Aust. J. Chem. **2014**, *67*, 1324–1329 http://dx.doi.org/10.1071/CH14149

Full Paper

Pyridyl- and Pyridylperoxy Radicals – A Matrix Isolation Study

André Korte,^A Artur Mardyukov,^A and Wolfram Sander^{A,B}

 ^ALehrstuhl für Organische Chemie II, Ruhr-Universität Bochum, D-44781 Bochum, Germany.
^BCorresponding author. Email: wolfram.sander@rub.de

The three isomeric pyridyl radicals $2\mathbf{a}-\mathbf{c}$ were synthesised using flash vacuum pyrolysis in combination with matrix isolation and characterised by infrared spectroscopy. The IR spectra are in good agreement with spectra calculated using density functional theory methods. The reaction of the pyridyl radicals 2 with molecular oxygen leads to the formation of the corresponding pyridylperoxy radicals $3\mathbf{a}-\mathbf{c}$. The peroxy radicals 3 are photolabile, and irradiation results in *syn-anti* isomerisation of $3\mathbf{a}$ and $3\mathbf{b}$ and ring expansion of all three isomers of 3.

Manuscript received: 14 March 2014. Manuscript accepted: 7 May 2014. Published online: 19 June 2014.

Introduction

Nitrogen-containing heterocycles are important constituents of coal, which on combustion produce large amounts of NO_x . Since coal is a highly complex mixture of compounds difficult to study directly, pyridine (1) has served as a simple model to investigate the combustion of nitrogen-containing heterocycles. Loss of a hydrogen atom of 1 results in the formation of the three isomeric pyridyl radicals 2 that, depending on the conditions, could either react with molecular oxygen to give the pyridyloxy radicals 3 (Scheme 1) or degrade further to small, highly unsaturated fragments. The thermal decomposition of pyridine has been investigated by a variety of methods, including shock tube^[1,2] and laser IR pyrolysis.^[3] In the shock tube pyrolysis cyanoacetylene was found as the principal nitrogen containing product at 1300 K, whereas at 1800 K HCN predominated.^[1] Other products observed were acetylene and hydrogen. These studies suggest that the primary step in the thermal decomposition of pyridine is the loss of one hydrogen atom to form pyridyl radicals 2, that subsequently ring-open to form highly unsaturated secondary radicals. Both the 2-pyridyl radical 2a and the 3-pyridyl radical 2b are involved in the formation of the stable small molecules observed in these experiments, whereas it was concluded that the 4-pyridyl radical 2c results in polymerisation and soot formation.

The thermal decomposition of pyridine (1) to give the isomeric pyridyl radicals 2 was also investigated in a series of theoretical studies.^[4–7] The CH dissociation energy of the *ortho* CH bond in 1 is ~105 kcal mol⁻¹, and thus is 5– 6 kcal mol⁻¹ lower than that of the two other CH bonds and of that of benzene.^[2,8] The key step of the thermal decomposition of 1 is therefore the formation of the 2-pyridyl radical 2a. The next step of the decomposition with an estimated activation barrier of 40.3 kcal mol⁻¹ is the rupture of the C(5)–N bond in 2a to form a nitrile radical.^[7] Breaking the C(3)–C(4) bond to produce an alkyne radical is calculated to have a considerably higher barrier.

The loss of a second hydrogen atom from the pyridyl radicals **2** leads to the isomeric didehydropyridines (pyridynes).^[9] These species have been investigated by matrix isolation spectroscopy,^[10,11] gas phase ion techniques,^[12,13] and by theoretical methods.^[14,15] Compared with the ring opening, these processes are energetically less favourable and therefore pyridynes are not discussed as intermediates in the combustion of pyridine (**1**). Despite the interest in the chemistry of pyridyl radicals **2**, the only matrix isolation and spectroscopic characterisation of these species was reported in 1972 by Kasai and McLeod using electron paramagnetic resonance (EPR) spectroscopy for their detection.^[16]

In the presence of molecular oxygen, pyridyl radicals **2** rapidly react to form pyridylperoxy radicals **3**, which subsequently split off oxygen atoms to pyridyloxy radicals or rearrange to a second generation of rather unstable radicals.^[17–19] The 2-pyridylperoxy radical **3a** was generated by pulse radiolysis of 2-chloro- or 2-bromopyridine in the presence of air.^[19] This technique allowed recording of a transient spectrum of **3a** with a maximum absorption at 440 nm. The mechanism of the rearrangements of **3** was studied in detail by Fadden and Hadad using density functional theory (DFT) methods.^[18] In pyridine flames, up to 80 products of the combustion of **1** were detected by synchroton photoionisation techniques, which demonstrates the complexity of these processes.^[20]

To investigate reactions of radicals with O_2 under the conditions of matrix isolation, argon matrices can be doped with small amounts (0.5–2%) of O_2 . As long as the argon matrix is kept at temperatures below 20 K, diffusion of O_2 is prevented and no reaction occurs. At temperatures above 25 K, the diffusion of O_2 becomes rapid, and the oxygenation can be directly monitored by IR or UV-vis spectroscopy. To induce this type of bimolecular reaction in matrices, it is mandatory to generate the radicals by flash vacuum pyrolysis (FVP) rather than by photolysis of a matrix-isolated precursor. The latter technique results in radical pairs which are trapped in close proximity or even in



Scheme 1. Primary processes in the combustion of pyridine (1).



Scheme 2. Synthesis of the phenyl radical 2 and phenylperoxy radical 7.

the same matrix cage. Annealing of these matrices results in recombination of the radical pair, rather than in bimolecular reactions with O_2 . In contrast, FVP of the precursor with subsequent trapping of the products in matrices results in radicals that are trapped in individual matrix cages. Annealing now preferentially leads to bimolecular reactions with O_2 .

This technique was successfully used in our laboratory for the synthesis and matrix isolation of the phenylperoxy radical 7.^[21] FVP of azobenzene produces phenyl radicals **6** which were trapped in argon matrices doped with 0.5–1% O₂. Under these conditions only small fractions of **6** react with O₂. Annealing of the matrix at 30–35 K allows the diffusion of O₂ and formation of the peroxy radical **7** (Scheme 2). Photolysis of **7** results in insertion of one oxygen atom into the ring to give lactone **8**, which on prolonged irradiation opens the ring to ketene **9**.

The same technique should also be applicable for the synthesis of pyridyl radicals 2 and pyridyl peroxy radicals 3. Here, we describe the matrix isolation and spectroscopic characterisation of the three isomeric radicals 2 and their oxygen trapping products 3.

Experimental

Matrix isolation experiments were performed by standard techniques using closed-cycle helium cryostats. Matrices were deposited at 3 K and annealing experiments performed between 25 and 35 K. FTIR spectra were recorded in the range between 400 and 4000 cm⁻¹ with a resolution of 0.5 cm⁻¹. FVP was carried out by slowly subliming the precursor through an 8 cm

quartz tube heated electrically with a tantalum wire. For broadband irradiations mercury high-pressure arc lamps with quartz optics, dichroic mirrors, and cut-off filters with 50% transmission at the specified wavelength were used.

All DFT calculations were performed with the *Gaussian* $09^{[22]}$ program package. The geometries were optimised using the unrestricted Becke, three-parameter, Lee–Yang–Parr (UB3LYP) method^[23–26] in combination with the cc-pVTZ basis set.^[27]

2-Iodopyridine (**4a**), 3-iodopyridine (**4b**), and 4-iodopyridine (**4c**) were purchased from Sigma–Aldrich and used without further purification. 2,2'-Azopyridine (**5a**) and 4,4'-azopyridine (**5c**) were prepared according to literature procedures.^[28]

3,3'-Azopyridine (5b)

To a solution of 124 mg (1.0 mmol) of 3-nitropyridine in 20 mL of ethanol, a solution of 160 mg (4.1 mmol) of NaOH in water was added dropwise. After addition of 260 mg (4.1 mmol) of zinc powder the resulting suspension was heated to reflux for 16 h. The solution was filtered while hot and the solvent evaporated. After chromatography (EtOAc/EtOH, 5:1) the crude product was crystallised from hot water. The product was obtained as yellow-orange needles with a melting point of 139–140°C; yield 36 mg (38 %). $\delta_{\rm H}$ (200 MHz, CDCl₃, 30°C) 9.26 (d, *J* 2.0, 1H), 8.79 (dd, *J* 4.9, 1H), 8.30 (ddd, *J* 8.2, 2.3, 1.6, 1H), 7.59 (dd, *J* 8.2, 4.9, 1H). m/z (70 eV) 184 [M⁺], 106 (36 %), 78 (70), 51 (64), 28 (100).

Results and Discussion

The pyridyl radicals 2a-c were synthesised by FVP of the corresponding iodopyridines 4 or azopyridines 5 at temperatures between 620 and 700°C with subsequent trapping of the products in argon at 10 K (Scheme 3). Both types of precursors resulted in the formation of pyridine (1), acetylene, HCN, and diacetylene as the major products. These products were identified by comparison of the matrix IR spectra obtained after the FVP with literature data. The pyridyl radicals 2 were generally formed in small amounts only.

The IR spectra recorded after FVP of **4a** or **5a** and trapping of the products in an argon matrix exhibited a series of weak absorptions at 1044, 941, 735, and 565 cm⁻¹ assigned to the 2-pyridyl radical **2a** by comparison with results from DFT calculations (Fig. 1). Both precursors **4a** and **5a** produce the same new bands, which confirms the assignment. Radical **2a** was also formed by 254 nm photolysis of matrix-isolated **4a**. Annealing of such a matrix at 30 K for several minutes results in the recombination of radical **2a** with the iodine atoms to give back precursor **4a**. Annealing of matrices containing **2a** produced by FVP of **4a**, on the other hand, does not lead to radical recombination since the diffusion of both **2a** and iodine atoms is slow under these conditions.

The 3-pyridyl radical **2b** was generated in a similar way by FVP of **4b** and **5b** at temperatures above 600°C. In addition to unreacted starting material and products such as acetylene, diacetylene, and HCN, a band at 671.7 cm⁻¹ and several weaker absorptions are assigned to **2b** (Fig. 2). These bands rapidly decrease in intensity if the matrix is irradiated with visible light ($\lambda \ge 420$ nm). Simultaneously, bands in the region between 3300 and 3100 cm⁻¹ appear, indicating the formation of terminal alkynes.

The 4-pyridyl radical 2c was obtained by FVP of 4c or 5c. The pyrolysis of 5c produces radical 2c in moderate yields and only small amounts of side products. The most intense absorption in the IR spectrum of 2c is the out-of-plane CH deformation mode at 750 cm^{-1} (Fig. 3). These absorptions are in good agreement with the IR spectrum of 2c, calculated at the



Scheme 3. Synthesis of the pyridyl radicals 2 and pyridylperoxy radicals 3.



Fig. 1. Matrix IR spectra showing the flash vacuum photolysis (FVP) of 2-iodopyridine **4a**. (a) **4a** in argon at 10 K. (b) FVP of **4a** at 620°C with subsequent trapping of the products in argon at 10 K. (c) IR spectrum of **2a** calculated at the UB3LYP/cc-pVTZ level of theory.



Fig. 2. Matrix IR spectra showing the flash vacuum photolysis (FVP) of 3-iodopyridine (**4b**). (a) **4b** in argon at 10 K. (b) FVP of **4b** at 620°C with subsequent trapping of the products in argon at 10 K. (c) Difference spectrum after irradiation ($\lambda \ge 420$ nm) of a matrix containing **2b**. Bands pointing downwards are disappearing during irradiation and are assigned to **2b**. (d) IR spectrum of **2b** calculated at the UB3LYP/cc-pVTZ level of theory.

UB3LYP/cc-pVTZ level of theory. FVP of the deuterated precursor d_4 -**5c** yields the deuterated pyridyl radical d_4 -**2c**.

Pyridylperoxy Radicals

The pyridylperoxy radicals 3a-c were generated by annealing argon matrices doped with 1-2% oxygen containing the



Fig. 3. Matrix IR spectra showing the flash vacuum photolysis (FVP) of 4-iodopyridine (**4c**). (a) **4c** in argon at 10 K. (b) FVP of **4c** at 620°C with subsequent trapping of the products in argon at 10 K. (c) IR spectrum of **2c** calculated at the UB3LYP/cc-pVTZ level of theory.

corresponding pyridyl radicals **2** at temperatures between 25 and 35 K. At these temperatures the diffusion of O_2 in argon becomes rapid, and thus bimolecular reactions are possible as long as the activation barrier is very small or zero. The disappearance of **2** and formation of **3** can be directly monitored by IR spectroscopy. After several minutes of annealing to allow for the diffusion of O_2 , the matrices are generally cooled back to 10 K. To study the photochemistry of the peroxy radicals **3**, the matrices were irradiated at 10 K with visible and UV light at various wavelengths. The relative energies of the regio isomers and conformers of **3** as well as the transition states connecting the conformers were calculated at the UB3LYP/cc-pVTZ level of theory (Fig. 4).

2-Pyridylperoxy Radical 3a

The 2-pyridylperoxy radical **3a** was synthesised by annealing argon matrices containing **2a** and 2% oxygen. New absorptions at 1599, 1465, 1429, 1301, 1260, 1177, 1125, 1039, 986, 804, 775, and 727 cm⁻¹ are assigned to **3a** (Fig. 5). If ¹⁸O₂ is used in the experiments, the bands at 1125 and 804 cm⁻¹ show large isotopic shifts of -56 and -12 cm⁻¹, respectively, as expected for the O–O and C–O stretching vibration (Figs S1 and S2 in the Supplementary Material). All other bands of **3a** show isotopic shifts of less than 1 cm⁻¹.

According to DFT calculations (UB3LYP/cc-pVTZ) the bimolecular reaction of 2a with oxygen is exothermic by 43.1 kcal mol⁻¹, and the *anti*-conformer of 3a is 1.8 kcal mol⁻¹

more stable than the *syn*-conformer (Scheme 4, Fig. 4). The two conformers are separated by an activation barrier of 4.46 kcal mol⁻¹. The IR spectrum of **3a** is in very good agreement with the spectrum calculated for *anti*-**3a** (Table S7, Supplementary Material), whereas the less stable *syn*-**3a** is not observed (Table S8, Supplementary Material). Visible light irradiation (> 415 nm), however, results in the formation of *syn*-**3a** and disappearance of the *anti*-isomer (Fig. 6). Subsequent annealing of the matrix for several minutes at 30 K again yields the spectrum assigned to *anti*-**3a**. This clearly demonstrates that the activation barrier for the isomerisation of *syn*-**3a** to *anti*-**3a** is small enough to be overcome at temperatures as low as 30 K, and that the *anti*-isomer, in agreement with the predictions from the DFT calculations.

Prolonged visible light irradiation ($\lambda > 415$ nm) results in the disappearance of **3a** and formation of a new product with a strong absorption at 1701 cm⁻¹ which is red-shifted by -23 cm⁻¹ if ¹⁸O₂ is used in the experiment. By comparison with DFT calculations the new product is assigned to the cyclic



Fig. 4. Relative energies of the *syn* and *anti* conformers of the pyridylperoxy radicals **3a–c** and of the transition states connecting the conformers calculated at the UB3LYP/cc-pVTZ level of theory. Values are given in kcal mol⁻¹ relative to the most stable isomer *anti-3a*.



Fig. 5. Matrix IR spectra showing the formation of the 2-pyridylperoxy radical **3a**. (a) Flash vacuum photolysis (FVP) of **4a** and deposition in argon at 10 K. (b) FVP of **4a** and deposition in argon containing 2 % oxygen at 10 K. (c) IR spectrum of *anti-***3a** calculated at the UB3LYP/cc-pVTZ level of theory.

carbamate radical **10** (Fig. 7). Radical **10** is also photolabile, and continuous photolysis with $\lambda > 415$ nm leads to new bands in the region between 2350 and 2050 cm⁻¹ which indicates ringopening and formation of alkynes or nitriles. Due to the complexity of these spectra we were not able to identify these products.

3-Pyridylperoxy Radical 3b

The reaction of **2b** with oxygen was carried out in a 0.5-2% O₂-doped argon matrix. During annealing at 35 K several IR absorptions assigned to the 3-pyridylperoxy radical **3b** increase in intensity (Fig. 8). Two absorptions at 799 and 796 cm⁻¹ are assigned to the out-of-plane deformation modes of the two conformers *syn*-**3b** and *anti*-**3b**, respectively. The assignment of the IR bands of **3b** were confirmed by ¹⁸O₂ isotopic labelling and comparison to the results of DFT calculations. Both



Fig. 6. Matrix IR spectra showing the photochemical conversion of *anti*-**3a** into *syn*-**3a**. (a) Spectrum calculated for *anti*-**3a** at the UB3LYP/cc-pVTZ level of theory. (b) Difference spectrum showing the $\lambda > 415$ nm photochemistry. Peaks pointing downwards are disappearing; peaks pointing upwards are appearing. (c) Spectrum of *syn*-**3a** calculated at the UB3LYP/ cc-pVTZ level of theory.



Fig. 7. Matrix IR spectra showing the long-time photochemistry ($\lambda > 415$ nm, 7 h) of *anti*-3a in argon/2 % O₂. (a) Spectrum of *anti*-3a calculated at the UB3LYP/cc-pVTZ level of theory. (b) Difference spectrum after prolonged irradiation with visible light ($\lambda > 415$ nm, 7 h). (c) Spectrum of the carbamate radical 10 calculated at the UB3LYP/cc-pVTZ level of theory.



Scheme 4. Photochemistry of pyridylperoxy radical 3a.



Fig. 8. Matrix IR spectra showing the formation of the 3-pyridylperoxy radical **3b**. (a) Flash vacuum photolysis (FVP) of **4b** and deposition in argon at 10 K. (b) FVP of **4b** and deposition in argon containing 2% oxygen at 10 K. (c) IR spectrum of *anti*-**3b** calculated at the UB3LYP/cc-pVTZ level of theory.



Fig. 9. Matrix IR spectra showing the photochemical conversion of *anti*-**3b** into *syn*-**3b**. (a) Spectrum calculated for *anti*-**3b** at the UB3LYP/cc-pVTZ level of theory. (b) Difference spectrum showing the $\lambda > 550$ nm photochemistry. Peaks pointing downwards are disappearing; peaks pointing upwards are appearing. (c) Spectrum of *syn*-**3b** calculated at the UB3LYP/cc-pVTZ level of theory.

conformers *syn*-**3b** and *anti*-**3b** are formed during annealing, which is in contrast to **3a** where only the *anti*-conformer is formed under similar conditions. This observation is in accordance with the DFT calculations, which give a slight energy difference of 0.7 kcal mol⁻¹ between the conformers (the *anti*-conformer being more stable) and an activation barrier of 3.9 kcal mol⁻¹ for the *anti*-*syn* isomerisation. Irradiation with visible light ($\lambda > 550$ nm) leads to a decrease of *anti*-**3b** and a simultaneous increase of *syn*-**3b** (Fig. 9). This isomerisation is reversed by irradiation with $\lambda > 515$ nm. Obviously, the two conformers are formed in photostationary equilibria with the relative amounts depending on the irradiation wavelength.

Prolonged irradiation results in the formation of intense bands between 1750 and 1680 cm^{-1} , and simultaneous disappearance of **3b**. The new bands in the carbonyl-stretching region suggest that ring expansion products are formed, but a definitive assignment was not possible. Experiments carried out with ¹⁸O₂ show the expected red-shifts of the carbonyl absorptions.

4-Pyridylperoxy Radical 3c

The 4-pyridylperoxy radical 3c was generated by annealing of O₂-doped matrices containing radical 2c. New bands at 1600,



Fig. 10. Matrix IR spectra showing the formation of the 4-pyridylperoxy radical **3c**. (a) Flash vacuum photolysis (FVP) of **4a** and deposition in argon containing 2% oxygen at 10 K. (b) IR spectrum of **3c** calculated at the UB3LYP/cc-pVTZ level of theory.



Fig. 11. Matrix IR spectra showing the photochemistry of **3c**. (a) Flash vacuum photolysis (FVP) of **4a** and deposition in argon containing 2% oxygen at 10 K. (b) Difference spectrum after irradiation with visible light ($\lambda \ge 420$ nm). (c) IR spectrum of **3c** calculated at the UB3LYP/cc-pVTZ level of theory.

1572, 1484, 1411, 1220, 1150, 1119, 990, 817, 808, and 508 cm^{-1} are assigned to **3c** (Fig. 10). If ${}^{18}\text{O}_2$ is used in the experiments, the bands at 1119 and 808 cm⁻¹ are red-shifted by -57 and -16 cm^{-1} , respectively, and therefore assigned to the O–O and C–O stretching vibrations of **3c**. As expected, only one conformer of **3c** is observed.

Irradiation of **3c** with blue light ($\lambda > 420 \text{ nm}$) results in the decrease of all bands assigned to **3c**, and formation of a strong and broad absorption at 2144 cm⁻¹ is observed. When ¹⁸O₂ is used in the experiments, new bands at 2118 and 2089 cm⁻¹ are found, together with the peak of C¹⁸O₂ at 2310 cm⁻¹. This suggests that a ketene is formed. Due to the low intensity of the other IR bands, a definitive assignment of the ketene was not possible (Fig. 11).

Conclusion

Pyridylradicals 2 can be synthesised by FVP of iodopyridines 4 or azopyridines 5 and trapping of the products in argon matrices. By-products of the FVP are pyridine 1 and fragmentation

products, in particular acetylene, HCN, and diacetylene. The fragmentation is driven by the formation of the very stable CN triple bond, and therefore the yield of pyridyl radicals is lower than that of phenyl radicals 6 from the analogous precursors iodobenzene or azobenzene. By carefully analysing the spectra and comparison with results from DFT calculations we were able to identify all three isomers of 2.

The bimolecular reaction of radicals 2 with O_2 was induced by annealing 1-2 % O₂-doped argon matrices containing 2 for several minutes at 25-35 K. This suggests that, as expected, the reaction between radicals 2 and O_2 has no thermal activation barrier. The only products observed are the pyridylperoxy radicals 3. For 3a and 3b two conformers, syn and anti, are possible, but only for 3b are both conformers observed after the thermal reaction between 2b and O₂, while for 3a the more stable anti-isomer is formed exclusively. The conformers form photostationary equilibria, and visible light irradiation results in syn-anti isomerisation. For both 3a and 3b the anti-conformers with the terminal oxygen atom pointing away from the nitrogen atom have the smaller dipole moment and are thermodynamically more stable by 1.84 and $0.67 \text{ kcal mol}^{-1}$, respectively. For both **3a** and **3b**, both the *syn*- and the *anti*-conformer can be generated by irradiation in photostationary equilibria. Even by annealing the matrices at temperatures above 30 K the conformers don't equilibrate thermally, which suggests a substantial thermal activation barrier for the isomerisation, in agreement with the calculations (Fig. 4). On the other hand, the thermal reaction between 2a and O2 produces syn-3a exclusively, while under similar conditions 2b reacts to a mixture of syn- and anti-**3b**. The reaction of the pyridyl radicals **3** with O_2 is exothermic, and the excess energy released might result in a syn-anti equilibration. Since the energy difference between syn- and anti-3b is small (the calculations are not accurate enough to reproduce these small differences reliably) both conformers could be formed in similar amounts in the matrix.

Prolonged visible light irradiation, or UV irradiation, results in the insertion of one oxygen atom into the pyridine ring to yield seven-membered heterocycles. Due to the low yields of these photoproducts, only 10 could be identified as the product of the rearrangement of 3a, whereas the photoproducts of 3b and 3c could not be identified. Overall, the reaction of the pyridyl radicals 2 with O_2 and the subsequent photochemistry follows the same path as that of the phenyl radical 6.

Supplementary Material

The ¹H- and ¹³C-NMR spectra of 3,3'-azopyridine and the spectroscopic and calculated data of the pyridyl radicals 2a-c and the pyridylperoxy radicals 3a-c are available on the Journal's website.

Acknowledgements

This work was financially supported by the Cluster of Excellence RESOLV (EXC 1069) funded by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

References

- J. C. Mackie, M. B. Colket, P. F. Nelson, J. Phys. Chem. 1990, 94, 4099. doi:10.1021/J100373A040
- [2] J. H. Kiefer, Q. Zhang, R. D. Kern, J. Yao, B. Jursic, J. Phys. Chem. A 1997, 101, 7061. doi:10.1021/JP970211Z

- [3] N. R. Hore, D. K. Russell, J. Chem. Soc., Perkin Trans. 2 1998, 2, 269. doi:10.1039/A706731C
- [4] X. L. Cheng, Y. Y. Zhao, Z. Y. Zhou, J. Mol. Struct. THEOCHEM 2004, 678, 17. doi:10.1016/J.THEOCHEM.2004.01.053
- [5] X. L. Cheng, J. Mol. Struct. THEOCHEM 2005, 731, 89. doi:10.1016/ J.THEOCHEM.2005.07.003
- [6] X. Cheng, L. Niu, Y. Zhao, Z. Zhou, Spectrochim. Acta A 2004, 60, 907. doi:10.1016/S1386-1425(03)00318-4
- [7] R. F. Liu, T. T. S. Huang, J. Tittle, D. H. Xia, J. Phys. Chem. A 2000, 104, 8368. doi:10.1021/JP000821Q
- [8] S. W. Wren, K. M. Vogelhuber, J. M. Garver, S. Kato, L. Sheps, V. M. Bierbaum, W. C. Lineberger, J. Am. Chem. Soc. 2012, 134, 6584. doi:10.1021/JA209566Q
- [9] M. Winkler, W. Sander, Aust. J. Chem. 2010, 63, 1013. doi:10.1071/ CH10113
- [10] H. H. Nam, G. E. Leroi, J. Am. Chem. Soc. 1988, 110, 4096. doi:10.1021/JA00220A092
- [11] M. Winkler, B. Cakir, W. Sander, J. Am. Chem. Soc. 2004, 126, 6135. doi:10.1021/JA039142U
- [12] S. L. Debbert, C. J. Cramer, Int. J. Mass Spectrom. 2000, 201, 1. doi:10.1016/S1387-3806(00)00160-3
- P. E. Williams, B. J. Jankiewicz, L. Yang, H. I. Kenttämaa, *Chem. Rev.* 2013, 113, 6949. doi:10.1021/CR400121W
- [14] C. J. Cramer, J. Am. Chem. Soc. 1998, 120, 6261. doi:10.1021/ JA9806579
- [15] C. J. Cramer, S. Debbert, Chem. Phys. Lett. 1998, 287, 320. doi:10.1016/S0009-2614(98)00192-4
- [16] P. H. Kasai, D. McLeod, Jr, J. Am. Chem. Soc. 1972, 94, 720. doi:10.1021/JA00758A007
- [17] J. E. Bennett, J. A. Howard, J. Am. Chem. Soc. 1973, 95, 4008. doi:10.1021/JA00793A029
- [18] M. J. Fadden, C. M. Hadad, J. Phys. Chem. A 2000, 104, 6088. doi:10.1021/JP0008492
- [19] Z. B. Alfassi, G. I. Khaikin, P. Neta, J. Phys. Chem. 1995, 99, 4544. doi:10.1021/J100013A026
- [20] Z. Tian, Y. Li, T. Zhang, A. Zhu, F. Qi, J. Phys. Chem. A 2008, 112, 13549. doi:10.1021/JP8066537
- [21] A. Mardyukov, W. Sander, Chem. Eur. J. 2009, 15, 1462. doi:10.1002/CHEM.200801546
- [22] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09 2009 (Gaussian, Inc.: Wallingford, CT).
- [23] A. D. Becke, J. Chem. Phys. 1993, 98, 5648. doi:10.1063/1.464913
- [24] S. H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 1980, 58, 1200. doi:10.1139/P80-159
- [25] C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 1988, 37, 785. doi:10.1103/ PHYSREVB.37.785
- [26] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, J. Phys. Chem. 1994, 98, 11623. doi:10.1021/J100096A001
- [27] R. A. Kendall, J. T. H. Dunning, R. J. Harrison, J. Chem. Phys. 1992, 96, 6796. doi:10.1063/1.462569
- [28] E. V. Brown, G. R. Granneman, J. Am. Chem. Soc. 1975, 97, 621. doi:10.1021/JA00836A025

