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Infrared Absorption Spectroscopy of the Phenyl Radical

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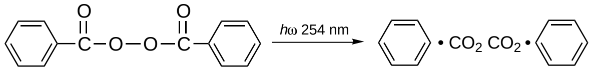
The phenyl radical (C_6H_5) is an important species in organic chemistry and combustion processes.[1−3] Despite numerous attempts, spectroscopic characterization of C_6H_5 is far from complete, due to its high reactivity. The energy of this radical has recently been[4] reported [$\Delta_f H_0(C_6H_5) = 84.3 \pm 0.6$ kcal mol^{-1}] and is derived from the bond energy of benzene [$D_0(C_6H_5{-}H) = 112.0 \pm 0.6$ kcal mol^{-1}]. In this paper we report the infrared absorption spectrum of the phenyl radical in an argon matrix at 12 K and propose assignments for the frequencies and intensities for *all* of the 24 IR active modes. Our assignments are supported by *ab initio* electronic structure calculations.

We observe the IR absorption spectrum of the phenyl radical in an Ar matrix at 12 K when we photolyze either the benzoyl peroxide, $C_6H_5CO_2{-}OCOC_6H_5$, or the anhydride, $C_6H_5CO{-}O{-}COC_6H_5$.[5] Acyl peroxides have long been known[7,8] to be a clean source of radicals which avoids radical/radical recombination in the matrix.



(1)

A 254-nm photon is certainly energetic enough [113 kcal mol^{-1}] to cleave the peroxy bond in the peroxide,[6] $DH_{298}(PhCO_2{-}OCOPh) \cong 34$ kcal mol^{-1}. In addition to the formation of phenyl radical from benzoyl peroxide, our IR spectra clearly show the growth of CO_2, as well as two side products or intermediates.[9] Kinetic studies show that the growth of CO_2 is coupled to the destruction of the acyl peroxide and that 1 mol of $C_6H_5CO_2{-}OCOC_6H_5$ produces 2 mol of CO_2 as (1) suggests. Furthermore, our irradiated matrix has an EPR spectrum that is identical with the known[10] EPR spectrum of C_6H_5 and which is consistent with a C_{2v} "σ radical", C_6H_5 $\tilde{X}\ {}^2A_1$.

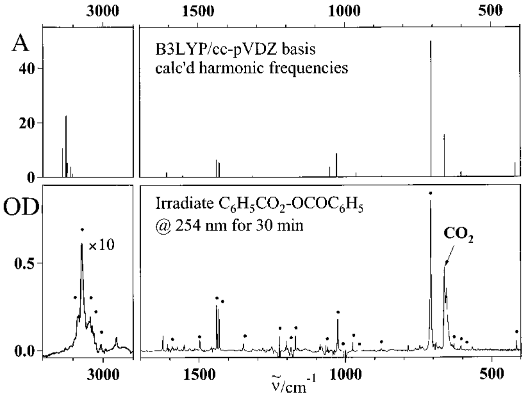


Figure 1. The experimental infrared absorption spectrum of phenyl radical (bottom) isolated in Ar matrix at 12 K where the fundamental vibrations are marked with dots (•). Calculated (Becke3LYP-DFT, unscaled) spectrum of C_6H_5 (top).

Product studies also confirm our observation of C_6H_5. Upon warming the irradiated matrix to 40 K, the IR spectrum of phenyl radical disappears and that of biphenyl appears.

$$[C_6H_5\,CO_2\,CO_2\,C_6H_5]_{12K} \xrightarrow{\Delta \text{ to } 40\text{ K}} C_6H_5{-}C_6H_5 + 2\,CO_2 \qquad (2)$$

The diffusion rates are much higher at 40 K and the two phenyl radicals that were separated by two CO_2 molecules can combine to form biphenyl. No other stable products were found after warming the matrix.

To find the IR absorptions of C_6H_5, we monitor the time course of infrared spectra as we photolyze $C_6H_5CO_2$-$OCOC_6H_5$, (1). We identify a set of bands that a) are produced at the same rate as benzoyl peroxide is destroyed *and* (b) disappear at the same rate as $C_6H_5{-}C_6H_5$ is produced upon warming the matrix.

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(5) The major impurity of benzoyl peroxide (Aldrich, 97%) is benzoic acid which was removed by sublimation at 60 °C onto the radiation shield prior to the deposition. The peroxide was sublimed into a stream of Ar (Spectra Gases, 99.9995% pure; 2 mmol min^{-1}) at 80−84 °C and condensed on a CsI or CaF_2 spectroscopic window. Benzoic anhydride (Lancaster, 98%) was distilled into a stream of Ar at 120 °C. Biphenyl (Aldrich, 99%) was used without further purification. In order to produce high optical quality matrices, the deposition target temperature was maintained at 27−29 K during the matrix preparation. In subsequent irradiations and spectral measurements, the sample temperature was kept at 12 K. Low-temperature samples were cooled with the aid of an Air Products closed-cycle He cryostat (DE-202). Spectral measurements were performed using a Nicolet Magna-550 FTIR with 0.5-cm^{-1} resolution. EPR spectra were measured using a Brucker-300 spectrometer. Photochemical transformations were achieved with a low-pressure Hg lamp.

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(9) During irradiation of benzoyl peroxide (1), two minor transient photochemical products were generated in addition to C_6H_5 radical and CO_2. The spectrum of the first intermediate, produced only at early stages of 254-nm irradiation (and later bleached by it), consists of the following absorptions (in cm^{-1}): 614 (m), 671 (m), 692 (s), 776 (w), 1039 (w), 1480 (vs), 1498 (w), 1522 (w), 1533 (m), and 1608 (m). It is unlikely that this compound is generated from impurities; it is always produced in a similar quantity relative to phenyl radical, regardless of the degree of peroxide purification. It does not contain distinct carbonyl-type absorptions, which seems to eliminate C_6H_5CO, but it could be a delocalized $C_6H_5CO_2$ radical without a distinct carbonyl stretch. The second intermediate compound has the following absorption lines (in cm^{-1}): 1066 (m), 1081 (m), 1200 (s), 1266 (m), and 1754 (m). This compound is generated in small quantities and is not bleached noticeably by 254-nm light. The EPR spectra of the photolyzed matrix contains no sign of the acyloxy radical, $C_6H_5CO_2$. This benzoyloxy radical has a lifetime of 10 ns at room temperature in solution, so it might be a stable intermediate in a 12 K matrix. Neither of our intermediates could be detected by EPR spectroscopy.

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(11) Our spectra are plots of $\tilde{\nu}$ *vs* optical density where OD $\equiv \log(I_o/I)$. We adopt $A(CO_2) = 485 \pm 15$ km mol^{-1},[20] and if the optical path, z/cm^{-1}, is known, we can use the IR absorption spectrum of CO_2 to measure the concentration of carbon dioxide in the matrix:

$$n/\text{mol cm}^{-3} = \frac{\ln(10)}{Az}\int_{\text{IR band}} d\tilde{\nu}\,[\text{OD}] \qquad (\text{A1})$$

A typical matrix is about [1 cm × 1 cm × 0.1 mm] and we monitor the background carbon dioxide; we find the integrated intensity about the two CO_2 ν_3 bands at 2345 and 2339 cm^{-1} to be 0.481 cm^{-1}. Consequently evaluation of (A1) leads to a concentration of CO_2 in the initial 12 K Ar matrix of 2.3×10^{-6} mol cm^{-3} or 2.3 mmol L^{-1}. Following irradiation of the $PhCO_2OCOPh$ matrix for 5 min at 254 nm, the carbon dioxide band grows substantially. When the area of the photolyzed CO_2 band is corrected for the small initial carbon dioxide contamination, we find that our irradiation has produced 103 mmol L^{-1} of CO_2.

(12) Carbon dioxide becomes an internal standard which permits us to extract the absolute infrared intensities for each of the phenyl radical fundamental frequencies. Because the phenyl radical and carbon dioxide are in the same matrix, $z(CO_2) = z(C_6H_5)$. The photolysis scheme in (1) produces one molecule of CO_2 for one of C_6H_5, $n(CO_2) = n(C_6H_5)$; hence we use (A1) to find:

$$[A(\text{phenyl})]^{-1}\int_{\text{phenyl}} d\tilde{\nu}\,[\text{OD}] = [A(CO_2)]^{-1}\int_{\text{carbon dioxide}} d\tilde{\nu}\,[\text{OD}] \qquad (\text{A2})$$

Use of expression A2 permits us to extract the intensities for all 24 IR active modes of C_6H_5.

We assign these bands to C_6H_5. In our spectra we find no traces of benzene or its isomers or other related compounds like benzynes, etc. Other species are only formed in small quantities, and there is a nearly quantitative conversion of benzoyl peroxide to C_6H_5 and CO_2. Thus, a comparison of the integrated intensity[11] of the CO_2 bands and those of phenyl enables us to estimate[12] the absolute infrared intensities of the bands for C_6H_5.

Figure 1 shows the IR absorption spectrum of the phenyl radical obtained from the photolysis of $C_6H_5CO_2{-}OCOC_6H_5$. This figure is assembled by (a) collecting an IR spectrum of $C_6H_5CO_2{-}OCOC_6H_5$, (b) measuring the IR spectrum following irradiation of the matrix at 254 nm for 30 min, and (c) finally subtracting the first spectrum from the second spectrum. Consequently, all of the features in this spectrum belong to C_6H_5, CO_2, and other minor products.

We identified the fundamental frequencies for phenyl radical by comparison with the frequencies and intensities from an *ab initio* density functional treatment electronic structure calculation (Becke3LYP-DFT).[13] For a C_{2v} phenyl radical, one expects 27 vibrational modes, $\Gamma_{vib} = 10\ a_1 \oplus 3\ a_2 \oplus 5\ b_1 \oplus 9\ b_2$, of which only 24 will be active in the infrared. Our assignments together with the set of (unscaled) *ab initio* harmonic frequencies $\{\omega_i\}$ are collected together in Table 1.[14] A visual comparison of the *ab initio* and experimental findings is made in Figure 1; the proposed 24 C_6H_5 fundamentals are marked by dots (•). Several groups have previously reported vibrational modes for the C_6H_5 radical[8,15−18] and our values are compatible with these earlier, partial assignments. Definitive assignments of the complete vibrational spectrum will still require selective isotope labeling, a careful polarization study of partially photooriented samples, and determination of the Raman spectrum.

Table 1. Infrared Absorption Spectrum of C_6H_5 ($\tilde{X}\ ^2A_1$)

exptl freq: Ar matrix (12 K)				harmonic vib freq[13] (unscaled)		
ν	sym	$\tilde{\nu}$/cm^{-1}	A/km mol^{-1}	ω/cm^{-1}	A/km mol^{-1}	assignment[a]
1	**a_1**	3085	3.1	3199	10.7	C−H sym s (predominantly $C_4{-}H_4$)
2		3071	0.2	3184	5.3	$C_{2,6}{-}H_{2,6}$ sym s ooph $C_4{-}H_4$ s
3		3052	0.2	3165	1.3	$C_{2,4,6}{-}H_{2,4,6}$ sym s ooph $C_{3,5}{-}H_{3,5}$ s
4		1499	2.2	1585	0.6	$C_{2,6}{-}C_{3,5}$ sym s; $C_{3,5}{-}H_{3,5}$ ip b
5		1441	8.7	1467	6.5	$C_1{-}C_{2,6}$ sym s; $C_{2,3,5,6}{-}H_{2,3,5,6}$ ip b
6		1080	2.2	1166	0.1	$C_{2,3,5,6}{-}H_{2,3,5,6}$ b
7		1027	7.9	1049	8.9	$C_1{-}C_{2,6}$ s
8		1011	0.2	1023	0.2	ring breathing mode
9		976	1.6	982	1.5	C−C−C b
10		605	1.4	615	1.8	$C_1{-}C_{2,6}$; $C_4{-}C_{3,5}$ b
11	**a_2**			966	0	
12				813	0	
13				400	0	
14	**b_1**	971	0.1	997	0.2	$C_{2,4,6}{-}H_{2,4,6}$ ooph $C_{3,5}{-}H_{3,5}$ b
15		878	0.9	891	0.3	$C_{2,4,6}{-}H_{2,4,6}$ b
16		708	55.9	719	50.3	C−H b
17		629	1.1	674	15.7	$C_{2,4,6}{-}H_{2,4,6}$ b
18		416	3.4	426	5.2	$C_{2,3,5,6}{-}H_{2,3,5,6}$ ooph $C_4{-}H_4$ and ring b
19	**b_2**	3073	10.6	3187	22.7	$C_{2,3}{-}H_{2,3}$ s $C_{5,6}{-}H_{5,6}$ as s
20		3060	0.1	3171	4.0	$C_{2,5}{-}H_{2,5}$ sym s ooph $C_{3,6}{-}H_{3,6}$ sym s
21		1593	0.1	1641	1.8	$C_{1,2}{-}C_{4,5}$ sym s ooph $C_{1,5}{-}C_{3,4}$ sym s
22		1433	6.3	1459	5.4	C−C s; $C_{3,4,5}{-}H_{3,4,5}$ b
23		1344	0.3	1343	0.4	Kekulè mode; $C_{3,5}{-}H_{3,5}$ ip b
24		1226	3.6	1293	0.1	$C_2{-}C_3$ s ooph $C_5{-}C_6$ s; C−H b
25		1086	0.1	1167	0.2	$C_{3,4,5}{-}H_{8,9,10}$ ip b
26		1067	1.1	1072	3.8	$C_2{-}C_3$ s ooph $C_5{-}C_6$ s
27		586	0.2	597	0.6	ring s

[a] Approximate mode description; for atom numbering, see ref 13; s = stretch; sym = symmetric; as = asymmetric; ooph = out-of-phase; ip = in-phase; b = bend.

One of the most important reactions in the environmental oxidation of aromatics is the reaction of C_6H_5 with oxygen. The kinetics of this radical/radical reaction is disputed: $C_6H_5 + O_2 \rightarrow C_6H_5O_2$.[19] We have observed the reaction of C_6H_5 with molecular oxygen in our matrix. Photolysis of $C_6H_5CO_2{-}OCOC_6H_5$ in an Ar matrix doped with O_2 produces the phenyl radical along with a species that was not formed when pure Ar was used. When the matrix is warmed up to 35 K, we observe the destruction of signals from C_6H_5 and this other species and the production of a new set of bands. None of the bands correspond to vibrational features of $C_6H_5{-}C_6H_5$, indicating that we are forming oxygenated compounds. Phenylhydroperoxyl radical, C_6H_5OO, is probably formed when we generate C_6H_5 in the oxygen matrix.

The results in this communication show that the phenyl radical can be cleanly and quantitatively prepared in a cryogenic matrix for spectroscopic studies. A close comparison is made between experimental C_6H_5 frequencies $\{\nu\}$ and intensities $\{A\}$ and modern electronic structure calculations of the phenyl radical, which shows that the calculations can be quite accurate.

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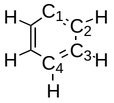
(13) Generally *ab initio* unrestricted Hartree−Fock vectors are spin-contaminated, but the Becke3LYP-DFT calculation produces a vector that is "nearly" a proper doublet; $\langle \tilde{X}\ ^2A_1 |\ S^2 |\ \tilde{X}\ ^2A_1 \rangle = 0.76$. While UHF harmonic frequencies are empirically scaled by roughly 90%, the Becke3LYP-DFT $\{\omega\}$ set are commonly scaled by 96%. Our matrix frequencies are expected to be within ±1% of the gas-phase values $\{\tilde{\nu}/\mathrm{cm}^{-1}\}$ and differ on average by 2.9% from the computed values for C_6H_5. The calculated structure for C_6H_5 is:



$r(C{-}H_2) = 1.092$ Å $\quad r(C{-}H_3) = 1.093$ Å $\quad r(C{-}H_4) = 1.092$ Å
$r(C_1{-}C_2) = 1.380$ Å $\quad r(C_2{-}C_3) = 1.406$ Å $\quad r(C_3{-}C_4) = 1.399$ Å
$\angle(C_1C_2C_3) = 116.6°$ $\quad \angle(C_2C_3C_4) = 120.2°$ $\quad \angle(C_3C_4C_5) = 120.7°$
$\angle(C_1C_2H) = 122.4°$ $\quad \angle(C_2C_3H) = 119.6°$ $\quad \angle(C_2C_1C_6) = 125.8°$

$A = 0.209\ \mathrm{cm}^{-1}$, $B = 0.186\ \mathrm{cm}^{-1}$, $C = 0.098\ \mathrm{cm}^{-1}$; $\kappa = -0.729$.

(14) The identification of some of the bands listed in Table 1 is difficult. In an attempt to gain access to the 670−645 cm^{-1} region, where the strong ν_{17} fundamental is predicted, we tried to generate C_6H_5 from several different precursors: benzil ($C_6H_5{-}CO{-}CO{-}C_6H_5$), benzophenone ($C_6H_5COC_6H_5$), benzoic anhydride, azobenzene ($C_6H_5N_2C_6H_5$), and benzoyl chloride (C_6H_5-COCl). Commonly this region of the infrared will be partially obscured by CO_2 which the peroxide photolysis generates. In an Ar matrix neither azobenzene nor benzil underwent any photodecomposition, even when short wavelength radiation at 186 nm (low-pressure He lamp) was used. No detectable amount of phenyl radical was generated from the irradiated benzoyl chloride. Benzoic anhydride definitely yields phenyl radical but it still produces CO_2. Benzoyl peroxide is the most effective precursor for C_6H_5. Comparison of intensities of CO_2 bands, when the radical is present in the matrix and after it is converted to biphenyl, suggests that indeed ν_{17} might be covered by CO_2 absorption. But we observe a band at 629 cm^{-1} that definitely originates from phenyl radical and cannot by explained as a combination or overtone. Therefore, we assign it as ν_{17}, in spite of the large intensity mismatch with theoretical predictions.

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