Curtius rearrangement.[1] The underlying reaction mechanism, particularly for photoinduced decomposition, has attracted extensive experimental and theoretical attention over the past few decades.[2−14] Two pathways for the decomposition have been proposed. One is a stepwise reaction that occurs by forming the carbonyl nitrene intermediate, RC(O)N, followed by intramolecular rearrangement to RNCO. The other is a concerted elimination of N_2 with the simultaneous formation of RNCO without involvement of the nitrene.

Although the involvement of nitrenes can be inferred by analysis of the complicated product mixtures resulting from photolysis of some carbonyl azides in solution, only very few triplet nitrenes have been detected by electron paramagnetic resonance spectroscopy (EPR).[11,15,16]

Benzoyl nitrene (PhC(O)N), generated by photolysis of benzoyl azide[2,7,9,10] or sulfilimine-based nitrene precursors,[17] has been detected by ultrafast IR spectroscopy and matrix-isolation IR and UV/vis spectroscopy. The absorption data and the absence of EPR signal suggested a singlet ground state for this nitrene,[10,18] although the sign of the calculated relative energy between the singlet and triplet (ΔE_{ST}) was found to depend on the applied methods.

A recent matrix-isolation study of the photolysis of the parent molecule $HC(O)N_3$ reported a failure to produce the parent carbonyl nitrene,[19] whose ground-state multiplicity has also been a matter of some controversy.[10,20,21] In contrast, formation of triplet carbonyl nitrenes was experimentally confirmed by EPR spectroscopy during the photolysis of alkoxycarbonyl azides ($ROC(O)N_3$), such as (4-acetylphenoxyl)carbonyl azide[11] and carbethoxy azide.[16]

Quite recently, the ground-state multiplicities of fluorinated acylnitrenes, including FC(O)N, were computationally rationalized.[22] For fluoroalkylcarbonyl azides (e.g., $CF_3C(O)N$), the electron-withdrawing effect of the fluorine was found to reduce the relative stability of the singlet configuration. However, because of direct conjugation between the fluorine and carbonyl, FC(O)N is electronically more closely related to the ROC(O)N nitrenes and a larger ΔE_{ST} is predicted.

Compared to the complicated photochemistry of most carbonyl azides in solution, high-temperature thermal decomposition in the gas phase seems to be much simpler; generally, only the Curtius-rearrangement product RNCO was isolated.[23] This experimental observation is consistent with the calculated potential energy surfaces (PES) of prototypical molecules like $HC(O)N_3$,[24] $CH_3C(O)N_3$,[6,9] and $ClF_2CC(O)N_3$,[25] for which the transition state of the concerted pathway is lower in energy than that of the stepwise pathway.

Interestingly, theoretical calculations predicted the preference of a stepwise dissociation for methoxycarbonyl azide ($CH_3OC(O)N_3$),[9] i.e., the activation barrier for forming $CH_3OC(O)N$ (126 kJ mol^{-1}) from the higher-energy conformer of the azide is lower than that of the concerted way to CH_3ONCO (154 kJ mol^{-1}) at the CBS-QB3 level of theory. However, all attempts to observe the nitrene intermediate $CH_3OC(O)N$ either by photolysis of $CH_3OC(O)N_3$ in solid noble gas matrices[26,27] or by pyrolysis of the azide in the gas

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phase[27,28] were unsuccessful. Instead, mainly the Curtius-rearrangement compound CH_3ONCO was detected.

Nevertheless, it was generally accepted that pyrolysis of carbonyl azides can hardly be used to produce carbonyl nitrenes, which were thought to be highly unstable against Curtius rearrangement in the gas phase. The close electronic relationship between the alkoxycarbonylnitrenes, whose ground states seem to be more clearly established by computational methods than alkylcarbonylnitrenes, and FC(O)N suggests that the latter might be an attractive target for attempting to observe the nitrene by thermal methods.

As a continuation of our interest in thermally persistent nitrene species,[29] we present here a rare example of a thermally produced triplet carbonyl nitrene, FC(O)N, in the gas phase. Additionally, the PES for its formation from $FC(O)N_3$ has been explored using quantum chemical calculations. Prior to this study, nitrene FC(O)N has been generated by ArF laser photolysis (193 nm) of matrix-isolated $FC(O)N_3$ at 16 K, and it has been characterized by IR (^{13}C, ^{15}N, ^{18}O-labeling), UV/vis, and EPR spectroscopy, allowing for the unambiguous confirmation of FC(O)N in this study.[30]

To verify a preference of stepwise decomposition of $FC(O)N_3$ via the nitrene intermediate FC(O)N, quantum chemical calculations on the PES of $FC(O)N_3$ were performed at both the B3LYP/6-311+G(3df) and CBS-QB3 levels of theory. The results are summarized in Figure 1.

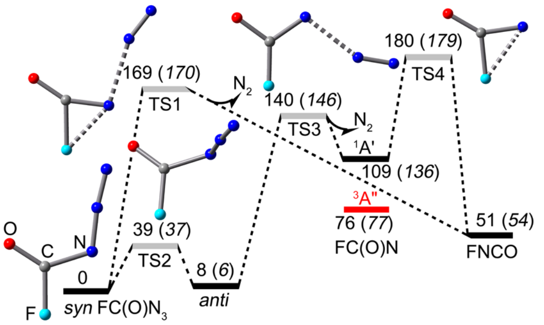

Figure 1. Calculated relative energies (kJ mol^{-1}) of the minima and transition states for the decomposition of $FC(O)N_3$ at the CBS-QB3 level of theory. The relative energies calculated at the B3LYP/6-311+G(3df) level are given in parentheses. The optimized structures of the transition states are shown.

Like most carbonyl azides,[9] two conformers, namely, *syn* and *anti*, are true minima. The *syn*/*anti* conformation refers to the relative position of C═O and N_3 with respect to the C–N bond. The *syn* conformer of the azide is slightly lower in energy than the *anti*. The calculated energy difference (8 kJ mol^{-1}, CBS-QB3) between these two conformers agrees with the experimental value of 6 ± 2 kJ mol^{-1}, as determined by IR spectroscopy.[31] The energy for the interconversion of these two conformers is 39 kJ mol^{-1}, which involves an out-of-plane rotation transition state (TS2) of the N_3 moiety. This small barrier allows for the facile enrichment of the higher-energy *anti* conformer upon heating.

Two pathways for the endergonic decomposition of $FC(O)N_3$ to produce FNCO are predicted. The computed barrier for the stepwise decomposition of the higher-energy *anti* conformer (132 kJ mol^{-1}) via the nitrene is lower than the concerted decomposition of the *syn* conformer (160 kJ mol^{-1}). This suggests that $FC(O)N_3$ should produce the nitrene upon heating. The barrier for the intramolecular rearrangement from the initially formed nitrene FC(O)N to isocyanate FNCO is only slightly higher (71 kJ mol^{-1}) than that for $CH_3OC(O)N$ (59 kJ mol^{-1})[9] at the same CBS-QB3 level. Such small rearrangement barriers exclude the observation of these two singlet intermediates during the thermal decomposition of their azide precursors.

However, in addition to the rearrangement reaction, intersystem crossing (ISC) is a potentially competitive process for the initially generated nitrene species. As for FC(O)N, the calculated ΔE_{ST} is 33 kJ mol^{-1}, which is the largest among all theoretically investigated carbonyl nitrenes such as HC(O)N (−0.5 kJ mol^{-1}, CCSD(T)/cc-pVQZ//CCSD(T)/cc-pVTZ),[10] $CH_3OC(O)N$ (24 kJ mol^{-1}, CBS-QB3),[9] $CF_2ClC(O)N$ (3 kJ mol^{-1}, CBS-QB3),[25] $CF_3C(O)N$ (15 kJ mol^{-1}, CR-CC(2,3)/6-311G(3df,2p)),[22] and $CH_3C(O)N$ (−17 kJ mol^{-1}, CBS-QB3; −1 kJ mol^{-1}, CR-CC(2,3)/6-311G(3df,2p);[9,22] the negative sign indicates that the calculated energy of the singlet is lower than the triplet. The large positive ΔE_{ST} and a close-shell singlet state due to intramolecular N–O interaction (singlet: r_{N-O} = 1.896 Å, ∠OCN = 97.9°; triplet: r_{N-O} = 2.272 Å, ∠OCN = 124.1°) imply that the singlet nitrene may rapidly relax to the triplet ground state through efficient ISC. The lower energy of the triplet nitrene state might provide a persistent minimum in that both endothermic reverse ISC and rearrangement to the isocyanate would have to occur. To ensure that there was no lower-energy pathway to forming the isocyanate from the triplet carbene, a fruitless search for a transition state was carried out at the B3LYP/6-311+G(3df) and CBS-QB3 levels. The rather high energy of triplet FNCO (209 kJ mol^{-1}, CBS-QB3) relative to the triplet nitrene rules out this potential thermal rearrangement. Thus, triplet FC(O)N should be a rare carbonyl nitrene that can be thermally produced in the gas phase and experimentally observed.

Flash vacuum pyrolysis of $FC(O)N_3$ in argon (1:500) at ca. 700 °C was performed, and the IR spectrum of the matrix-isolated decomposition products is shown in Figure 2B. In addition to the IR bands of the undecomposed azide precursor, the bands of the Curtius rearrangement product FNCO

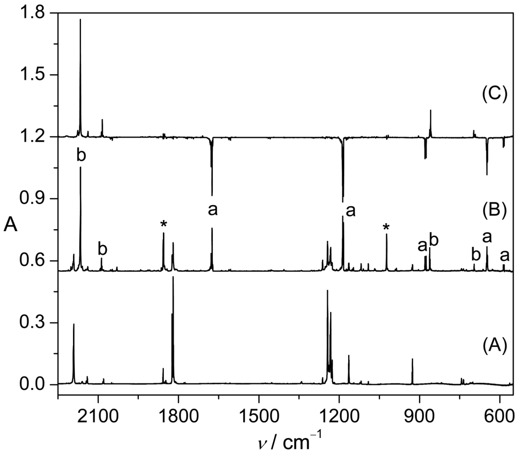

Figure 2. (A) IR spectrum of Ar-matrix isolated $FC(O)N_3$, (B) IR spectrum of Ar-matrix isolated pyrolysis (ca. 700 °C) products of $FC(O)N_3$, and (C) IR difference spectrum showing the changes after irradiation (λ > 335 nm, 10 min) of the matrix associated with spectrum B. The IR bands of FC(O)N (a), FNCO (b), and FCO (*) are labeled in spectrum B.

(marked by b in Figure 2B) and the triplet nitrene intermediate FC(O)N (marked by a in Figure 2B) can be clearly identified by comparison with the IR data reported in the previous photolysis experiments.[30] Due to the change in the matrix surroundings between the pyrolysis and photolysis experiments, the main band positions of FNCO (2166, 2085, 859, and 698 cm^{-1}) and FC(O)N (1675, 1187, 879, 649, and 587 cm^{-1}) are slightly shifted compared to the previous data for FNCO (2175, 2096, 861, and 702 cm^{-1}) and FC(O)N (1681, 1194, 880, 647, and 589 cm^{-1}), respectively. The assignment is further confirmed by the subsequent photoinduced ($\lambda > 335$ nm) conversion from FC(O)N to FNCO.

In the IR spectrum, there are two additional new bands at 1856 and 1023 cm^{-1} (marked by * in Figure 2B). They belong to the radical FCO (1857 and 1023 cm^{-1}).[32] The most straightforward way of forming FCO is the cleavage of the C−N bond in $FC(O)N_3$. However, the rather high C−N bond dissociation energy in *syn*-$FC(O)N_3$ (342 kJ mol^{-1}, CBS-QB3) and the absence of the IR band for N_3 radical (1657.5 cm^{-1})[33] imply that there is another route to form FCO during pyrolysis of $FC(O)N_3$. As has been shown above, pyrolysis of $FC(O)N_3$ efficiently yields triplet FC(O)N, which may dimerize into a diazene compound, FC(O)NNC(O)F. Secondary thermolysis of the diazene would result in N_2 and two FCO radicals. Structural optimization of this dimer at the B3LYP/6-311+G(3df) level reveals C_i molecular symmetry (OCNN = 83.4°, CNNC = 180°) with two long C−N bonds (1.433 Å) bridged by a short central N═N bond (1.230 Å). The thermal instability of FC(O)NNC(O)F can be partially inferred by the calculated low dissociation energy of 122 kJ mol^{-1} (→ 2 FCO + N_2, CBS-QB3). Dimerization reactions have already been observed for a number of triplet nitrenes such as $CH_3OC(O)N$[27] and FSO_2N.[29] A similar decomposition product (FSO_2) of the nitrene dimer was also obtained from the pyrolysis of FSO_2N_3, in which the thermally persistent triplet sulfonyl nitrene FSO_2N was produced in the gas phase with an estimated yield of about 66%.[29]

According to the observed and calculated intensities of the characteristic IR bands of $FC(O)N_3$ (1820 cm^{-1}), FC(O)N (1675 cm^{-1}), FNCO (2175 cm^{-1}), and FCO (1023 cm^{-1}), about 83% of the azide decomposes at ca. 700 °C, and the yields of FC(O)N, FNCO, and FCO are roughly estimated to be 49, 13, 21%, respectively.

In summary, we have found that carbonyl azide $FC(O)N_3$ can undergo stepwise decomposition upon thermolysis. This produces a thermally persistent triplet carbonyl nitrene FC(O)N in the gas phase with an estimated yield about 49%. The experimental observations show good agreement with the computational results, demonstrating that the activation barrier for the stepwise decomposition is energetically favored over the concerted formation of the corresponding isocyanate FNCO. The thermal persistence of triplet FC(O)N not only will contribute to the fundamental knowledge of rich nitrene chemistry butl also will enable future structural characterization of a carbonyl nitrene for the first time using gas-phase spectroscopy methods such as high-resolution IR or microwave spectroscopy.

EXPERIMENTAL METHODS

Matrix IR spectra were recorded on an FT-IR spectrometer in reflectance mode using a transfer optic at a resolution of 0.5 cm^{-1}. A KBr beam splitter and an MCT detector were used in the region 4000−500 cm^{-1}. The freshly purified $FC(O)N_3$ was mixed with argon gas (1:500) in a 1 L stainless steel storage container. Then, a small amount of the mixture was passed through a quartz furnace (i.d., 1.0 mm; length, 30 mm), which was heated (voltage, 6.1 V; current, 2.2 A) over a length of ca. 10 mm by a platinum wire (o.d., 0.25 mm; resistance, 0.8 Ω) prior to deposition on the cold rhodium-plated copper matrix support at 16 K in high vacuum. While not directly measured, under these conditions, the expected residence time in the hot zone is well under 1 ms. Details of the matrix apparatus have been described elsewhere.[34] Photolysis experiments were performed using a high-pressure mercury lamp (150 W) by conducting the light through water-cooled quartz lenses combined with a cutoff filter ($\lambda > 335$ nm). Geometry optimizations and harmonic frequency calculations were performed using the B3LYP[35] method with the 6-311+G(3df) basis set. Complete basis method (CBS-QB3) was also used.[36] Temperature corrections were all made at 298.15 K. Local minima were confirmed by vibrational frequency analysis, and transition states were further confirmed by intrinsic reaction coordinate (IRC) calculations.[37,38] All calculations were performed using the Gaussian 03 software package.[39]

ASSOCIATED CONTENT

Supporting Information

Molecular structures, coordination, and energies calculated at the B3LYP/6-311+G(3df) and CBS-QB3 levels of theory using the Gaussian 03 software package. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Curtius, T. *Ber. Dtsch. Chem. Ges.* **1890**, *23*, 3023−3033.

(2) Vyas, S.; Kubicki, J.; Luk, H. L.; Zhang, Y.; Gritsan, N. P.; Hadad, C. M.; Platz, M. S. *J. Phys. Org. Chem.* **2012**, *25*, 693−703.

(3) Kubicki, J.; Zhang, Y.; Xue, J.; Luk, H. L.; Platz, M. *Phys. Chem. Chem. Phys.* **2012**, *14*, 10377−10390.

(4) Kubicki, J.; Zhang, Y.; Vyas, S.; Burdzinski, G.; Luk, H. L.; Wang, J.; Xue, J.; Peng, H.-L.; Pritchina, E. A.; Sliwa, M.; Buntinx, G.; Gritsan, N. P.; Hadad, C. M.; Platz, M. S. *J. Am. Chem. Soc.* **2011**, *133*, 9751−9761.

(5) Kubicki, J.; Zhang, Y.; Wang, J.; Luk, H. L.; Peng, H.-L.; Vyas, S.; Platz, M. S. *J. Am. Chem. Soc.* **2009**, *131*, 4212−4213.

(6) Tarwade, V.; Dmitrenko, O.; Bach, R. D.; Fox, J. M. *J. Org. Chem.* **2008**, *73*, 8189−8197.

(7) Wentrup, C.; Bornemann, H. *Eur. J. Org. Chem.* **2005**, *21*, 4521−4524.

(8) Zabalov, M. V.; Tiger, R. P. *Russ. Chem. Bull. Int. Ed.* **2005**, *54*, 2270−2280.

(9) Liu, J.; Mandel, S.; Hadad, C. M.; Platz, M. S. *J. Org. Chem.* **2004**, *69*, 8583−8593.

(10) Pritchina, E. A.; Gritsan, N. P.; Maltsev, A.; Bally, T.; Autrey, T.; Liu, Y.; Wang, Y.; Toscano, J. P. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1010−1018.
(11) Sigman, M. E.; Autrey, T.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 4297−4305.
(12) McConaghy, J. S.; Lwowski, W. *J. Am. Chem. Soc.* **1967**, *89*, 4450−4456.
(13) Berry, R. S.; Cornell, D.; Lwowski, W. *J. Am. Chem. Soc.* **1963**, *85*, 1199.
(14) Wasserman, E. *Prog. Phys. Org. Chem.* **1971**, *8*, 319−336.
(15) Lwowski, W. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 897−906.
(16) Autrey, T.; Schuster, G. B. *J. Am. Chem. Soc.* **1987**, *109*, 5814−5820.
(17) Desikan, V.; Liu, Y.; Toscano, J. P.; Jenks, W. S. *J. Org. Chem.* **2008**, *73*, 4398−4414.
(18) Kuck, V. J.; Wasserman, E.; Yager, W. A. *J. Phys. Chem.* **1972**, *76*, 3570−3571.
(19) Zeng, X. Q.; Bernhardt, E.; Beckers, H.; Banert, K.; Hagedorn, M.; Liu, H. *Angew. Chem., Int. Ed.* **2013**, *52*, 3503−3506.
(20) Harrison, J. F.; Shalhoub, G. *J. Am. Chem. Soc.* **1975**, *97*, 4172−4176.
(21) Mavridis, A.; Harrison, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 7651−7655.
(22) Sherman, M. P.; Jenks, W. S. *J. Org. Chem.* **2014**, *79*, 8977−8983.
(23) Falvey, D. E.; Gudmundsdottir, A. D. *Nitrenes and Nitrenium Ions*; John Wiley & Sons, Inc.: Hoboken, NJ, 2013; Vol. *6*.
(24) Banert, K.; Berndt, C.; Hagedorn, M.; Liu, H.; Anacker, T.; Friedrich, J.; Rauhut, G. *Angew. Chem., Int. Ed.* **2012**, *51*, 4718−4721.
(25) Ramos, L. A.; Zeng, X. Q.; Ulic, S. E.; Beckers, H.; Willner, H.; Della Védova, C. O. *J. Org. Chem.* **2012**, *77*, 6456−6462.
(26) Wilde, R. E.; Srinivasan, T. K. K.; Lwowski, W. *J. Am. Chem. Soc.* **1971**, *93*, 860−863.
(27) Teles, J. H.; Maier, G. *Chem. Ber.* **1989**, *122*, 745−748.
(28) Dyke, J. M.; Levita, G.; Morris, A.; Ogden, J. S.; Dias, A. A.; Algarra, M.; Santos, J. P.; Costa, M. L.; Rodrigues, P.; Andrade, M. M.; Barros, M. T. *Chem.—Eur. J.* **2005**, *11*, 1665−1676.
(29) Zeng, X. Q.; Beckers, H.; Willner, H. *J. Am. Chem. Soc.* **2013**, *135*, 2096−2099.
(30) Zeng, X. Q.; Beckers, H.; Willner, H.; Grote, D.; Sander, W. *Chem.—Eur. J.* **2011**, *17*, 3977−3984.
(31) Mack, H.-G.; Védova, C. O. D.; Willner, H. *J. Mol. Struct.* **1993**, *291*, 197−209.
(32) Jacox, M. E. *J. Mol. Spectrosc.* **1980**, *80*, 257−271.
(33) Amicangelo, J. C.; Collier, J. R.; Dine, C. T.; Saxton, N. L.; Schleicher, R. M. *Mol. Phys.* **2007**, *105*, 989−1002.
(34) Schrader, B. *Infrared and Raman Spectroscopy, Methods and Applications*; VCH: Weinheim, Germany, 1995.
(35) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.
(36) Montgomery, J. A., Jr.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **2000**, *112*, 6532−6542.
(37) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363−368.
(38) Hratchian, H. P.; Schlegel, H. B. *J. Chem. Theory Comput.* **2005**, *1*, 61−69.
(39) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; et al. *Gaussian 03*, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2003.