

- T. Preiss, H. P. Reisenauer, B. A. Hess, Jr., L. J. Schaad, *J. Am. Chem. Soc.* **1994**, *116*, 2014–2018.
- [4] R. W. Hoffmann, R. Schüttler, *Chem. Ber.* **1975**, *108*, 844–855.
- [5] We thank Prof. E.-U. Würthwein, Universität Münster, for drawing our attention to this fact in 1993 (MP2/6–31G** calculations, unpublished results).
- [6] a) K. Tanaka, M. Yoshimine, *J. Am. Chem. Soc.* **1980**, *102*, 7655–7662; b) W. J. Bouma, R. H. Nobes, L. Radom, C. E. Woodward, *J. Org. Chem.* **1982**, *47*, 1869–1875; c) M. Yoshimine, *J. Chem. Phys.* **1989**, *90*, 378–385.
- [7] R. Hochstrasser, J. Wirz, *Angew. Chem.* **1989**, *101*, 183–185; *Angew. Chem. Int. Ed. Engl.* **1989**, *26*, 805.
- [8] Gaussian 94, Revision B.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh PA, **1995**.
- [9] The isotopomer [D₂]**1** was prepared according to ref. [4] from quadricyclanone and nonadeuterotrimethylsulfoxonium chloride.
- [10] a) G. Maier, H. P. Reisenauer, T. Sayrac, *Chem. Ber.* **1982**, *115*, 2192–2201; b) G. Maier, H. P. Reisenauer, T. Sayrac, *Chem. Ber.* **1982**, *115*, 2202–2213.
- [11] For a review on the oxirene problem, see a) E. Lewars, *Chem. Ber.* **1983**, *83*, 519–534; see also b) E. Lewars, *J. Mol. Struct. (Theochem)* **1996**, *360*, 67–80, and references therein; c) G. Maier, C. Schmidt, H. P. Reisenauer, E. Endlein, D. Becker, J. Eckwert, B. A. Hess, Jr., L. J. Schaad, *Chem. Ber.* **1993**, *126*, 2337–2352; reference [6].
- [12] W. Sander, G. Bucher, S. Wierlacher, *Chem. Rev.* **1993**, *93*, 1583–1621.
- [13] If CH₂ is replaced by SiH₂ the CO complex H₂Si·CO is calculated to be the global minimum on the CH₂OSi potential-energy surface and can be isolated in a cryogenic matrix: G. Maier, H. P. Reisenauer, H. Egenolf in *Organosilicon Chemistry IV – From Molecules to Materials* (Eds: N. Auner, J. Weis), VCH, Weinheim, in press.
- [14] G. Vacek, J. M. Galbraith, Y. Yamaguchi, H. F. Schaefer III, R. H. Nobes, A. P. Scott, L. Radom, *J. Phys. Chem.* **1994**, *98*, 8660–8665.

Isonitroso Hydrogen (Hydroxy Nitrene, HON)**

Günther Maier,* Hans Peter Reisenauer, and Michael De Marco

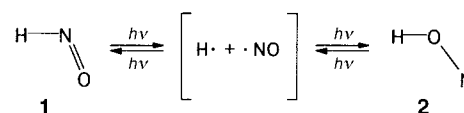
Dedicated to Professor Heinrich Nöth on the occasion of his 70th birthday

The importance of nitroso hydrogen HNO (**1**) for combustion, atmospheric chemistry, astrophysics, and particularly theoretical chemistry is demonstrated in a multitude of papers published on this topic.^[1] According to the results of some theoretical studies the existence of isonitroso hydrogen HON (**2**) besides HNO (**1**) is anticipated, but to the best of our knowledge there is no experimental evidence for that. Herein we describe the first matrix isolation and IR-spectroscopic

identification of isonitroso hydrogen (**2**) in solid argon at 10 K.

For the generation of HON (**2**) the same method can be used, which was employed by Jacox and Milligan 15 years ago to produce and to identify HNO (**1**) IR spectroscopically in an argon matrix.^[2] Thus, hydrogen atoms are generated by exposing a H₂/Ar mixture to a microwave discharge and deposited together with a NO/Ar mixture on a 10 K cold spectroscopic window. Under these conditions a NO radical and a hydrogen atom can recombine to form HNO (**1**). In the meantime we know that HON (**2**) is also generated within this process in a small amount. Alternatively one can produce the same products by passing a mixture of NO, H₂, and argon (ratio: 1:2:250) or of H₂, N₂, O₂, and argon (ratio: 4:1:1:500) through a microwave discharge.

Independent of the chosen method of generation we found strong IR absorptions of HNO (**1**) and small bands, which we assign to HON (**2**). The identification of **2** is based mainly on the investigation of the photochemistry of the already known HNO (**1**) isomer. Moreover, further products (NH, N₂O, N₂O₂, N₂O₃, HNO₂, NO₂, OH, H₂O, HO₂, CO, CO₂) could be observed in various amounts. In analogy with the photoisomerization of nitrosyl cyanide (ONCN) to isonitrosyl cyanide (NOCN),^[3] the thermodynamically more stable nitroso hydrogen (**1**) was converted into the less stable isonitroso hydrogen (**2**). During irradiation of HNO (**1**) in solid argon at 10 K with monochromatic light of the wavelength $\lambda = 313$ nm, the HNO bands at 2715.1, 1562.2, and 1504.3 cm⁻¹ decrease, while two new absorptions arise at 3467.2 and 1095.6 cm⁻¹, which we assign to HON (**2**). At the same time the NO band (1871.4 cm⁻¹) increases. If the wavelength is changed to $\lambda = 254$ nm the HON absorptions decrease, while the HNO bands increase. During this second irradiation the NO band continues to grow. All these observations point to a photochemical equilibrium between HNO (**1**) and HON (**2**), which is presumably reached by the



dissociation of the two isomers into NO radicals and H atoms. The position of the equilibrium depends on the wavelength of light used for the irradiation. The increase of the NO concentration during the photoisomerization is caused by cage escape of H atoms, which are rather mobile even at 10 K in solid argon.^[4]

Irradiation with very short (248, 193, 185 nm) and long (> 330 nm) wavelengths does not lead to any observable isomerization. The identification of isonitroso hydrogen (**2**) is based essentially on the comparison of the experimental and calculated IR spectra. Figure 1 shows a difference spectrum, which documents the photoisomerization between **1** and **2**. Furthermore the corresponding calculated IR spectra (Gaussian package of programs)^[5] are included for comparison. In addition the D- (Figure 2) and ¹⁵N-isotopomers of HON (**2**) have been investigated. All results (BLYP^[6] and QCISD/6-311++G**) are compiled in Table 1.

[*] Prof. Dr. G. Maier, Dr. H. P. Reisenauer, Dipl.-Chem. M. De Marco
Institut für Organische Chemie der Universität
Heinrich-Buff-Ring 58, D-35392 Giessen (Germany)
Fax: (+49) 641-99-34309

[**] This work was supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft.

Table 1. Experimental ($[\text{cm}^{-1}]$, argon matrix, 10 K) and calculated vibrational spectra (BLYP and QCISD/6-311++G**) of four isotopomers of HON (relative intensities are given in parentheses).

	Type ^[a]			HON	HO ¹⁵ N	DON	DO ¹⁵ N
ν_1	A'	OH str	exp.	3467.2 (19)	3466.4 (19)	2563.6 (28)	2564.6 (20)
			calcd ^[b]	3479.8 (27)	3479.8 (27)	2532.8 (30)	2532.8 (31)
			calcd ^[c]	3780.3 (42)	3780.3 (44)	2751.9 (42)	2751.9 (43)
ν_2	A'	NO str	exp.	— ^[d]	— ^[d]	1149.0 (100)	1127.9 (100)
			calcd ^[b]	1157.7 (0)	1145.7 (0)	1092.2 (100) ^[i]	1071.6 (100) ^[k]
			calcd ^[c]	1232.1 (1)	1222.4 (5)	1171.1 (100) ^[j]	1149.2 (100) ^[l]
ν_3	A'	bend	exp.	1095.6 (100)	1085.6 (100)	868.8 (79)	867.2 (74)
			calcd ^[b]	1030.2 (100) ^[e]	1020.7 (100) ^[g]	815.2 (70)	813.6 (72)
			calcd ^[c]	1142.5 (100) ^[f]	1129.1 (100) ^[h]	895.8 (81)	893.9 (52)

[a] str=stretching vibration, bend=bending vibration. [b] BLYP/6-311++G**. [c] QCISD/6-311++G**. [d] Not measurable due to too low intensity. [e] Absolute intensity: 163 km mol^{-1} . [f] Absolute intensity: 177 km mol^{-1} . [g] Absolute intensity: 160 km mol^{-1} . [h] Absolute intensity: 168 km mol^{-1} . [i] Absolute intensity: 76 km mol^{-1} . [j] Absolute intensity: 95 km mol^{-1} . [k] Absolute intensity: 73 km mol^{-1} . [l] Absolute intensity: 93 km mol^{-1} .

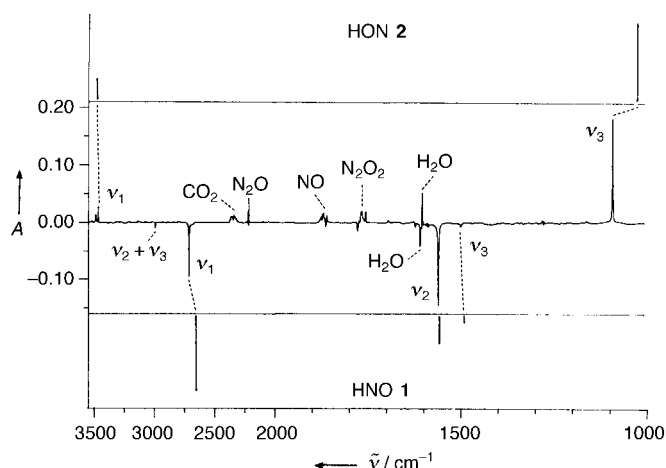


Figure 1. Calculated (BLYP/6-311++G**) and experimental IR spectra of HNO (**1**) and HON (**2**). Theoretical spectrum for HON (**2**) at the top and for HNO (**1**) at the bottom. Difference spectrum (Ar matrix, 10 K) of the photochemical isomerization of **1** to **2** in the middle. The investigated matrix was produced by cocondensation of a mixture of NO/Ar (ratio: 4:1000) with H atoms, which were generated by microwave discharge of a mixture of H_2/Ar (ratio: 8:1000).

For the triatomic bent molecule HON (**2**), as well as for HNO (**1**), three IR active fundamental vibrations are expected. However, for isomer **2** due to the low intensity of the NO stretching vibration (ν_2), which is coupled with the HON bending mode (ν_3), only two absorptions could be observed. They are attributed to the bending mode (ν_3 ; 1095.6 cm^{-1}), which is mixed with the NO stretching vibration (ν_2) and the OH stretching vibration (ν_1 ; 3467.2 cm^{-1}). The calculated IR spectrum of DON predicts an increase of the intensity of the now uncoupled NO stretching vibration. Indeed, three new bands were observed during the photoisomerization of DNO, which we assign to the bending mode (ν_3 ; 868.8 cm^{-1}), the NO stretching vibration (ν_2 ; 1149.0 cm^{-1}), and the OD stretching vibration (ν_1 ; 2563.6 cm^{-1}) of DON ([D]**2**) (Figure 2). The comparison of the calculated and experimental band shifts of the isotopomers HON, HO¹⁵N, DON, and DO¹⁵N (Table 1) are in good agreement again. The spectra of DON and DO¹⁵N are particularly informative because all three fundamental vibrations are observable.

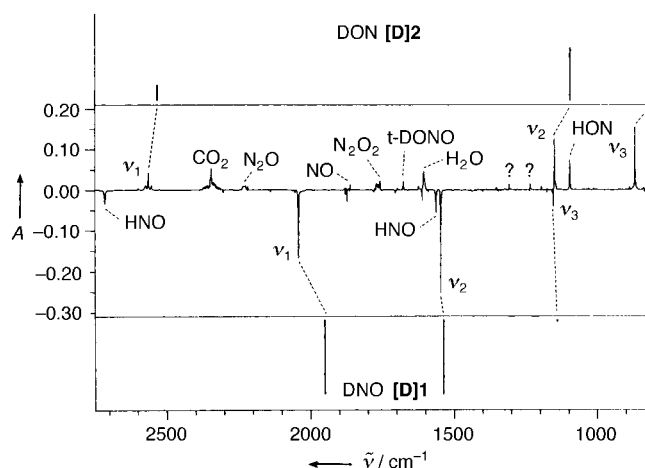


Figure 2. Calculated (BLYP/6-311++G**) and experimental IR spectra of DNO ([D]**1**) and DON ([D]**2**). Theoretical spectrum for DON ([D]**2**) on the top and for DNO ([D]**1**) at the bottom. Difference spectrum (Ar matrix, 10 K) of the photochemical isomerization of [D]**1** to [D]**2** in the middle. The investigated matrix was produced by cocondensation of a mixture of NO/Ar (ratio: 4:1000) with D atoms, which were generated by microwave discharge of a mixture of D_2/Ar (ratio: 8:1000).

How does the UV/Vis spectrum of **2** look? During irradiation of HNO (**1**) with light of the wavelength $\lambda = 313 \text{ nm}$ one observes the decrease of its characteristic sharp bands at 688, 709, and 761 nm,^[7] new absorptions in the range between 230 and 1100 nm cannot be detected. Nevertheless, **2** must absorb below 300 nm, since this compound is photochemically stable against irradiation with wavelengths above 300 nm, but, irradiation with $\lambda = 254 \text{ nm}$ light causes isomerization to **1**.

What is the multiplicity of the ground state of isonitroso hydrogen (**2**)? Calculation of the potential energy surface of the system HNO/HON shows a singlet ground state for HNO (**1**), which is also the global minimum.^[1, 8] However, for HON (**2**) a triplet ground state is predicted. The energy gap between singlet and triplet of approximately 20 kcal mol^{-1} supports the assumption that under our conditions the triplet ground state of **2** is present. Indeed, the experimental IR spectrum fits much better to the calculated spectrum of the triplet molecule (see ref. [8] and our own calculations).^[9] Thus, the isomerization of HNO to HON involves a change of multiplicity. Calculations reported by Guadagnini et al.^[8] correspond with

results from our experiment in so far as the dissociation to H and NO is lower in energy than a cyclic transition state for the direct reaction of **1** to **2** on the singlet as well as the triplet potential-energy surface.

What can we say about the geometry of **2**? The calculations^[8] reveal a typical O–H bond length for isonitroso hydrogen (**2**) ($d = 0.984 \text{ \AA}$; $\text{trans-HONO: } d(\text{OH}) = 0.98 \text{ \AA}$). The N–O bond length ($1.323 \text{ \AA}$) is very long and lies between a double ($\text{trans-HONO: } d(\text{N=O}) = 1.20 \text{ \AA}$) and a single bond ($\text{trans-HONO: } d(\text{N–O}) = 1.46 \text{ \AA}$). These structural data of isonitroso hydrogen (**2**) express the character of a nitrene. In other words: This molecule should be regarded as “hydroxy nitrene”.

Received: July 27, 1998 [Z 12206 IE]
German version: *Angew. Chem.* **1999**, *111*, 113–115

Keywords: ab initio calculations • isomerizations • matrix isolation • nitrenes • photochemistry

- [1] D. H. Mordaunt, H. Flöthmann, M. Stumpf, H.-M. Keller, C. Beck, R. Schinke, K. Yamashita, *J. Chem. Phys.* **1997**, *107*, 6603–6615, and references therein.
- [2] M. E. Jacox, D. E. Milligan, *J. Mol. Spectrosc.* **1973**, *48*, 536–559.
- [3] G. Maier, H. P. Reisenauer, J. Eckwert, M. Naumann, M. De Marco, *Angew. Chem.* **1997**, *109*, 1785–1787; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1707–1709.
- [4] K. H. Gödderz, N. Schwentner, M. Chergui, *J. Chem. Phys.* **1996**, *105*, 451–458.
- [5] Gaussian 94, Revision B.1: M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Alatham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Derees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzales, J. A. Pople, Gaussian Inc., Pittsburgh, PA, USA, **1995**.
- [6] Review: L. J. Bartolotti, U. Flurchick, *Rev. Comput. Chem.* **1996**, *7*, 187–216.
- [7] G. W. Robinson, M. McCarty, Jr., *Can. J. Phys.* **1958**, *63*, 1590–1591.
- [8] R. Guadagnini, G. C. Schatz, S. P. Walch, *J. Chem. Phys.* **1995**, *102*, 774–783.
- [9] In principle it should be possible to verify the triplet multiplicity of the HON ground state by ESR spectroscopy. However, since the relevant signal is expected to lie outside the range of our ESR spectrometer, we have not carried out measurements.

Palladium-Mediated Dynamic Kinetic Resolution: Stereoselective Synthesis of Vicinal Diamines**

Gregory R. Cook,* P. Sathya Shanker, and
Ketheeswaran Pararajasingham

The palladium-catalyzed allylic substitution reaction has emerged as a powerful methodology in organic synthesis.^[1] The stereoselective variants have focussed primarily on enantioselective processes which utilize chiral ligands and achiral substrates.^[2] When chiral substrates are used, the configuration of the allylic leaving group controls the configuration of the product through a double inversion mechanism. In contrast, little attention has been paid to diastereoselectivity in the nucleophilic addition to π -allyl palladium complexes with an adjacent stereocenter,^[2–4] and a study of the asymmetric induction by acyclic substrates in intermolecular reactions has not been previously reported.^[5] For stereocenters outside of the allyl framework to control the addition of a nucleophile, the palladium complex must be able to undergo rapid allyl inversion (Figure 1). Our interest in dynamic transition metal complexes^[6] has led us to probe the diastereoselectivity in such a system, and our results are reported herein. This process constitutes an example of palladium-mediated dynamic kinetic resolution.^[3b, 7]

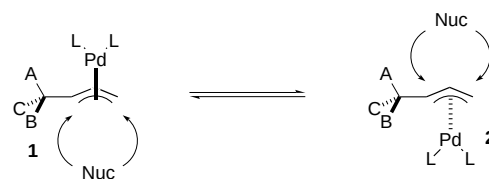


Figure 1. Selectivity issues in dynamic diastereomeric complexes (see text for details).

Several issues of regio- and stereoselectivity need to be addressed when considering the allylic substitution reaction. The palladium-catalyzed reaction usually favors addition at the less substituted terminus. For complexes **1** and **2** (Figure 1), this mode of reactivity must be reversed in order to generate a new stereocenter. While many allyl complexes are configurationally stable, rapid equilibration is common, and this usually results in loss of allyl stereochemistry. For selectivity in a diastereoselective process, such as described here, the rate of π -allyl inversion relative to the rate of nucleophilic addition is important (Figure 1).

We have shown^[6] that chiral 5-vinyloxazolidinones **3** derived from α -amino acids react with palladium(0) catalysts to afford 5-vinyloxazolines **6** by oxidative insertion, loss of CO_2 , and subsequent cyclization at the amide oxygen atom (Scheme 1). The oxazoline products were obtained with

[*] Prof. G. R. Cook, P. S. Shanker, K. Pararajasingham
Department of Chemistry
North Dakota State University
Fargo, ND 58105 (USA)
Fax: (+1) 701-231-8831
E-mail: grcook@plains.nodak.edu

[**] We thank the National Science Foundation (OSR 9452892) and North Dakota State University for support of this project.