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Matrix Isolation and Spectroscopic Characterization of the Phenylperoxy Radical and Its Rearranged Products

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Abstract: The phenylperoxy radical **1** has been synthesized by the reaction of the phenyl radical **2** with ${}^{3}O_{2}$. Radical **1** could be either generated in the gas phase and subsequently trapped in solid argon at 10 K, or directly synthesized in argon matrices. By reacting **2** as well as its perdeuterated isotopomer $[D_{5}]$ -**2** with ${}^{16}O_{2}$ and with ${}^{18}O_{2}$, respectively, the four isotopomers $[H_{3}]$ - ${}^{16}O_{2}$ -**1**,

$[D_5]^{-16}O_2$ -1, $[H_5]^{-18}O_2$ -1, and $[D_5]^{-18}O_2$ -1 were matrix-isolated and characterized by IR spectroscopy. The experimental IR spectra are in excellent agreement with results from DFT calculations. Ir-

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radiation of **1** with visible light produces the 2-oxepinoxy radical **5** in a clean reaction. Subsequent irradiation results in ring-opening and formation of several conformers of ketoketene **6**. The radicals **1**, **5**, and **6** play an important role in the combustion of aromatic hydrocarbons and could now be isolated and spectroscopically characterized for the first time.

Introduction

The phenylperoxy radical 1 is the primary product of the reaction of the phenyl radical 2 with molecular oxygen. This reaction is considered to be of key importance in the combustion of aromatic hydrocarbons^[1,2] and in the degradation of benzene in the troposphere.^[3,4] Due to the high CH bond dissociation energy of 113 kcalmol⁻¹ in benzene,^[5] the phenyl radical 2 is one of the most reactive organic radicals, and the reaction of 2 with molecular oxygen to give the peroxy radical $\mathbf{1}$ is exothermic by 46.3 kcalmol⁻¹ according to ab initio G2M calculations.^[6] This highly exothermic primary step of the oxidation of 2 is followed by a complex sequence of secondary reactions.^[6,7] The kinetics of the 2 +³O₂ reaction has been studied with the cavity-ring-down method by measuring the appearance of $\mathbf{1}$,^[8] and from these data a small negative activation barrier of -0.32 kcalmol⁻¹ was determined. Variational transition state theory reveals that the reaction of 2 with ${}^{3}O_{2}$ is barrierless,^[9] and thus the

reaction rate should be at the diffusion limit. At very high temperatures the main fate of **1** is to lose an oxygen atom $O(^{3}P)$ and form the phenoxyl radical **3**, which is still an exothermic reaction. The phenoxyl radical subsequently eliminates CO to yield the cyclopentadienyl radical $C_{5}H_{5}$. In cross-beam reactions between **2** and $^{3}O_{2}$ an oxygen atom is abstracted from molecular oxygen to produce **3** and $O(^{3}P)$ atoms.^[10] Under these conditions the phenyl peroxy radical **1** is an extremely short-lived intermediate with lifetimes below 10 fs.

Despite its importance in various processes the phenyl peroxy radical **1** has not yet been isolated or characterized spectroscopically. By cavity-ring-down spectroscopy a very weak and broad, structureless absorption in the visible region between 495 and 525 nm was found which could be used for kinetic measurements but which is not suitable for the spectroscopic identification of 1.^[4,9] In aqueous solution, a broad peak with a maximum at 490 nm has been assigned to 1.^[11,12] According to DFT calculations the transitions of **1** in the visible region of the spectrum are due to intramolecular charge transfer and thus very sensitive to the solvent polarity.^[12]

In contrast to **1**, the phenyl radical **2** has been trapped in inert gas matrices and characterized spectroscopically in great detail.^[13–16] Basically, two methods can be used for the matrix isolation of **2**: the photodissociation of a matrix-isolated precursor or flash vacuum pyrolysis (FVP) of a precursor with subsequent trapping of the products in low temperature matrices. To investigate the thermal reaction of **2** with



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Supporting information (IR spectra of deuterated 1 and its photoproducts and tables with Z-matrices and energies of 1, 5, and three conformers of 6) for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200801546.

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 ${}^{3}O_{2}$ in low temperature matrices, the matrix has to be annealed at approximately two-thirds of its melting point to allow the diffusion of the trapped oxygen molecules. Since the matrix photodissociation necessarily produces radical pairs trapped in the same matrix cage, the subsequent annealing of these matrices results in unwanted radical recombination instead of reactions with other trapped molecules (e. g. oxygen) in most cases. FVP with subsequent trapping in matrices, on the other hand, produces radicals in individual matrix cages. Now the reaction with oxygen molecules can efficiently compete with radical recombination.

Here, we report the matrix isolation and IR spectroscopic characterization of the phenyl peroxy radical **1** and several of its isotopomers. In addition, a second important isomer, the 2-oxepinoxy radical **5**, could also be characterized.

Results and Discussion

Various precursors, such as nitrosobenzene, iodobenzene, benzoyl peroxide, or benzoic anhydride, have been used as precursors for the matrix isolation of $2^{[13,17]}$ In our experiments we use azobenzene (4) as a new thermal precursor of 2. FVP of 4 at temperatures between 600 and 700 °C with subsequent trapping with a large excess of argon at 10 K produces 2 in good yields (Scheme 1). By-products found in these matrices are nitrogen (invisible in the IR), benzene (formed via hydrogen abstractions from 2), and traces of acetylene (product of the thermal fragmentation of 2). The phenyl radical 2 was characterized by comparison of its matrix infrared spectrum with literature data.^[13,17] FVP of perdeuterated azobenzene [D₁₀]-4 results in the formation of [D₅]-2, again its IR spectrum is in good agreement with the data reported in literature.

To synthesize the oxygen trapping products of **2**, the argon was doped with 2% O₂. FVP of **4** in O₂-doped argon again resulted in the formation of **2**, benzene, and acetylene. In addition, new strong to medium IR absorptions are found at 1481.2, 1463.9, 905.1, 751.9, and 679.2 cm⁻¹ (Figure 1, Table 1). If ${}^{18}O_2$ is used in the FVP, these bands show only very small isotopic shifts of less than 1 cm⁻¹. However, a



Scheme 1. Reaction of the phenyl radical 2 with molecular oxygen.

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weaker band at 1122.9 cm^{-1} shows a huge redshift of -67.2 cm^{-1} which clearly indicates a OO stretching vibration. Other large redshifts are found for a weak absorption at 793.9 cm⁻¹ (-15.6 cm⁻¹) assigned to a CO stretching vibration and at 607.2 cm⁻¹ (-11.8 cm⁻¹) assigned to a COO deformation mode. A comparison of the newly formed bands in O₂-doped matrices with the results of DFT calculations (UB3LYP/cc-pVTZ) of the phenylperoxy radical **1** shows an excellent agreement. The two perdeuterated isotopomers [D₅]-**1** and [D₅]-¹⁸O₂-**1** were also synthesized and a careful analysis of their spectra confirms the assignment of the phenylperoxy radical (Figure 2, Table 1). These experiments clearly show that the phenyl radical **2** reacts with molecular oxygen in the gas phase to produce **1**. The phenoxyl radical **3** was not observed under these conditions.

The matrix produced after FVP of 4 in 2% O₂-doped argon followed by trapping of the products at 10 K contains both the phenylperoxy radical 1 and the phenyl radical 2. At 10 K the matrix is very rigid and does not permit the diffusion of oxygen. However, annealing at 30-35 K results in the rapid diffusion of oxygen, which allows one to investigate the thermal reaction of 2 with ${}^{3}O_{2}$ under the conditions of matrix isolation (see Figure 1S in the Supporting Information). The reaction of triplet carbenes with ${}^{3}O_{2}$ had been investigated previously in a similar way.^[18-20] Theses reactions proceed within several minutes and can be directly monitored by IR spectroscopy. Warming a matrix containing 2 and excess ${}^{3}O_{2}$ from 10 K to 35 K results in a rapid decrease of 2 and the concurrent formation of 1. The formation of 1 in a thermal reaction at temperatures as low as 30 K indicates a very small or no activation barrier for this reaction, in accordance with theoretical predictions.^[9]

Matrices containing **1** show a slight orange color caused by a broad absorption with a maximum around 480 nm. This finding is in accordance with the broad band in the visible region observed in cavity-ring-down experiments.^[8] Irradiation of this band (argon, 10 K, $\lambda > 400$ nm) rapidly results in the disappearance of all bands assigned to **1** and formation of a new set of bands (Figure 3). The strongest IR band of the new compound at 1726.9 cm⁻¹ shows a strong ¹⁸O isotope shift of -30.7 cm⁻¹ and is thus assigned to a C=O

stretching vibration (Table 2, see Figure 2S in the Supporting Other Information). strong bands are found at 1307.9, 1095.8, and 724.9 cm⁻¹. The IR spectra of a number of isomers of 1 were calculated by using DFT, and an excellent agreement was found for the 2-oxepinoxy radical 5. The IR frequencies, intensities, and isotopic shifts of all four isotopomers closely match the calculated data.

The rearrangement of **1** to **5** is obviously a multistep reac-

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Figure 1. IR spectra showing the products of the FVP of **4** in 2% O_2 -doped argon with subsequent trapping at 10 K. a) Spectrum obtained after FVP with ${}^{16}O_2$. b) Spectrum of **1** calculated at the UB3LYP/cc-pVTZ level of theory. c) Spectrum obtained after FVP with ${}^{18}O_2$. d) Spectrum of ${}^{18}O_2$ -1 calculated at the UB3LYP/cc-pVTZ level of theory. Bands of remaining precursor **4** are marked *, bands of the phenyl radical **2** are marked \square and bands of benzene are marked \bigcirc .

Table 1. IR spectroscopic data of four isotopomers of the phenyl peroxy radical 1.

Mode ^[a]	C ₆ H ₅ ¹⁶ O ¹⁶ O (1)		$C_6H_5^{18}O^{18}O^{(18}O_2-1)$		$C_6 D_5^{16} O^{16} O([D_5]-1)$		$C_6 D_5^{18} O^{18} O([D_5]^{-18} O_2^{-1})$		Sym.	Assignment
	argon ^[b]	DFT ^[c]	argon ^[b]	DFT ^c	argon ^[b]	DFT ^[c]	argon ^[b]	DFT ^[c]	2	U
33	3118.7	3227.7 (3)	3117.9	3227.7 (3)	-	2387.7 (3)	_	2387.7 (3)	A′	C ² –H str.
32	3189.1	3201.9 (8)	3187.2	3201.9 (8)	2318.9	2372.8 (15)	-	2372.8 (15)	\mathbf{A}'	C ^{4,5,6} –H str.
31	3089.3	3193.8 (18)	3086.9	3193.8 (18)	-	2362.5 (19)	_	2362.5 (19)	\mathbf{A}'	C ^{3,4,6} –H str.
30	3070.8	3183.4 (15)	3070.5	3183.4 (15)	2285.4	2351.2 (19)	_	2351.2 (19)	\mathbf{A}'	C ^{3,5} –H str.
28	_	1643.9 (5)	-	1643.4 (5)	1583.4 (9)	1612.2 (3)	1582.4 (9)	1611.7 (3)	\mathbf{A}'	CCC str. as.
26	1481.2 (52)	1514.2 (27)	1480.8 (55)	1513.9 (27)	1355.5 (17)	1384.1 (11)	1353.2 (30)	1382.4 (15)	\mathbf{A}'	C ^{2,3,4,5} –H def.
25	1463.9 (12)	1498.6 (8)	1462.7 (10)	1498.1 (8)	1347.6 (32)	1376.0 (23)	1346.5 (37)	1375.7 (23)	\mathbf{A}'	C ^{4,5} –H def.
23	1313.1 (3)	1345.6 (1)	1312.4 (2)	1344.6 (1)	1297.7 (7)	1336.8 (3)	1297.0 (7)	1336.6 (2)	\mathbf{A}'	$C^{3,5}$ –H def./ ν str.
20	1122.9 (8)	1175.1 (8)	1055.7 (8)	1108.1 (5)	1126.0 (8)	1178.3 (11)	1068.1 (14)	1114.6 (7)	\mathbf{A}'	O–O str.
19	-	1129.2 (0)	1109.6 (3)	1130.2 (5)	-	1112.8 (3)	1007.6 (3)	1106.2 (7)	\mathbf{A}'	$C^{1}-O^{7}$ str/ $C^{2,6}$ -H def.
18	1067.7 (4)	1098.1 (8)	1071.1 (2)	1096.1 (3)	814.5 (9)	830.6 (11)	813.1 (18)	829.6 (11)	\mathbf{A}'	C ^{2,4,6} –H def.
17	1018.5 (9)	1040.9 (5)	1017.3 (4)	1040.5 (5)	809.4 (9)	824.0 (11)	807.6 (14)	822.5 (7)	\mathbf{A}'	C ^{2,3,5,6} –H def.
13	905.1 (12)	940.5 (10)	904.9 (14)	940.4 (10)	754.3 (21)	783.8 (15)	753.8 (26)	783.6 (15)	$A^{\prime\prime}$	C ^{2,4,6} –H wag.
11	793.9 (2)	807.9 (1)	778.3 (2)	792.3 (1)	-	761.6 (3)	-	748.6 (3)	\mathbf{A}'	C^1 – O^7 str/ $C^3C^4C^5$ def.
10	751.9 (100)	777.3 (98)	751.3 (100)	777.1 (98)	624.3 (20)	642.7 (26)	624.4 (21)	642.6 (23)	$A^{\prime\prime}$	C ^{2,3,4,5,6} -H wag.
9	679.2 (22)	702.9 (38)	679.2 (24)	702.9 (38)	547.3 (100)	562.4 (96)	547.0 (100)	562.1 (100)	$A^{\prime\prime}$	C ^{2,4,6} -H wag.
8	615.1 (9)	628.5 (3)	_	626.7 (0)	595.0 (28)	608.0 (19)	572.3 (20)	586.6 (19)	\mathbf{A}'	ring def. in plane
7	607.2 (5)	621.8 (8)	595.4 (3)	604.8 (10)	582.1 (11)	597.9 (7)	-	423.1 (3)	\mathbf{A}'	$C^1O^7O^8$ def.
6	480.8 (7)	499.3 (10)	479.7 (8)	498.4 (10)	429.3 (37)	433.8 (42)	429.5 (30)	433.2 (42)	$A^{\prime\prime}$	ring def. out of plane

[a] Mode numbers based on the $C_6H_5^{16}O^{16}O$ isotopomer. [b] Argon matrix at 10 K. Wavenumbers in cm⁻¹, relative intensities in parenthesis. [c] Calculated at the UB3LYP/cc-pVTZ level of theory.

tion. The formation of a spirodioxiranyl radical from 1 as an intermediate which rearranges to 5 via a dioxy triradical has been shown by computations to be a feasible mechanism.^[2,21,22] These and other proposed intermediates of the rearrangement are expected to be highly labile and are not observed during the photolysis of 1. According to DFT cal-

culations by Merle and Hadad the addition of a further molecule of oxygen at one of the three possible positions is endothermic by $9-13 \text{ kcal mol}^{-1}$ with activation barriers of 17- 18 kcal mol^{-1} . Thus, a further addition of molecular oxygen to **5** is not expected under the conditions of matrix isolation.

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Figure 2. IR spectra showing the products of the FVP of $[D_5]$ -4 in 2% O₂-doped argon with subsequent trapping at 10 K. a) Spectrum obtained after FVP with ${}^{16}O_2$. b) Spectrum of $[d_5]$ -1 calculated at the UB3LYP/cc-pVTZ level of theory. c) Spectrum obtained after FVP with ${}^{16}O_2$. d) Spectrum of $[D_5]$ -1 calculated at the UB3LYP/cc-pVTZ level of theory. c) Spectrum obtained after FVP with ${}^{16}O_2$. d) Spectrum of $[D_5]$ -1 calculated at the UB3LYP/cc-pVTZ level of theory. c) Spectrum obtained after FVP with ${}^{16}O_2$. d) Spectrum of $[D_5]$ -1 calculated at the UB3LYP/cc-pVTZ level of theory. Bands of remaining precursor 4 are marked *, bands of the phenyl radical 2 are marked \Box and bands of benzene are marked \odot .



Figure 3. Difference IR spectra showing the photochemistry ($\lambda > 400$ nm) of 1, matrix-isolated in argon at 10 K. Bands pointing downwards are disappearing during irradiation and assigned to 1. Bands pointing upwards are appearing and assigned to 5. a) IR spectrum of 1 calculated at the UB3LYP/cc-pVTZ level of theory. b) Difference IR spectrum of the ¹⁶O₂ isotopomer. c) IR spectrum of 5 calculated at the UB3LYP/cc-pVTZ level of theory.

Prolonged irradiation of matrix-isolated **5** at 10 K with visible light ($\lambda > 400$ nm) results in the complete photolysis of **5** and formation of a new compound with intense IR absorptions in the region between 2150–2050 cm⁻¹ and 1650–1600 cm⁻¹ (see Figure 4S and 5S, and Table 7S in the Supporting Information). The bands in both regions show con-

siderable ¹⁸O-isotopic shifts, which suggests ketene groups for the bands between 2150–2050 cm⁻¹ and enones for the bands between 1650–1600 cm⁻¹. Since some of these bands grow at different rates during the photolysis, we assume that a mixture of at least two compounds is formed. It is therefore tempting to assign ketoketene 6 and its conformers and configurational isomers to the photoproduct of 5. However, since the IR spectra calculated for various geometrical isomers of 6 are very similar, an assignment to one of the isomers was not possible. In a study by Fadden and Hadad for the ring-opening of 5 to ketoketene 6 a thermal activation barrier of 23.4 kcal mol⁻¹ was calculated,^[23] while two other rearrangements of 5 were found to proceed via considerably higher activation barriers. Our experiments do not allow us to determine if the ring-opening is a photochemical or a hot ground state reaction. Regardless of this, the product observed is that which is formed with the lowest predicted activation barrier.

Conclusion

The phenyl radical 2 rapidly reacts with molecular oxygen to produce the phenoxylperoxy radical 1 both in the gas phase and in argon matrices. Phenoxyl radical 3 is not formed under these conditions. This indicates that the activation barrier for the oxygen addition to 2 is very low and that, despite the high exothermicity of this reaction, the pri-

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Table 2. IR spectroscopic data of four isotopomers of the 2-oxepinoxy radical 5.

Mode ^[a]	C ₆ H ₅ ¹⁶ O ¹⁶ O (5)		C ₆ H ₅ ¹⁸ O ¹⁸ O (¹⁸ O ₂ -5)		$C_6 D_5^{16} O^{16} O([D_5]-5)$		$C_6 D_5^{18} O^{18} O ([D_5]^{-18} O_2^{-5})$		Sym.	Assignment
	argon ^[b]	DFT ^c	argon ^[b]	DFT ^c	argon ^[b]	DFT ^[c]	argon ^[b]	DFT ^[c]	•	-
28	1726.9 (100)	1790.0 (99)	1696.2 (100)	1754.4 (99)	1724.8 (100)	1787.7 (99)	1691.7 (100)	1751.4 (99)	А	C=O str.
27	1575.8 (13)	1609.2 (14)	1574.8 (16)	1609.2 (14)	1533.3 (16)	1564.5 (16)	1531.3 (23)	1563.0 (17)	А	C ⁵ C ⁶ str
26	1515.8 (5)	1553.6 (3)	1514.6 (1)	1552.1 (2)	1443.8 (12)	1472.9 (15)	1438.1 (26)	1467.0 (13)	А	C ² C ³ str
25	1429.7 (1)	1472.6 (2)	1428.3 (2)	1471.3 (3)	1361.6 (6)	1408.1 (4)	1360.7 (10)	1407.9 (4)	А	$C^{2,3}$ –H def./ C^{3} – C^{4} str.
24	1415.8 (1)	1447.4 (1)	-	1446.6 (0)	1228.1 (10)	1255.5 (4)	1222.2 (8)	1249.9 (3)	А	C ^{5,6} –H def./ring str.
23	1375.8 (9)	1412.8 (8)	1375.4 (5)	1410.5 (6)	1177.2 (9)	1193.6 (7)	1167.4 (13)	1186.3 (6)	А	C ^{2,3,4} –H def./C ¹ C ² str.
22	1307.9 (18)	1339.6 (13)	1297.2 (15)	1329.8 (12)	1092.6 (33)	1079.2 (10)	1070.2 (52)	1057.5 (10)	А	$C^{5,6}$ –H def./ C^1O^8 str.
21	1235.5 (2)	1259.2 (1)	1234.2 (2)	1259.2 (1)	1010.1 (6)	1015.8 (5)	1009.7 (15)	1014.4 (5)	А	C ^{2,3} –H def.
20	1177.4 (2)	1208.5 (1)	_	1206.1 (1)	_	909.9 (0)	_	905.1 (0)	А	C ^{4,5} –H def.
19	1095.8 (25)	1083.9 (14)	1083.4 (10)	1072.5 (13)	-	944.7 (0)	-	944.2 (0)	А	C ¹ O ⁸ str./C ^{4,5} –H def.
18	1029.6 (7)	1048.7 (4)	1016.7 (3)	1039.1 (5)	_	867.9 (0)	_	862.4 (0)	А	ring str.
17	-	1002.0 (0)	-	1001.9 (0)	-	809.6 (0)	-	809.5 (0)	А	C ^{2,3,4} -H wag.
16	_	953.6 (0)	_	952.4 (0)	837.2 (4)	849.9 (2)	836.8 (7)	848.4 (2)	А	ring str.
15	_	950.0 (0)	_	950.0 (0)	760.2 (3)	769.5 (2)	_	768.3 (1)	А	C ^{5,6} –H wag.
14	888.5 (6)	887.9 (2)	881.3 (8)	879.0 (3)	-	815.8 (0)	-	813.1 (0)	А	ring str.
13	833.4 (3)	860.5 (3)	832.5 (6)	860.1 (3)	748.5 (6)	764.2 (3)	746.4 (6)	762.1 (4)	А	ring str./C ^{2,4,6} -H wag.
12	797.9(2)	805.7 (1)	796.3 (1)	804.1 (1)	-	671.1 (0)	-	670.1 (0)	А	C ^{2,3,4,5,6} -H wag
11	-	805.6 (2)	784.0 (4)	789.7 (2)	_	768.4 (3)	_	755.9 (1)	А	C ² C ¹ O ⁸ def
10	724.9 (19)	746.2 (11)	723.9 (22)	745.1 (12)	584.6 (3)	600.3 (1)	584.4 (6)	599.8 (1)	А	C4.5,6-H wag
9	694.2 (4)	687.5 (5)		671.6 (5)	669.8 (5)	657.7 (4)	659.2 (7)	643.0 (4)	А	C ¹ O ⁸ str
8	623.9 (5)	644.3 (3)	621.7 (5)	642.1 (3)	_	507.4 (2)	_	505.4 (2)	А	C ^{2,3,4,5} -H wag
7	527.8 (2)	550.6 (1)	_	549.4 (0)	450.9 (5)	468.5 (2)	450.6 (7)	468.2 (2)	А	ring def. out of plane
6	-	513.4 (0)	-	497.7 (0)	-	498.5 (0)	-	483.4 (0)	А	C^1O^7 def.

[a] Mode numbers based on the $C_6H_5^{16}O^{16}O$ isotopomer. [b] Argon matrix at 10 K. Wavenumbers in cm⁻¹, relative intensities in parenthesis. [c] Calculated at the UB3LYP/cc-pVTZ level of theory.

mary product 1 can efficiently dissipate the excess energy without fragmentation. Loss of oxygen from 1 obviously requires a higher thermal excitation in high-temperature processes or in cross-beam experiments. This is of relevance to tropospheric chemistry, since the phenyl radical 2 can be produced in the troposphere from benzene via H-abstraction by OH radicals. The phenyl radical 2 will be efficiently quenched by oxygen to form peroxy radical 1. Under these conditions it is not expected that 1 cleaves to phenoxyl radical **3** and $O(^{3}P)$. Formation of triplet oxygen atoms would regenerate ozone and subsequently OH radicals. The photochemical rearrangement of 1 by visible light produces another intermediate of importance in the oxidation of benzene: the 2-oxepinoxy radical 5. This radical was also characterized by IR spectroscopy. Further irradiation finally leads to the cleavage of the ring and formation of a mixture of several conformers of ketoketene 6. Our experiments do not allow us to determine if the photochemical steps which lead to 5 and 6 proceed on an excited surface or if these reactions are hot ground state reactions. Nevertheless, the products found in the matrix are the products that have been predicted by ab initio and DFT calculations to be formed with the smallest activation barriers. These products are thus also relevant for the thermal combustion of benzene.

Experimental Section

Azobenzene and $[D_{10}]$ azobenzene: Azobenzene 4 (Acros Organics 99.8%) was used without further purification. The perdeuterated azobenzene $[D_{10}]$ -4 was synthesized according to a literature procedure.^[24]

¹³C NMR (50.33 MHz, CDCI₃, 25 °C, TMS): $\delta_{\rm C}$ =152.99, 78.06, 77.43, 76.79 ppm; MS (RI, 70 eV): (*m*/*z*, %): 192 [*M*⁺], 110, 82, 54, 45.

Matrix isolation: Matrix isolation experiments were performed by standard techniques^[25] using a closed-cycle helium cryostat and a CsI spectroscopic window cooled to 10 K. FTIR spectra were recorded with a standard resolution of 0.5 cm⁻¹, using a N₂(1)-cooled MCT detector in the range 400–4000 cm⁻¹. UV spectra were recorded in the spectroscopic range 800 to 200 nm with a standard resolution of 0.02 nm, using a Varian UV/Vis NIR spectrophotometer from a sample deposited on a sapphire window cooled to 10 K by a closed cycle cryostat. Flash vacuum pyrolysis (FVP) was carried out by slowly subliming azobenzene **4** through a 7 cm quartz tube heated electrically with a tantalum wire. Broadband irradiation was carried out with mercury high-pressure arc lamps in housings equipped with quartz optics and dichroic mirrors in combination with cutoff filters (50% transmission at the wavelength specified).

Computational methods: Optimized geometries and vibrational frequencies of all species were calculated at the UB3LYP^[26–28] level of theory using the 6–311+G(d,p) polarized valence-triple- basis set^[29,30] and Dunning's cc-pVTZ^[31–33] basis sets. All DFT calculations were carried out with Gaussian 03.^[34]

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