Radicals

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Interaction and Reaction of the Phenyl Radical with Water: A Source of OH Radicals**

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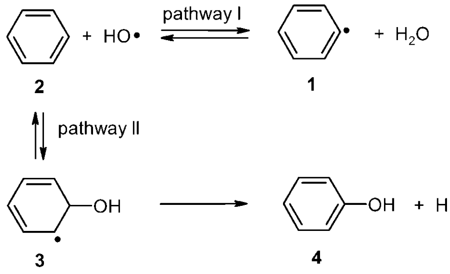
The phenyl radical (**1**) and the hydroxyl radical OH$^{\bullet}$ are highly reactive intermediates that play key roles in many reaction mechanisms. Gas-phase reactions of these radicals are of particular importance for our understanding of processes such as the combustion of hydrocarbons at high temperatures or the degradation of aromatic compounds in the troposphere at ambient temperature. Reaction with the hydroxyl radical is the only known pathway for the removal of benzene (**2**) from the troposphere. Owing to this fundamental importance, a large number of experimental and theoretical studies in this field have been described.[1–8]

An interesting, little-studied aspect of radical chemistry is the role of weakly bound noncovalent complexes.[9] Complexes between radicals and water and other highly polar compounds might stabilize the radicals and thus modulate their reactivity. The method of choice for investigating these complexes is matrix-isolation spectroscopy.[10,11] Although the inert-gas matrix introduces some degree of distortion into the trapped complexes, it could be shown in many instances that the spectra of even very weakly bound van der Waals complexes can be reproduced well by gas-phase calculations. Herein, we present evidence that both the phenyl radical (**1**) and the hydroxyl radical form noncovalent complexes that are of importance for understanding the reactivity of these species.

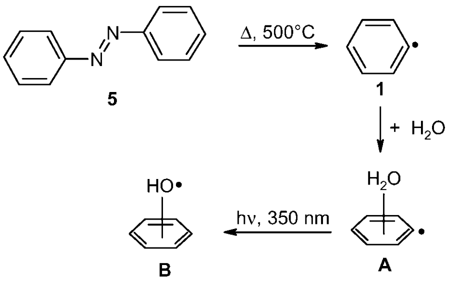
There are two pathways for the reaction of benzene (**2**) with OH: I) hydrogen abstraction to give radical **1** and water, and II) addition to yield the 2-hydroxycyclohexadienyl radical **3** (Scheme 1). At higher temperatures, phenol (**4**) can be formed from **3** through the loss of a hydrogen atom. The thermochemistry of these reactions was evaluated by using G3 theory.[7] According to these calculations, the hydrogen abstraction, I, is exothermic by 4.2 kcal mol^{-1} with an activation energy of 5.3 kcal mol^{-1}. The calculated reaction energy is in accordance with a simple estimation from the experimental bond enthalpies (DH$_{298}$) of the CH bond in benzene (112.9 kcal mol^{-1}) and the OH bond in water (118.8 kcal mol^{-1}): an enthalpy difference of 5.9 kcal mol^{-1}.[12] The addition reaction, II, is more exothermic (−16.2 kcal mol^{-1}) according to the G3 calculation,[7] and the activation barrier (2.8 kcal mol^{-1}) is lower than that of reaction I.



Scheme 1. Pathways for the reaction of the hydroxyl radical with benzene (**2**).

To gain insight into the systems benzene/OH$^{\bullet}$ and phenyl radical/H$_2$O, we investigated the photochemical reaction of the phenyl radical with water in low-temperature argon matrices. The phenyl radical (**1**) can be produced in high yields by flash vacuum pyrolysis of azobenzene (**5**) at 500 °C and trapping of the products in argon at 10 K (see the Supporting Information for experimental details).[13] The only by-products observed by IR spectroscopy in these matrices are benzene (**2**), formed by hydrogen abstraction from surface contaminants of the pyrolysis oven, and traces of acetylenes and other alkynes formed by ring opening of the phenyl radical at higher temperatures.

When the matrix is doped with 1 % water (Scheme 2), several additional bands, which were absent for matrices containing only the pyrolysis products of **5** or only 1 % water, were observed in the IR spectrum. The intensity of these bands increased when the matrix was annealed at temperatures between 25 and 35 K. At these temperatures, the diffusion of matrix-isolated water becomes rapid, and aggre-



Scheme 2. Synthesis of the phenyl radical (**1**) and its reaction with water.

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gates of water molecules as well as aggregates between water and other trapped molecules are formed.

One set of the new bands was assigned readily to the well-known complex between benzene (**2**) and water.[14] In the **2**$\cdots H_2O$ complex, the strong out-of-plane (oop) deformation mode of **2** at 675.0 cm^{-1} is blue-shifted to 682.0 cm^{-1} (+7.0 cm^{-1}; Figure 1). This shift was taken as evidence for an interaction of the water molecule with the π system of **2**. A second set of new IR bands was observed at 3618.0, 711.4, and 659.8 cm^{-1}. These bands are close to the water OH stretching vibration at 3639.4 cm^{-1}[15] and to two b_1-symmetrical oop deformation vibrations of radical **1** at 705.8 and 657.4 cm^{-1}.[16] The band at 711.4 cm^{-1} is blue-shifted from the band of **1** at 705.8 cm^{-1} by 5.6 cm^{-1}, in the same way as the band of the **2**$\cdots H_2O$ complex at 682.0 cm^{-1} is blue-shifted from the corresponding band of **1**. It was thus tempting to conclude that this new compound was a complex between **1** and water. To confirm this assignment, five isotopomers of the complex, $C_6H_5\cdots H_2O$, $C_6D_5\cdots H_2O$, $C_6H_5\cdots D_2O$, $C_6D_5\cdots D_2O$, and $C_6H_5\cdots H_2{}^{18}O$, were matrix-isolated (Table 1). For all isotopomers, the shifts of the IR bands were very similar to those of the corresponding isotopomers of the benzene–water complex.

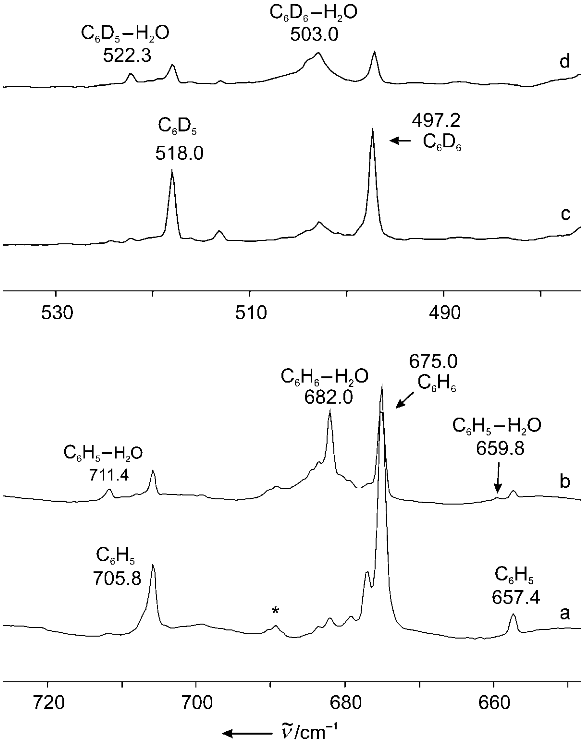

Figure 1. IR spectra showing the formation of a complex between the phenyl radical (**1**) and water in solid argon. a) IR spectrum obtained after trapping the products of the flash vacuum pyrolysis (FVP) of azobenzene (**5**) in argon doped with 1% water at 10 K. b) IR spectrum of the matrix in (a) after warming to 40 K and cooling back down to 10 K. c) IR spectrum after FVP of the perdeuterated $[D_{10}]$**5** as a precursor of $[D_5]$**1** under conditions similar to those for (a). d) IR spectrum of the matrix in (c) after warming to 40 K and cooling back down to 10 K.

Table 1: IR spectroscopic data for the complex between the phenyl radical (**1**) and water. Calculated frequencies (UM05-2X/6-311++G-(2d,2p)) are given in italics underneath the experimental frequencies (argon, 10 K); the frequency shift upon the formation of the complex from the corresponding monomers is given in parenthesis.

	OH stretch	CH oop deform.	CH oop deform.
H_2O[14,15,20]	3639.4		
	3894.2		
D_2O[14,15,20]	2658.8		
	2806.5		
$H_2{}^{18}O$[21]	3630.7		
	3886.1		
C_6H_5[16]		705.8	657.4
		734.0	*681.8*
C_6D_5[16]		518.0	–
		535.3	
$C_6H_5\cdots H_2O$	3618.0 (−21.4)	711.4 (+5.6)	659.8 (+2.4)
	3863.5 (−30.7)	*739.3 (+5.3)*	*682.6 (+0.8)*
$C_6D_5\cdots H_2O$	3618.0 (−21.4)	522.3 (+4.3)	–
	3863.5 (−30.7)	*540.0 (+4.7)*	
$C_6H_5\cdots D_2O$	2645.1 (−13.7)	711.8 (+6.0)	659.8 (+2.4)
	2787.1 (−19.4)	*739.3 (+5.3)*	*682.6 (+0.8)*
$C_6D_5\cdots D_2O$	2645.1 (−13.7)	522.3 (+4.3)	–
	2787.1 (−19.4)	*539.9 (+4.6)*	
$C_6H_5\cdots H_2{}^{18}O$	3610.5 (−20.2)	711.5 (+5.7)	659.5 (+2.1)
	3854.7 (−31.4)	*739.3 (+5.3)*	*682.6 (+0.8)*

The structure, energy of complexation, and IR spectra of several weakly bound complexes between **1** and H_2O were calculated by using the UM05-2X functional[17] with a large 6-311++G(2d,2p) basis set (see the Supporting Information for computational details). Since standard functionals, such as B3LYP, fail to estimate dispersion energies (and thus are not reliable for the calculation of weakly bound complexes, such as **1**$\cdots H_2O$), and CCSD(T) with a large basis set is prohibitively expensive, we used the UM05-2X functional, which was developed for the calculation of van der Waals complexes. The most stable complex, **A** (Scheme 2), is stabilized by an OH⋯π hydrogen bond by −3.77 $kcal\,mol^{-1}$ (Figure 2). This value is in excellent agreement with the binding energy of −3.69 $kcal\,mol^{-1}$ obtained from a single-point coupled-cluster calculation (RHF-UCCSD(T)/6-311++G(2d,2p)//UM05-2X/6-311++G(2d,2p)). After corrections for the zero-point vibrational energy (ZPE) and basis set superposition errors (BSSE), the binding energy of complex **A** is still −2.39 $kcal\,mol^{-1}$, which demonstrates that radical **1** is stabilized considerably by the interaction with water. Other complexes between **1** and water have also been identified, but these complexes are less stable. A comparison of the matrix IR spectrum of the **1**$\cdots H_2O$ complex with that calculated for **A** reveals an excellent agreement and thus confirms the assignment (Table 1).

Complex **A** proved to be photolabile upon irradiation with near-UV light. Irradiation of the matrix for several minutes with light of wavelength $\lambda > 350$ nm resulted in the bleaching of **A** (all three observed IR bands disappeared simultaneously) and the formation of a new compound **B** with IR bands at 3502.2, 1482.8, 1040.3, and 684.2 cm^{-1} (Figure 3, Table 2). Other bands in the spectrum were not affected (for example, the benzene–water complex does not show any

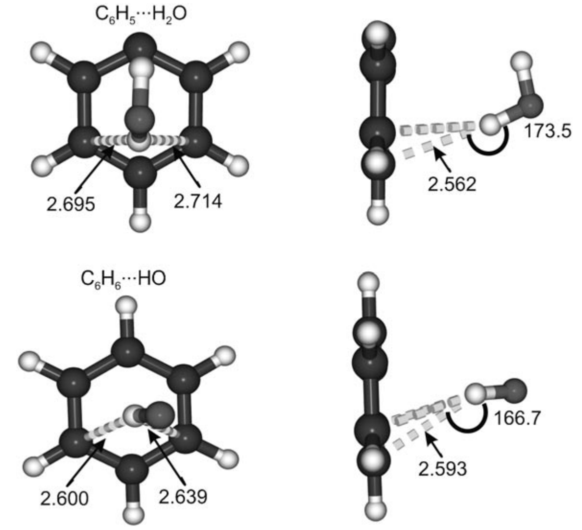

Figure 2. Structures and some geometrical data of the complexes between the phenyl radical and water (top) and benzene and the hydroxyl radical (bottom).

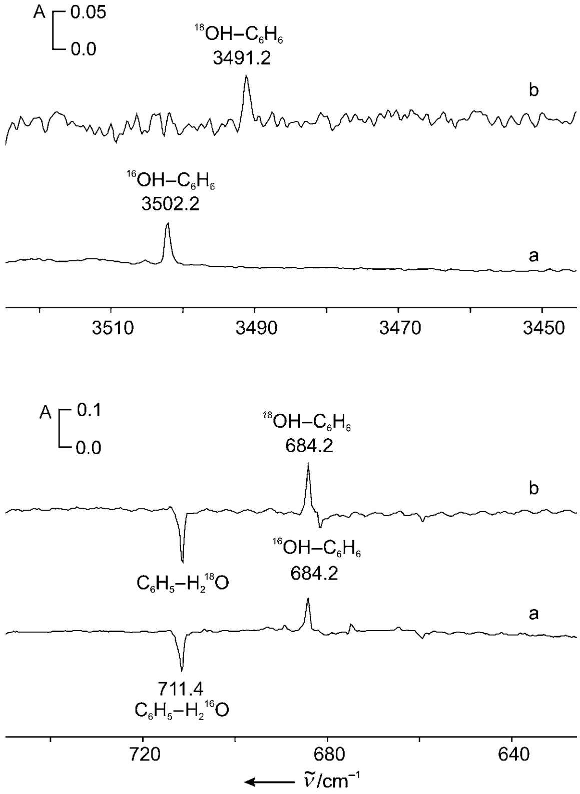

Figure 3. IR difference spectra showing the photochemical transformation of **1**···H_2O into **2**···OH. A = absorbance. a) Bands pointing downwards assigned to **1**···H_2O disappear and bands pointing upwards assigned to **2**···OH appear after irradiation for 5 min with light of wavelength $\lambda > 350$ nm. b) The equivalent experiment with $H_2{}^{18}O$.

photochemistry). The vibrations of **B** at 1482.8, 1040.3, and 684.2 cm^{-1} closely resemble the vibrations of matrix-isolated **2** at 1483.3, 1040.8, and 675.0 cm^{-1}.[14] In compound **B**, the oop deformation mode of benzene is blue-shifted to 684.2 cm^{-1}, in analogy with the blue shift observed for the benzene–water complex.[14] We therefore concluded that **B** was a π complex of benzene. The other two benzene vibrations in **B** showed very small red shifts of less than 1 cm^{-1} with respect to "free" matrix-isolated **2** but could be assigned clearly to **B** and not to free benzene by monitoring the intensity changes during irradiation.

When D_2O was used in the experiments, the ν_4 vibration of benzene (**2**) in **B** showed a very large isotope shift to 614.2 cm^{-1}, as expected for [D$_1$]benzene (Table 2; see also the Supporting Information). The band is blue-shifted by 6.0 cm^{-1} from that observed for matrix-isolated [D$_1$]**2** and thus indicates the formation of a π complex with [D$_1$]**2** as one component. This result demonstrates clearly that radical **1** abstracts a deuterium atom from D_2O to give [D$_1$]**2** during irradiation. What remains from the water molecule is an OD radical (or an OH radical if unlabeled water is used). It was thus tempting to conclude that compound **B** is a weakly bound complex between **2** and the OH radical.

This assignment was corroborated by an analysis of the OH-stretching region of the IR spectrum of **B**. The fourth observed IR absorption of **B** at 3502.2 cm^{-1} is red-shifted by 46 cm^{-1} with respect to the OH stretching vibration of the OH radical at 3548.2 cm^{-1} in solid argon.[18,19] This red shift indicates the formation of a strong hydrogen bond, as expected for **B**. With D_2O instead of H_2O, the vibration at 3502.2 cm^{-1} was red-shifted by 918.8 cm^{-1}, and with $H_2{}^{18}O$ by 11 cm^{-1} (Table 2). These results prove that this band is indeed due to an OH stretching vibration. The presence of other OH-

Table 2: IR spectroscopic data for the complex between benzene (**2**) and the hydroxyl radical. Calculated frequencies (UM05-2X/6-311++G(2d,2p)) are given in italics underneath the experimental frequencies (argon, 10 K); the frequency shift upon the formation of the complex from the corresponding monomers is given in parenthesis.

	OH stretch	ring deform.	ring deform.	CH oop deform.
OH[18,22]	3548.2			
	3803.6			
OD[18,22]	2616.1			
^{18}OH[18,22]	3537.1			
C_6H_6[16]		1483.3	1040.8	675.0
		1546.3	*1081.1*	*698.0*
C_6D_6[16]		1334.7	816.3	497.2
C_6H_5D[16]		1480.2	1036.9	608.2
$C_6H_6\cdots OH$	3502.2 (−46)	1482.8 (−0.5)	1040.3 (−0.5)	684.2 (+9.2)
	3759.5 (−44.1)	*1545.0 (−1.3)*	*1080.1 (−1.0)*	*711.7 (+13.7)*
$C_6HD_5\cdots OH$	3502.2 (−46)	–	–	–
$C_6H_5D\cdots OD$	2583.4 (−32.7)	–	–	614.2 (+6.0)
$C_6D_6\cdots OD$	2583.4 (−32.7)	–	–	504.6 (+7.4)
$C_6H_6\cdots{}^{18}OH$	3491.2 (−45.9)	1482.7 (−0.6)	1040.9 (+0.1)	684.2 (+9.2)

containing compounds, such as water or phenol, can be excluded by comparison of their known matrix IR spectra with the matrix IR spectrum of **B**.

The observation that the ^{18}O isotopic shift of the OH radical in **B** of $-11\ \text{cm}^{-1}$ is identical to that of the matrix-isolated OH radical and markedly different from that of H_2O serves as additional evidence that **B** is a complex of the OH radical. Finally, the calculated IR spectrum of the **2**···OH π complex is in excellent agreement with the matrix IR spectrum of **B** (Table 2). In particular, the predicted shifts of the IR bands of the OH and benzene fragments match the experimental values almost perfectly.

The crucial question remains as to why a complex between benzene **2** and the OH radical is observed at all: Why does this complex not immediately react further to give radical **3** (pathway II, Scheme 1)? The activation barriers for this reaction have been predicted at the B3LYP level of theory by Tokmakov and Lin[7] using a 6-311++G(d,p) basis set to be absent (to $-0.8\ \text{kcal mol}^{-1}$) and by Hadad and Platz et al.[8] with a smaller basis set (6-311+G(d,p)) to $1.22\ \text{kcal mol}^{-1}$. G3 theory gave a barrier of $2.8\ \text{kcal mol}^{-1}$,[7] which is still very low, even under the conditions of matrix isolation in cryogenic matrices.

However, the barrier is considerably higher if OH and benzene form a stabilized prereactive complex. The stabilization energy of such a prereactive complex had been calculated by Tokmakov and Lin[7] to be -1.8 and $-2.6\ \text{kcal mol}^{-1}$ at the B3LYP/6-311++G(d,p) and G3 level of theory, respectively. The complex was found to be very flexible with respect to movements of the OH molecule across the benzene π system. At the UM05-2X/6-311++G(2d,2p) level of theory we found a stabilization energy of $-4.71\ \text{kcal mol}^{-1}$ for complex **B**. As expected, this value is considerably larger than the stabilization calculated with the B3LYP functional. This stabilization increases the barrier to the addition reaction and thus enables the isolation of the OH complex in the matrix. It is also interesting to note that complex **B** is slightly more stable than complex **A**. As a result, the endothermicity of hydrogen-atom transfer from water to the phenyl radical is decreased.

In summary, we have isolated and characterized complexes between the phenyl radical and water and between the hydroxyl radical and benzene for the first time. We observed light-driven hydrogen-atom transfer from water to the phenyl radical within these complexes. Our results demonstrate the importance of radical complexes for the radical reactivity. We expect that this phenomenon is also of importance for the understanding of radical reactions in biological media.

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[1] T. Seta, M. Nakajima, A. Miyoshi, *J. Phys. Chem. A* **2006**, *110*, 5081–5090.
[2] B. Bohn, C. Zetzsch, *Phys. Chem. Chem. Phys.* **1999**, *1*, 5097–5107.
[3] R. Volkamer, B. Klotz, I. Barnes, T. Imamura, K. Wirtz, N. Washida, K. H. Becker, U. Platt, *Phys. Chem. Chem. Phys.* **2002**, *4*, 1598–1610.
[4] C.-C. Chen, J. W. Bozzelli, J. T. Farrell, *J. Phys. Chem. A* **2004**, *108*, 4632–4652.
[5] S. Raoult, M.-T. Rayez, J.-C. Rayez, R. Lesclaux, *Phys. Chem. Chem. Phys.* **2004**, *6*, 2245–2253.
[6] J. S. Poole, X. Shi, C. M. Hadad, M. S. Platz, *J. Phys. Chem. A* **2005**, *109*, 2547–2551.
[7] I. V. Tokmakov, M. C. Lin, *J. Phys. Chem. A* **2002**, *106*, 11309–11326.
[8] M. P. DeMatteo, J. S. Poole, X. Shi, R. Sachdeva, P. G. Hatcher, C. M. Hadad, M. S. Platz, *J. Am. Chem. Soc.* **2005**, *127*, 7094–7109.
[9] R. Crespo-Otero, E. Sanchez-Garcia, R. Suardiaz, L. A. Montero, W. Sander, *Chem. Phys.* **2008**, *353*, 193–201.
[10] A. Mardyukov, E. Sanchez-Garcia, P. Rodziewicz, N. L. Doltsinis, W. Sander, *J. Phys. Chem. A* **2007**, *111*, 10552–10561.
[11] E. Sánchez-García, A. Mardyukov, A. Tekin, R. Crespo-Otero, L. A. Montero, W. Sander, G. Jansen, *Chem. Phys.* **2008**, *343*, 168–185.
[12] S. J. Blanksby, G. B. Ellison, *Acc. Chem. Res.* **2003**, *36*, 255–263.
[13] A. Mardyukov, W. Sander, *Chem. Eur. J.* **2009**, *15*, 1462–1467.
[14] A. Engdahl, B. Nelander, *J. Phys. Chem.* **1985**, *89*, 2860–2864.
[15] G. P. Ayers, A. D. E. Pullin, *Spectrochim. Acta Part A* **1976**, *32*, 1629–1639.
[16] A. V. Friderichsen, J. G. Radziszewski, M. R. Nimlos, P. R. Winter, D. C. Dayton, D. E. David, G. B. Ellison, *J. Am. Chem. Soc.* **2001**, *123*, 1977–1988.
[17] Y. Zhao, D. G. Truhlar, *Acc. Chem. Res.* **2008**, *41*, 157–167.
[18] B. M. Cheng, Y. P. Lee, J. F. Ogilvie, *Chem. Phys. Lett.* **1988**, *151*, 109–115.
[19] A. Engdahl, G. Karlstrom, B. Nelander, *J. Chem. Phys.* **2003**, *118*, 7797–7802.
[20] G. P. Ayers, A. D. E. Pullin, *Spectrochim. Acta Part A* **1976**, *32*, 1641–1650.
[21] G. P. Ayers, A. D. E. Pullin, *Spectrochim. Acta Part A* **1976**, *32*, 1689–1693.
[22] A. Engdahl, B. Nelander, *J. Chem. Phys.* **2005**, *122*, 126101.