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Structure and infrared spectrum of 2-hydroxyphenyl radical

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Abstract

Infrared spectrum of 2-hydroxyphenyl, C_6H_4 -OH, produced from 2-iodophenol in a low-temperature argon matrix upon UV irradiation ($\lambda > 280$ nm) was measured with an FT-IR spectrophotometer. This radical was found to be less stable by 120 kJ mol⁻¹ than phenoxyl, C_6H_5 -O, by a density functional theory calculation. Two final photoproducts were identified as cyclopentadieny-lidenemethanone and 4-iodo-2,5-cyclohexadienone in analogy with the photoproducts of 2-chloro and 2-bromophenols. A kinetic analysis shows that the latter is produced via 2-hydroxyphenyl by hydrogen migration and iodine recombination while the former is produced by Wolff rearrangement after elimination of hydrogen iodide. © 2004 Elsevier B.V. All rights reserved.

1. Introduction

Phenoxyl radical, C_6H_5 -O, is well known as a transient species in chemical and biological processes such as combustion of aromatic compounds [1] and protein redox reactions [2]. The molecular structure and chemical properties of this radical have been studied extensively by electron-spin resonance, electronic absorption, resonance Raman, and infrared spectroscopies [3]. For example, the infrared spectra of this radical including isotopic species were measured in low-temperature matrices [4].

In contrast, many fewer studies have been made on 2-hydroxyphenyl radical, C_6H_4 -OH, which is an isomeric structure of phenoxyl, because 2-hydroxyphenyl is much less stable than phenoxyl. Kasai and McLeod Jr. [5] observed the ESR spectrum of an intermediate produced from 2-iodophenol in an argon matrix and identified it from the splitting pattern as 2-hydroxyphenyl. Schuler et al. [6] reported the conversion of hydroxyphenyl to phenoxyl in aqueous solutions by ESR spectroscopy. No other spectroscopic studies have been reported to our knowledge.

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In the present Letter, we report an infrared spectrum of 2-hydroxyphenyl produced from 2-iodophenol in a low-temperature argon matrix upon UV irradiation, from which the structure of this radical has been determined with an aid of a density functional theory (DFT) calculation. Furthermore, a kinetic analysis for the growth behavior of 2-hydroxyphenyl and final photoproducts is performed to elucidate the photoreaction mechanism of 2-iodophenol. The obtained reaction mechanism is compared with the results of our previous studies for 2-chloro [7] and 2-bromophenols [8].

2. Experimental and calculation methods

The sample of 2-iodophenol (Aldrich, 98% purity) was premixed with argon (Nippon Sanso, 99.9999% purity) after vacuum distillation. The mixing ratio of sample/ rare gas was 1/1000, and the deposition time was about 1 h. The premixed gas was deposited on a CsI plate, cooled by a closed-cycle helium refrigerator (Iwatani, Model CW303), at about 10 K. Spectra of the matrix sample were measured with an FT-IR spectrophotometer (JEOL, Model JIR-WINSPEC50). The spectral resolution was 0.5 cm⁻¹, and the number of accumulation was 64. UV radiation from a superhigh-pressure mercury

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lamp was used to induce photodissociation, where a UV-28 cutoff optical filter (HOYA) was used to choose radiation energy ($\lambda > 280$ nm). Other experimental details were reported elsewhere [9,10].

The DFT calculations were performed by using the GAUSSIAN 03 program [11] with the basis set of 6-31++G**, where Becke's three-parameter hybrid density functional [12], in combination with the Lee–Yang–Parr correlation functional (B3LYP) [13], was used to optimize geometrical structures and to estimate vibrational wavenumbers of 2-hydroxyphenyl and phenoxyl radicals.

3. Results and discussion

3.1. Infrared spectra of 2-hydroxyphenyl and final products

Infrared spectral changes caused by photodissociation were observed when 2-iodophenol in an argon matrix was irradiated by UV light through a UV-28 cutoff optical filter. A difference spectrum between the spectra measured after 10-min and before irradiation is shown in Fig. 1a, where the decreasing and increasing bands represent the reactant, 2-iodophenol, and photoproducts, respectively. The bands marked with an open circle are assignable to an intermediate because their intensity increased at the beginning of irradiation time and decreased afterwards. A typical intensity change of the 1233 cm⁻¹ band is shown in Fig. 2. The maximum



Fig. 1. Infrared spectra of 2-hydroxyphenyl: (a) observed difference spectrum between spectra measured after 10-min minus before UV irradiation ($\lambda > 280$ nm), (b) and (c) calculated spectral patterns of *syn* and *anti* obtained at the DFT/B3LYP/6-31++G** level. A scaling factor of 0.98 was used. Symbols \bigcirc , \Box , and \triangle represent an intermediate (2-hydroxyphenyl) and final products (cyclopentadienylidene-methanone and 4-iodo-2,5-cyclohexadienone), respectively.



Fig. 2. Time dependence of infrared band intensity. Symbols \bigcirc , \Box , and \triangle represent the bands appearing at 1233 (2-hydroxyphenyl), 896 (cyclopentadienylidenemethanone) and 1257 cm⁻¹ (4-iodo-2,5-cyclo-hexadienone). Solid lines represent calculated values obtained by least-squares fitting, where Scheme 3 was assumed for photoreaction mechanism.

amount is found at the irradiation time of 10 min. The wavenumbers of the bands, which showed the same intensity change, are summarized in Table 1. A reasonable interpretation is that 2-hydroxyphenyl is produced from 2-iodophenol by elimination of iodine atom upon UV irradiation in the matrix, as shown in Scheme 1, where the conformation of the reactant, 2-iodophenol, is assumed to be syn in analogy with 2-chloro [7] and 2bromophenols [8] in consideration of the intramolecular hydrogen bonding. This radical also has two conformations around the C-O bond as drawn in Fig. 3; we call them syn and anti, where the hydrogen atom positions in the hydroxyl group of the former and the latter are near and far from the unpaired electron, respectively. The optimized geometries of syn- and anti-2-hydroxyphenyl were obtained by a DFT calculation, which showed that both conformers are planer. The anti conformer is estimated by this calculation to be less stable than syn by 7.7 kJ mol⁻¹. Their bond lengths and angles of the optimized geometries are compared in Table 2. The corresponding bond lengths of anti and syn are agree within 0.003 Å, but the C3-H9 length in anti is slightly longer. This finding suggests repulsion between H8 and H9 atoms, which is supported by the fact that the C2–C3–H9 and C2–O7–H8 angles in anti are larger than the corresponding values in *syn*.

The calculated infrared spectral patterns of *syn* and *anti* are compared with the observed spectrum in Fig. 1. The spectral pattern for *syn* is found to reproduce the observed spectrum more satisfactorily than *anti*. Even if the less stable *anti* is produced upon UV irradiation, it is probably converted immediately to the more stable *syn* in a low-temperature matrix by hydrogen tunneling like hydroquinone derivatives [14–16]. The calculated wavenumbers and the relative intensities of the two conformers for 2-hydroxyphenyl are compared with the observed values in Table 1.

Table 1 Wavenumbers (cm⁻¹) and relative intensities of 2-hydroxyphenyl

Observed		Calculated					
v	Intensity	Syn		Anti			
		v ^a	Intensity	v ^a	Intensity		
		3739	57	3749	39		
		3144	8	3143	8		
		3133	9	3129	7		
		3125	3	3118	<1		
		3118	<1	3088	10		
b	b	1613	50	1625	27		
b	b	1557	11	1550	27		
1448	80	1452	59	1467	16		
1440	71	1445	33	1441	26		
1325	4	1328	2	1325	20		
1284	5	1295	5	1285	100		
1233	69	1237	87	1258	12		
1163	34	1153	90	1157	18		
		1148	1	1149	20		
1094	8	1085	13	1088	28		
1021	12	1017	12	1023	5		
		960	<1	958	<1		
		947	<1	940	<1		
896	c	906	2	899	1		
820	30	811	21	810	18		
		809	5	798	2		
728	100	725	60	726	54		
		620	<1	615	<1		
		613	<1	612	<1		
		511	<1	512	<1		
		508	1	509	3		
		403	4	404	5		
		380	10	389	6		
		359	100	322	70		
		220	1	216	2		

^aCalculated by DFT/B3LYP/6-31++G**. A scaling factor of 0.98 was used.

^bDisturbed by vibrational rotational lines of H₂O in atmosphere.

^cOverlapped with bands of final products.



Scheme 1.

There are some photoproducts bands unassigned to 2-hydroxyphenyl in the infrared spectrum measured after UV irradiation. A spectrum measured after the 2-h irradiation is compared with those of 2-chloro [7] and 2-bromophenols [8] in Fig. 4. The bands marked with an open square show the same growth behavior as the strong band appearing at 2134 cm⁻¹ in the C=C=O stretching region. These bands correspond with those of cyclopentadienylidenemethanone (CPM) identified as a final product in the photoreactions of 2-chloro and 2-bromophenols. On the other hand, the bands marked with an open triangle show the same growth behavior as the



Fig. 3. Two possible conformations of 2-hydroxyphenyl with atom numbering.

Table	2									
Bond	lengths	(Å)	and	bond	angles	(°)	for	optimized	geometry	of
2-hyd	roxypher	nyl								

Parameter ^a	Syn	Anti
r(C1–C2)	1.3825	1.3842
r(C2–C3)	1.4043	1.4058
r(C3–C4)	1.3970	1.3995
r(C4–C5)	1.3994	1.3968
r(C5–C6)	1.4068	1.4081
<i>r</i> (C6–C1)	1.3753	1.3737
r(C2–O7)	1.3687	1.3680
r(O7–H8)	0.9671	0.9665
r(C3–H9)	1.0865	1.0895
r(C4–H10)	1.0859	1.0859
r(C5–H11)	1.0859	1.0859
r(C6–H12)	1.0863	1.0866
θ(C1-C2-C3)	116.59	116.38
θ(C2–C3–C4)	119.88	120.23
θ(C3–C4–C5)	121.33	121.12
θ(C4-C5-C6)	119.46	119.33
θ(C5–C6–C1)	116.99	117.45
θ(C6–C1–C2)	125.75	125.49
θ(C1–C2–O7)	124.46	119.99
θ(C3–C2–O7)	118.95	123.63
θ(C2–O7–H8)	109.12	109.71
θ(C2–C3–H9)	118.65	119.59
θ(C3-C4-H10)	119.03	119.03
θ(C4–C5–H11)	120.65	120.64
θ(C5–C6–H12)	121.13	120.97

^a Atom numbering is given in Fig. 3.

strong band appearing at 1680 cm^{-1} in the C=O stretching region. These bands are similar to those of 4-bromo-2,5-cyclohexadienone identified as a final product in the photolysis of 2-bromophenol [8]. Hence, we tentatively assign these bands to 4-iodo-2,5-cyclohexadienone (CHD). To confirm this assignment, we tried to perform a DFT calculation to obtain the optimized geometry and infrared spectral pattern for CHD but in vain, because no suitable basis set for iodine atom was available.

3.2. Mechanism of photoreaction

The intensity changes of the 896 cm⁻¹ (CPM) and 1257 cm⁻¹ (CHD) bands are compared with that of the



Fig. 4. Comparison of infrared spectra of final products: (a) 2-iodo-, (b) 2-bromo-, (c) 2-chlorophenols. Irradiation time was 2 h. Bands marked with \Box and \triangle are assigned to cyclopentadienylidenemethanone and 4-halogeno-2,5-cyclohexadienone, respectively. A band marked with \times is due to water.

1233 cm⁻¹ band (2-hydroxyphenyl) in Fig. 2. The 896 cm⁻¹ band increases rapidly in the beginning of photoreaction, implying that CPM is produced from 2-iodophenol by one-step reaction. On the other hand, the 1257 cm⁻¹ band shows a clear induction period in the initial irradiation time, implying that CHD is produced by two-step reaction. The intensity of the 1257 cm⁻¹ band increases as that of the 1233 cm⁻¹ band decreases during prolonged irradiation, while that of the 896 cm⁻¹ band remains constant after 90-min irradiation. Therefore, we conclude that CHD is produced from 2-iodophenol via 2-hydroxyphenyl, as shown in Scheme 2.

When hydrogen iodide is eliminated by UV irradiation, ketocarbene is produced form 2-iodophenol. Since ketocarbene is reactive, the final product CPM is produced immediately by Wolff rearrangement. This reaction pathway is found in the photoreaction of 2-chloro [7] and 2-bromophenols [8]. On the other hand, 2-hydroxyphenyl is produced by elimination of iodine atom from 2-iodophenol. The hydrogen atom



Scheme 2.



Scheme 3.

in the hydroxyl group migrates to the unpaired electron by absorption of the second photon with electron rearrangement, which may be phenoxyl radical in an electronically excited state. Then another final product CHD is produced by recombination with iodine atom. A similar final product, 4-bromo-2,5-cyclohexadienone, was identified in the photoreaction of 2-bromophenol with an aid of a DFT calculation [8].

To confirm this photoreaction mechanism, we tried to determine the rate constants of k_1 , k_2 , and k_3 in Scheme 2. The following equations can be derived by solving the rate formulae:

$$\frac{A_{\rm CPM}}{\varepsilon_{\rm CPM}} = \frac{A_0 k_1}{k_1 + k_2} \left(1 - e^{-(k_1 + k_2)t} \right),\tag{1}$$

$$\frac{A_{\rm HPR}}{\varepsilon_{\rm HPR}} = \frac{A_0 k_2}{k_3 - k_2 - k_1} \left(e^{-(k_1 + k_2)t} - e^{-k_3 t} \right),\tag{2}$$

$$\frac{A_{\text{CHD}}}{\varepsilon_{\text{CHD}}} = A_0 k_2 \left\{ \frac{1}{k_1 + k_2} \left(1 - e^{-(k_1 + k_2)t} \right) - \frac{1}{k_3 - k_2 - k_1} \left(e^{-(k_1 + k_2)t} - e^{-k_3t} \right) \right\},$$
(3)

where A and ε represent absorbance and absorption coefficients, respectively, for the 896 (CPM), 1233 (HPR: 2-hydroxyphenyl) and 1257 cm⁻¹ (CHD) bands. In the least-squares fitting, the absorbance of 2-iodophenol at $t = 0, A_0$, was fixed to the experimental value measured before UV irradiation, while the ratio of $\varepsilon_{HPR}/\varepsilon_{CPM}$ was fixed to the value of 3.0 obtained by the DFT calculation. Then the five parameters among seven were variable in the least-squares analysis. However, a significant discrepancy between the observed and calculated values was found in the decreasing behavior of 2-hydroxyphenyl and the increasing behavior of CHD in the prolonged irradiation time. This finding suggests that a portion of 2-hydroxyphenyl cannot be converted to CHD by recombination with iodine atom. Then we considered diffusion of the iodine atom eliminated from 2-iodophenol in the photoreaction mechanism (Scheme 3), where the rate constants k_4 and k'_4 denote the leaving and returning rates of iodine atom, respectively. A numerical integral method was used in the least-squares fitting. The obtained rate constants are 0.011 ± 0.001 , 0.034 ± 0.001 , 0.133 ± 0.022 , 0.219 ± 0.025 and $0.015 \pm$ 0.002 min⁻¹, for k_1 , k_2 , k_3 , k_4 and k'_4 , respectively, where the uncertainties represent standard deviation. The calculated values are drawn in solid lines in Fig. 2. It is found that the calculated values are consistent with the observed values.

In the photoreaction of 2-chloro and 2-bromophenols, no infrared spectrum of 2-hydroxyphenyl was detectable. This fact implies that chlorine and bromine atoms are more reactive than iodine in matrices. The chlorine atom withdraws the hydrogen atom in the hydroxyl group and causes elimination of hydrogen chloride. As a result, 2-hydroxyphenyl and CHD are not produced upon UV irradiation (see Fig. 4c). On the other hand, bromine atom migrates to produce CHD more easily than iodine because of the smaller size of bromine than iodine; this implies that the rate constant k_3 in the photoreaction of 2-bromophenol is too large for the radical to survive in the matrix. If this is the case, then the rate constant k_3 for 2-iodophenol in a xenon matrix should be larger than that in an argon matrix because the matrix cage made of xenon atoms is larger than that of argon and favors migration of iodine atom for recombination. We performed a similar experiment on 2-iodophenol using xenon gas. No infrared spectrum of 2-hydroxyphenyl was observable, as expected.

4. Concluding remarks

The infrared spectrum of 2-hydroxyphenyl has been observed in UV photolysis of 2-iodophenol in an argon matrix. The conformation around the C–O bond of the radical is determined to be *syn* by a comparison of the observed spectrum with the calculated spectral patterns obtained by DFT calculations. Namely, the hydrogen atom of the hydroxyl group lies closer to the unpaired electron. Final photoproducts are assigned to cyclopentadienylidenemethanone and 4-iodo-2,5-cyclohexadienone in analogy with the photoreaction of 2-chloro and 2-bromophenols. A kinetic analysis has shown that 4-iodo-2,5-cyclohexadienone is produced via 2-hydroxyphenyl, where the recombination with iodine atom is partially disturbed by argon atoms.

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