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[18] EPPS: 3-[4-(2-hydroxyethyl)-1-piperazino]propanesulfonic acid. The polymer (ca. 5 mg, ca. 1.2 µmol peptide) was incubated with the metal salt (1 µmol) and the test substrates **3a,b** (1 µmol).

[19] To exclude sequence-specific adsorption effects, the following control experiments were carried out: a) The hydroxyindolyl phosphate **3b** was hydrolyzed enzymatically and oxidized to the indigo dye **5** in an aerated solution of alkaline phosphatase from *bovine intestinal mucosa* (EC 3.1.3.1; Sigma; 20 U mg^{-1}). Exposure of about 2500 beads of the undecapeptide library to the resulting deeply colored suspension did not afford stained beads. b) When TentaGel S–NH_2 was swollen in an aqueous solution of the above alkaline phosphatase, exposure to the reagent **3b** resulted in a deep turquoise stain of all beads.

[20] MES: 2-morpholinoethanesulfonic acid.

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[23] Uncomplexed Zr^{4+} as the cause of the observed acceleration appears very unlikely according to the following control experiments: At constant Zr concentration, a duplication of the peptide concentration does not result in a decrease of the rate of hydrolysis. On the other hand, at constant peptide concentration, an increase of the Zr concentration results in an increase of the rate of hydrolysis. Complex formation is furthermore indicated by resonance shifts observed in the NMR spectra of peptide **A** upon addition of Zr^{4+}.

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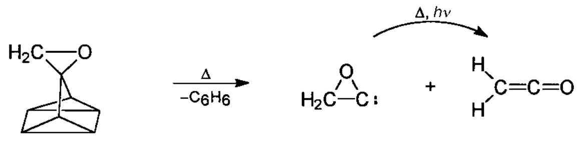
Oxiranylidene[**]

Günther Maier,* Hans Peter Reisenauer, and
Michael Cibulka

Fourteen years ago we could generate cyclopropenylidene by high vacuum flash pyrolysis of a quadricyclane derivative, synthesized by Hoffmann et al.,[1] and identify it spectroscopically in a rare gas matrix.[2] This was the starting point for intensive studies on the C_3H_2 potential-energy surface.[3] Consequently we tried to synthesize oxiranylidene (**2**) by using the quadricyclane derivative **1** as a precursor. This compound in particular was used because Hoffmann and Schüttler[4] had detected ketene (**3**) on thermolysis of **1** in an earlier experiment. The question as to whether oxiranylidene (**2**) is the primary product of this reaction could not be answered at that time. It was logical to resume the search for **2** with techniques available today (high vacuum flash pyrolysis in combination with matrix-isolation). This was especially tempting because of the great theoretical interest in oxiranylidene (**2**). Ab initio calculations predict that it should be a minimum on the C_2H_2O potential-energy surface with a considerable energy barrier to isomerization.[5, 6] Therefore it should be possible to detect **2** in a cryogenic matrix. Herein we show that besides ketene (**3**) and ethynol (**4**),[7] oxiranylidene (**2**) is indeed an observable C_2H_2O species.

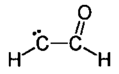


1 **2** **3**

$H-C\equiv C-OH$

4

5



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If one pyrolyzes polycycle **1** under high vacuum (quartz tube: diameter 8 mm; heating zone 5 cm; approximately 10^{-5} mbar; 500 °C) and deposits the resulting products together with nitrogen or argon as the matrix material on a cold (10 K) CsI window, the absorptions listed in Table 1 in addition to those of benzene and ketene (**3**) can be found in the IR spectrum. The bands are sharp in solid nitrogen, but split in argon because of matrix effects. Their intensity depends on the conditions of the pyrolysis and is highest if a temperature is chosen under which some starting material is still detectable in the condensate. When the temperature is raised up to 600 °C the absorptions listed in Table 1 diminish and those of ketene (**3**) become enlarged. The bands of **2** also decrease if the matrix-isolated pyrolysate is irradiated ($\lambda = 313$ nm), while the absorptions of **3** grow simultaneously. These observations and the good agreement between the experimental and the calculated (MP2/6-311++G**, B3LYP/6-311++G**)[8] spectrum (Table 1, Figure 1) confirm that the thermal cleavage of polycycle **1** leads, as expected, to oxiranylidene (**2**). The five fundamental vibrations with the highest calculated intensities are observed. No weak CH stretching vibrations at about 3000 cm^{-1} were detectable. Oxiranylidene (**2**) is converted into ketene (**3**) either under the conditions of the pyrolysis or on irradiation of the matrix after the thermolysis of **1**. The calculated IR spectrum for the singlet ground state **S-2** corresponds well with the experimental one. In contrast, the expected IR spectrum for the triplet carbene **T-2** looks quite different (Figure 1).

Table 1. Observed IR absorptions (N_2 matrix, 10 K; relative intensities in parentheses) and calculated vibrational spectra (MP2/6-311++G**, B3LYP/6-311++G**) of oxiranylidene (**2**).

		Type	$\tilde{\nu}_{N_2,exp}$ [cm^{-1}]	$\tilde{\nu}_{calcd}$ [cm^{-1}] (MP2)	$\tilde{\nu}_{calcd}$ [cm^{-1}] (B3LYP)
ν_7	a″	CH_2 str.	–	3313 (7)	3241 (10)
ν_1	a′	CH_2 str.	–	3189 (2)	3128 (4)
ν_2	a′	ring def. + CH_2 scis.	1470.8 (46)	1554 (61)	1528 (73)
ν_3	a′	CH_2 scis. + ring def.	1375.1 (50)	1438 (55)	1417 (64)
ν_8	a″	CH_2 rock.	–	1139 (3)	1116 (3)
ν_4	a′	CH_2 wag. + ring def.	1078.5 (16)	1118 (38)	1094 (42)
ν_9	a″	CH_2 twist	–	902 (4)	884 (4)
ν_5	a′	ring def. + CH_2 wag.	830.1 (100)	860 (100)[a]	838 (61)
ν_6	a′	ring def.	778.1 (29)	815 (59)	823 (100)[b]

[a] Absolute intensity: 52 $km\,mol^{-1}$. [b] Absolute intensity: 53 $km\,mol^{-1}$.

The structural elucidation of oxiranylidene (**2**) is confirmed by the result of the flash pyrolysis of the precursor [D_2]**1**[9] with a deuterated three-membered ring. Again the experiment is in good agreement with the calculations (Table 2, Figure 2). The surprising splitting of the strongest band in the IR spectrum of [D_2]**2** into two signals of nearly the same intensity at 1419.4 and 1400.6 cm^{-1} is the result of a Fermi resonance of the fundamental vibration ν_2 with the overtone of the fundamental vibration ν_6 of [D_2]**2** at 706.3 cm^{-1}.

The UV spectrum of the matrix-isolated pyrolysis products shows a weak, structureless band at $\lambda_{max} = 324$ nm. It is very likely that oxiranylidene (**2**) is responsible for this absorption, because it vanishes in the previously mentioned photoisomerization **2**→**3**, which is fastest with light of wavelength $\lambda = 313$ nm, slower with $\lambda = 254$ nm, and is not observed at all at $\lambda \geq 366$ nm.

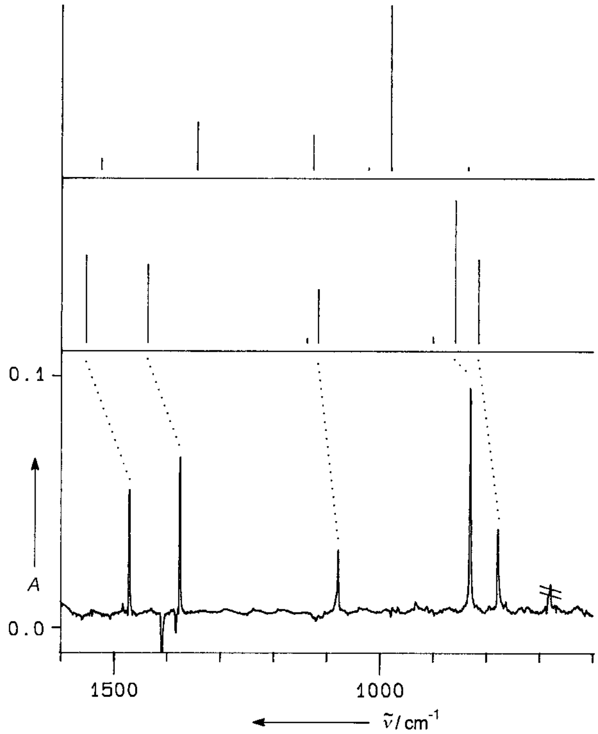

Figure 1. Selected region of the experimental (N_2 matrix, 10 K, bottom) and calculated (MP2/6-311++G**, middle) IR spectrum of oxiranylidene (**S-2**), as well as the calculated IR spectrum (MP2/6-311++G**, top) of triplet oxiranylidene **T-2**. The experimental spectrum is a difference spectrum of the photoisomerization **2**→**3** (the bands with positive values diminish upon irradiation).

Table 2. Observed IR absorptions (N_2 matrix, 10 K; relative intensities in parentheses) and calculated vibrational spectra (MP2/6-311++G**, B3LYP/6-311++G**) of [D_2]oxiranylidene ([D_2]**2**).

		Type	$\tilde{\nu}_{N_2,exp}$ [cm^{-1}]	$\tilde{\nu}_{calcd}$ [cm^{-1}] (MP2)	$\tilde{\nu}_{calcd}$ [cm^{-1}] (B3LYP)
ν_7	a″	CD_2 str.	–	2474 (8)	2419 (8)
ν_1	a′	CD_2 str.	–	2307 (2)	2262 (3)
$\nu_2/2\nu_6$	a′	ring def. + CD_2 scis.	1419.4 (85)[a]	1489 (100)[b]	1467 (100)[c]
$\nu_2/2\nu_6$	a′		1400.6 (81)[a]		
ν_3	a′	CD_2 scis.	1050.2 (21)	1090 (9)	1070 (8)
ν_4	a′	CD_2 wag. + ring def.	960.3 (57)	1001 (38)	974 (37)
ν_8	a″	CD_2 rock.	–	868 (4)	852 (3)
ν_5	a′	ring def.	780.1 (100)	811 (42)	821 (42)
ν_6	a′	CD_2 wag.	706.3 (94)	722 (56)	708 (46)
ν_9	a″	CD_2 twist	–	687 (5)	673 (4)

[a] Fermi resonance $\nu_2/2\nu_6$. [b] Absolute intensity: 57 $km\,mol^{-1}$. [c] Absolute intensity: 67 $km\,mol^{-1}$.

The investigation of oxiranylidene (**2**) was of interest to us also because of our earlier attempts[10] on matrix isolation of oxirene (**5**).[11] If **2** behaved as a normal alkylcarbene with an α-hydrogen atom, a 1,2-hydrogen migration to give oxirene (**5**) should occur easily.[12] However, this reaction cannot be observed.

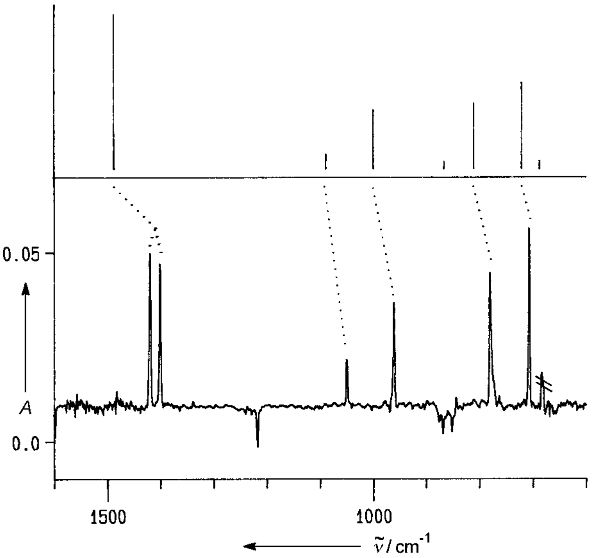

Figure 2. Selected region of the experimental (N_2 matrix, 10 K, bottom) and the calculated (MP2/6-311++G**, top) IR spectrum of [D_2]oxiranylidene (**S**-[D_2]**2**). The experimental spectrum is a difference spectrum of the photoisomerization [D_2]**2**→[D_2]**3** (the bands with positive values diminish upon irradiation).

Altogether the experiments and theoretical predictions give a consistant picture.[5, 6] In order to be able to compare the relevant stationary points, they were again calculated on the B3LYP/6-311++G** level of theory[8] (Scheme 1). The following conclusions can be drawn: a) The C_2H_2O isomer that is next highest in energy to ethynol (**4**)[7] (relative energy: 37.2 kcal mol^{-1}) was found with oxiranylidene (**2**) (relative energy on the level of theory used: 66.7 kcal mol^{-1}). b) Unlike formylcarbene (**6**) oxiranylidene (**2**) has a singlet ground state. c) The energy barrier for the ring-opening **2**→**3** is 30.6 kcal mol^{-1} lower than the barrier for a 1,2-hydrogen migration. The transition state **TS(2→3)** of the former reaction looks like a $CH_2\cdot CO$ complex.[13] The TS of the energetically disfavored reaction path (**2**→**6**) leads to formylcarbene (**6**) rather than oxirene (**5**).[6b] d) There seems to be no chance to generate C_2H_2O species other than **3**, **4**, and **2**. Even if **S-6** was formed from **S-2** it should react to ketene (**3**) via **TS(6→3)** nearly without any activation and hence compete with the conversion into the ground state **T-6**.[6b] The widely discussed formylcarbene/oxirene isomerization[6, 10–12] is also believed not to be observable experimentally, even if oxirene (**5**) is, in contrast to earlier calculations,[6] a true minimum.[14] The energy difference between oxirene (**5**), formylcarbene (**S-6**), and the transition state, which links **5** and **S-6**, is so small that isomerization to ketene (**3**) will occur immediately.

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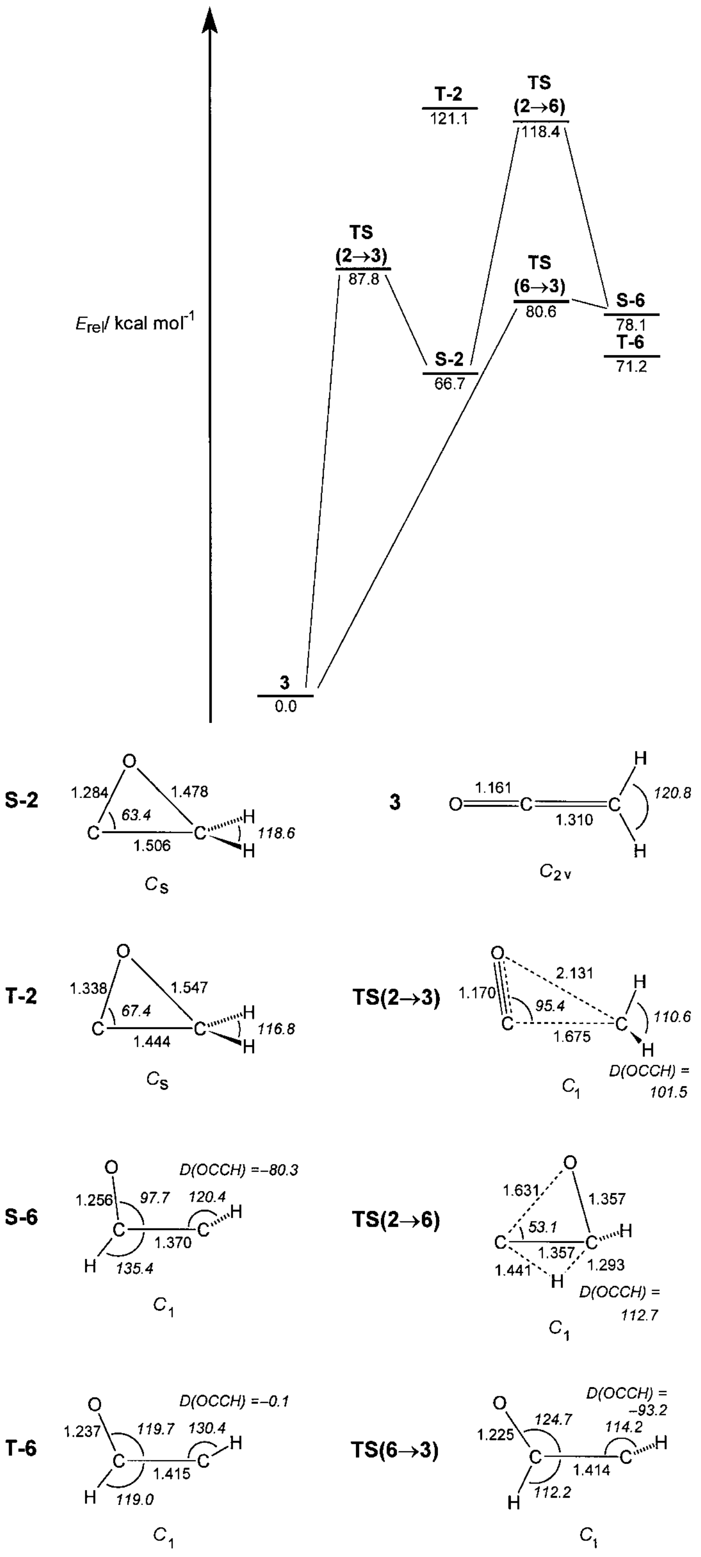

Scheme 1. Calculated (B3LYP/6-311++G**) relative energies (including zero point vibrational energies) and structures of relevant C_2H_2O minima and related transition structures **TS**. Distances in Å, angles in degrees (italic; D = dihedral angle).

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Isonitroso Hydrogen (Hydroxy Nitrene, HON)**

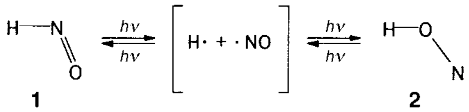
Günther Maier,* Hans Peter Reisenauer, and Michael De Marco

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 H_2/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, H_2, and argon (ratio: 1:2:250) or of H_2, N_2, O_2, 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, N_2O, N_2O_2, N_2O_3, HNO_2, NO_2, OH, H_2O, HO_2, CO, CO_2) 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]



1 **2**

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 comparision. In addition the D- (Figure 2) and ^{15}N-isotopomers of HON (**2**) have been investigated. All results (BLYP[6] and QCISD/6-311++G**) are compiled in Table 1.

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