Isolation of the Phenyl Cation in a Solid Argon Matrix[**]

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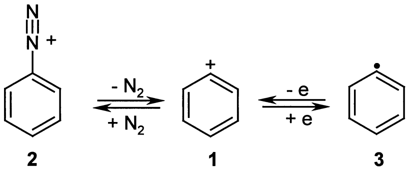
The phenyl cation (**1**) is of fundamental importance to organic chemistry and one of the most reactive molecules known.[1] Its existence as a reaction intermediate was postulated more than fifty years ago by Waters.[2] Since that time, a large number of reports dealing with the chemistry of **1** in solution,[3] the physical properties of **1** in the gas phase,[4] and theoretical descriptions of the electronic structure[5–7] of **1** have appeared in the literature. Evidence that **1** is indeed formed as a transient species in solution stems from $^{14}N_2/^{15}N_2$ exchange experiments with the benzene diazonium ion (**2**) and from kinetic measurements of the dediazoniation of **2** [Eq. (1)].[8]

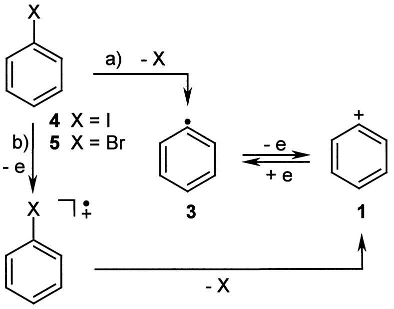


(1)

Owing to its extreme electrophilicity and reactivity, **1** is very short-lived in the condensed phase, and, in contrast to the phenyl radical (**3**),[9] has never been isolated or characterized spectroscopically. Neither NMR investigations in magic acid[10] nor time-resolved spectroscopy[11] made a direct observation of the phenyl cation possible. Although mass spectrometry and ICR spectroscopy provided some insight into the gas-phase reactivity of **1**,[12] no detailed conclusions concerning structural features and electronic properties can be drawn from these experiments. Especially the ground-state multiplicity of **1** and the gap between the lowest singlet ($^1A_1$) and triplet state ($^3B_1$) has been subject to some debate.[1, 5–7] From the analysis of the photoelectron spectrum of **3** it was concluded that the singlet state is 31 kJ mol^{-1} lower in energy than the triplet state.[13] Recent ab initio calculations predict a larger singlet–triplet gap of 75–80 kJ mol^{-1} [6] or even 103 kJ mol^{-1}.[7]

The technique of isolation in low-temperature noble gas matrices has proven to be a viable method for the characterization of highly reactive neutral species such as carbenes and radicals. In a series of papers Andrews et al. reported on the matrix isolation of cations produced by photoionization of neutral precursors with the short-wavelength light from a noble gas discharge source.[14, 15] In these experiments the major tool for the identification of the cations was UV/Vis spectroscopy. Here we describe the matrix isolation and first IR spectroscopic characterization of the elusive phenyl cation (**1**), generated by vacuum UV photolysis of iodobenzene (**4**) and bromobenzene (**5**).

The C–I bond dissociation energy for **4** is 2.8 eV (274 kJ mol^{-1}),[16] and irradiation at 254 nm (corresponding to 473 kJ mol^{-1}) of **4**, matrix isolated in argon at 8 K, readily produces the phenyl radical (**3**) in high yield [Eq. (2)]. The product was identified by comparison with literature data.[9] The vertical ionization potential of **3** is 9.0 ± 0.2 eV[6, 7] and that of **4** is 8.7 eV.[17] Thus the light emitted from an argon resonance source (105–107 nm $\hat{=}$ 11.6–11.8 eV)[15] should be sufficiently energetic to ionize both species and in addition cause the C–I bond in **4** to break.[18]



(2)

In a typical experiment, **4** was slowly sublimed with a large excess of argon and deposited on a cold spectroscopic window (CsI) at 8 K. During the deposition (2–3 h) the gas phase and the matrix formed on top of the CsI window were irradiated with the intense light of an argon discharge lamp. The IR spectrum of the matrix (Figure 1 a) reveals that despite the intense irradiation a substantial amount of unchanged starting material **4** is still present. Newly formed products are the phenyl radical (**3**), acyclic photoproducts of **4** along with small

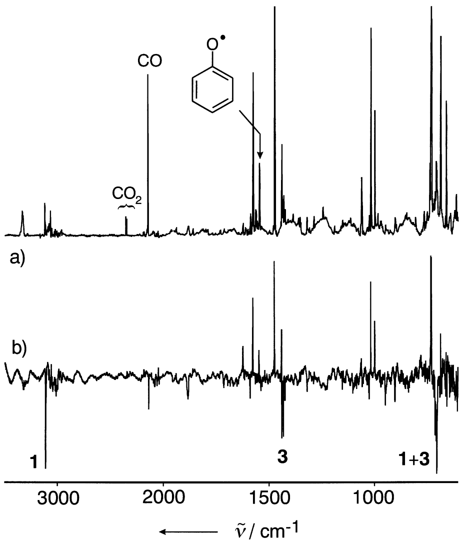


Figure 1. IR detection of the phenyl cation (**1**). a) IR spectrum of iodobenzene (**4**) after argon resonance irradiation; b) difference spectrum of the same matrix showing the bleaching of **1** and **3**; the bands pointing downwards disappear during irradiation with $\lambda > 400$ nm, whereas absorptions of **4** and the phenoxyl radical increase in intensity.

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amounts of CO, CO_2, and the phenoxyl radical. CO_2 is always a contaminant, formed by the oxidation of traces of organic compounds in the microwave discharge, and the intense vacuum UV irradiation leads to the cleavage of CO_2 into CO and oxygen atoms. Reaction of the oxygen atoms with **3** subsequently results in the formation of the phenoxyl radical.

Besides these products, a novel compound with an intense IR absorption at 3110 cm^{-1} is observed. Neither **4** nor **3** nor any of their products formed on conventional matrix photolysis exhibit IR absorptions between 3100 and 3200 cm^{-1}. On irradiation with visible light ($\lambda > 400$ nm), all absorptions of **3** as well as the 3110 cm^{-1} absorption are rapidly bleached (Figure 1 b). The presence of an intense band at 3110 cm^{-1} is in good agreement with calculations of the phenyl cation (**1**) at various levels of theory, which predict a high-frequency absorption, the asymmetric CH stretching vibration of the *ortho*-hydrogen atoms, to be the most intense absorption in the IR spectrum (Table 1).

Table 1. Comparison of calculated (B3LYP/cc-pVDZ) with experimental IR data of **1** and **3**. The frequencies are unscaled, and only bands with more than 10 % of the intensity of the strongest absorption are listed.

Species	Mode	Sym.	B3LYP/cc-pVDZ $\tilde{\nu}$ [cm^{-1}]	B3LYP/cc-pVDZ I [km mol^{-1}]	Ar, 8 K $\tilde{\nu}$ [cm^{-1}]
1 ($^1A_1$)	3	b_2	412	22	
	7	b_1	699[a]	136	713
	15	b_2	1098	43	
	19	a_1	1350	37	
	22	b_2	1802	33	
	23	a_1	3182	26	
	24	b_2	3183	24	
	25	a_1	3222	28	
	26	b_2	3236	204	3110
	27	a_1	3240	47	
1 ($^3B_1$)	4	b_1	591	18	
	6	b_1	739	57	
	19	a_1	1405	105	
	20	b_2	1409	42	
	21	b_2	1486	52	
	25	a_1	3206	21	
	26	b_2	3215	38	
3 ($^2A_1$)	5	b_1	673	14	655
	6	b_1	721	52	703
	13	a_1	1048	9	1027
	19	b_2	1457	5	1432
	20	a_1	1466	7	1438
	25	a_1	3183	5	3071
	26	b_2	3186	22	3073
	27	a_1	3198	10	3085

[a] This band is considerably blue-shifted (20–30 cm^{-1}) if an argon "solvation shell" is modeled by adding several argon atoms around **1**. In contrast, the solvation effects on the CH stretching vibration at 3110 cm^{-1} cancel out almost completely if a larger number of argon atoms is considered.

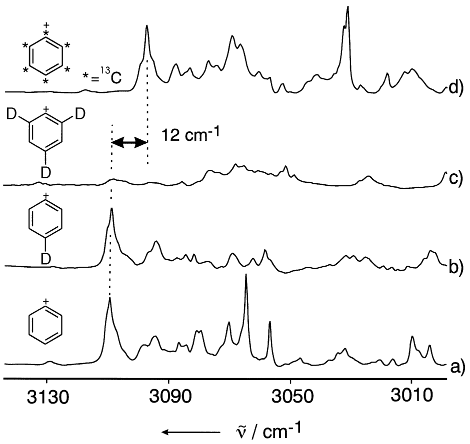

Figure 2. IR spectra obtained after argon resonance irradiation of bromobenzene (**5**) and several of its isotopomers. a) **1**; b) [4-D_1]-**1**; c) [2,4,6-D_3]-**1**; d) [$^{13}C_6$]-**1**. All spectra were recorded under identical experimental conditions. The highest frequency absorptions disappear during irradiation with $\lambda > 400$ nm.

Argon resonance irradiation of bromobenzene (**5**) during deposition of a matrix produces a similar product mixture, and in particular the strong, photolabile 3110 cm^{-1} absorption is also observed (Figure 2). The major difference is the very low yield of phenyl radicals, which allows observation of the second strongest IR absorption of **1** at 713 cm^{-1}. This band is assigned to the in-phase, out-of-plane CH deformation mode. With **4** as precursor this signal is hidden under the strong absorptions of **3** in the same region of the spectrum. The phenyl cation (**1**) is thus produced by two independent precursors. The ground state of **1** is the $^1A_1$ singlet state, while a triplet ground state ($^3B_1$) is not compatible with the experimental findings (Table 1).

To support the assignment of the 3110 and 713 cm^{-1} bands, several isotopomers of **1** were generated from the corresponding labeled halobenzenes [$^{13}C_6$]-**5**, [D_5]-**5**, [2,4,6-D_3]-**5**, and [4-D_1]-**5**. In the completely ^{13}C-labeled isotopomer [$^{13}C_6$]-**1** the absorptions at 3110 and 713 cm^{-1} are red-shifted by 12 and 5 cm^{-1}, respectively, in excellent agreement with the predictions of 11 and 5 cm^{-1} at the B3LYP/cc-pVDZ level of theory.[19] Selective deuteration of the *para* position in [4-D_1]-**1** hardly effects the 3110 cm^{-1} absorption, while this band completely disappears for both of the *ortho*-deuterated isotopomers [2,4,6-D_3]-**1** and [D_5]-**1** (Figure 2). Thus, the selective deuteration confirms the assignment of the 3110 cm^{-1} absorption to the asymmetric CH stretching vibration of the *ortho*-hydrogen atoms. According to the DFT calculations, the CD stretching vibrations are much lower in intensity than the corresponding CH stretching vibrations, and therefore could not be assigned unequivocally in the product mixture. The selective deuteration also reveals that under the reaction conditions no hydrogen migration occurs, as no isotopic scrambling is observed.[20] The barrier for the [1,2]-hydrogen migration was calculated to be 197 kJ mol^{-1} (2.04 eV) at the B3LYP/cc-pVTZ level of theory and is thus much higher than for aliphatic carbocations.

Two mechanisms for the formation of **1** by argon resonance irradiation of halobenzenes have to be considered [Eq. (2)]: a) photochemical dissociation of the C–X bond to give **3** and X atoms and subsequent ionization of **3**, or b) photoionization of the halobenzene to give the corresponding radical cation, which in a second step yields **1** under loss of X atoms. Both processes are energetically feasible, but they cannot be discriminated by our experiments. The electrons released upon photoionization are efficiently trapped by the X atoms or by traces of impurities (e.g. O atoms). Recombination of **1** and X$^-$ or of **3** and X during the formation of the matrix yields

4 or **5**, respectively, which explains the high amount of unchanged starting material.

Chemical evidence for the matrix isolation of the phenyl cation (**1**) stems from trapping experiments with molecular nitrogen. If the argon is doped with 5–10% N_2, the intensity of the 3110 cm^{-1} absorption decreases and a very strong absorption at 2327 cm^{-1} is observed (Figure 3). Higher concentrations of N_2 result in weaker 3110 and stronger 2327 cm^{-1} bands, which indicates that **1** can be "titrated" with N_2. With $^{15}N_2$ as trapping reagent a red shift of 78 cm^{-1} is observed for the 2327 cm^{-1} band, and thus this absorption can unambiguously be assigned to the N≡N stretching vibration of the benzene diazonium ion (**2**). At the B3LYP/cc-pVDZ level of theory this vibrational mode of **2** corresponds to the most intense absorption at 2350 cm^{-1} (unscaled), and a red shift of 79 cm^{-1} is expected upon $^{15}N_2$ labeling.[21] In solid benzene diazonium chloride this absorption was observed at 2302 cm^{-1}, and the $^{15}N_2$ isotopomer exhibits a similar red shift of 75 cm^{-1}.[22] The N≡N stretching vibration in matrix-isolated **2** is unaffected by H/D exchange within the phenyl moiety, again in perfect agreement with theoretical predictions.

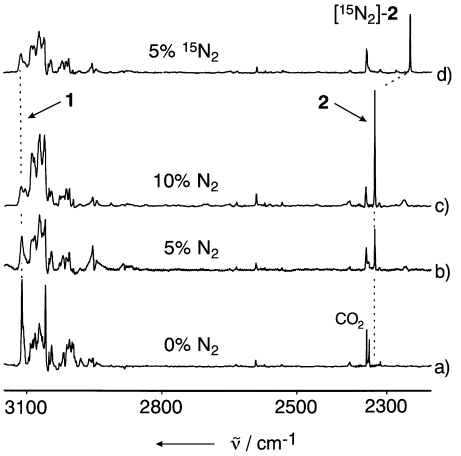

Figure 3. a)–c) "Titration" of **1** with $^{14}N_2$ and d) trapping of **1** with $^{15}N_2$. Spectra a)–c) are recorded under identical experimental conditions. The splitting of the CO_2 band in pure argon (spectrum a) is attributed to matrix site effects[23] and disappears when the argon lattice is disturbed by larger amounts of N_2. The 2327 cm^{-1} band of **2** is well separated from these absorptions. In $^{15}N_2$-**2** the N≡N stretching vibration is red-shifted by 78 cm^{-1} (spectrum d). The N_2 concentrations given are estimated values.

Our results clearly indicate that the phenyl cation (**1**) has been isolated and spectroscopically characterized in the condensed phase for the first time. The IR data of **1** are in good agreement with DFT-calculated spectra for the $^1A_1$ symmetrical singlet state, while predictions for the lowest triplet state ($^3B_1$) are not supported by the experimental finding. Thus, the long-standing question of the ground-state multiplicity of **1** can now be experimentally answered.

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