

set of useful empirical rules to guide conformational assignments for molecules of this type.

While the trans lone-pair effect may not be the dominant interaction with respect to conformational stability, it appears to be the most useful feature for identifying rotational isomers by means of infrared spectroscopy. Namely, the frequencies of the OH and CH stretching vibrations are governed largely by the existence of a trans lone-pair interaction, although the band separation may vary. On the other hand, the OH stretching vibration apparently is insensitive to the gauche effect, as exemplified by the single, sharp OH

absorption band arising from the two most stable conformers of hexafluoropropane-2,2-diol. Since this insight has been gained largely by CNDO/2 calculations, we believe that this method can be used as a reliable tool by the spectroscopist for the purpose of conformational analysis.

Acknowledgment. We gratefully acknowledge the financial support of the National Research Council of Canada and the University of Calgary Data Centre. One of us (H. W.) wishes to thank the University for financial support for part of this work.

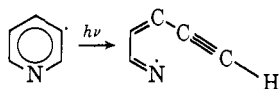
2-Hydroxyphenyl and 2-Methoxyphenyl Radicals. Matrix-Isolation Electron Spin Resonance Study

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Contribution from the Union Carbide Corporation, Tarrytown Technical Center, Tarrytown, New York 10591. Received August 23, 1973

Abstract: 2-Hydroxyphenyl and 2-methoxyphenyl radicals generated in argon matrices were examined by electron spin resonance spectroscopy. Both radicals were found to be σ radicals and were found to isomerize under thermal or photoexcitation to phenoxy and phenoxyethyl radicals as the result of intramolecular hydrogen abstraction from the respective substituent group.

An electron spin resonance (esr) study of phenyl radicals isolated in argon matrix revealed that the radical is stable against uv ($\lambda > 250$ nm) irradiation.¹ The radical must also possess substantial thermal stability, since it is the only radical observed when produced by pyrolysis ($500 \approx 700^\circ$) of phenyl iodide. Pyridyl radicals,² on the other hand, have been found to undergo readily a ring-rupture rearrangement when irradiated with uv light, e.g.



We report here the results of a matrix-isolation esr study of 2-hydroxyphenyl and 2-methoxyphenyl produced from 2-iodophenol and 2-iodoanisole, respectively. Both radicals were found to be σ radicals despite the essentially nonbonding lone-pair electrons at the oxygen p_π orbital. Most interestingly, it was found that thermal or photoexcitation of these radicals leads to intramolecular hydrogen abstraction by the radical center from the substituent group.

Experimental Section

The cryostat-spectrometer assembly that would permit isolation of reactive species in rare-gas matrices and observation of their esr spectra has been detailed earlier.³ The matrix is formed upon a cold finger (a sapphire rod) which is attached to the bottom of the inner liquid helium dewar. The design was such that the entire

inner dewar can be rotated about and moved along its vertical axis. During the course of the present study, the lower section of the inner dewar was extensively modified in order to achieve a variable temperature capability. The essential features of the modification are depicted in Figure 1. The cold finger is now attached to the bottom of the lower can which is cooled by a liquid-helium flow from the upper reservoir and heated by a resistive coil wound around it. With this arrangement it was possible to vary and maintain the temperature of the lower can from 4.6°K up with the accuracy of $\pm 0.5^\circ$ K. The temperature is monitored by a Chromel vs. gold (0.07 at. % Fe) thermocouple,⁴ the cold junction of which is imbedded in the wall of the upper reservoir. From the change in the intensity of an esr signal related to the Boltzmann distribution, it was concluded that, when the temperature of the lower can is changed (within the range covered, 4.6–20°K), the matrix comes to thermal equilibrium with the can in less than 0.5 min.

In the case of pyrolysis the precursor (2-iodophenol or 2-iodoanisole) was passed through a resistively heated quartz tube and trapped in an argon matrix being formed upon the cold finger. In the case of photolysis, an argon matrix containing the precursor was prepared and then irradiated with uv through the side quartz window. In the case of the dissociative photoelectron transfer process,⁵ an argon matrix containing the precursor molecules and Na atoms (the atomic ratio Ar:precursor:Na being roughly 1000:10:1) was prepared and then irradiated with red light ($\lambda > 580$ nm). A high-pressure mercury arc (GE, AH-6) equipped with appropriate filters (Corning 7-54 for uv, and 2-62 for $\lambda > 580$ nm) was used for these experiments. Unless mentioned otherwise, all the spectra were obtained while the matrix was maintained at 4.6°K. The frequency of the spectrometer locked to the sample cavity was 9.430 GHz. 2-Iodophenol and 2-iodoanisole were obtained from Aldrich Chemicals and purified further by sublimation.

2-Hydroxyphenyl Radicals

Figure 2 shows the esr spectrum obtained when an argon matrix containing 2-iodophenol was irradiated

(1) P. H. Kasai, E. Hedaya, and E. B. Whipple, *J. Amer. Chem. Soc.*, **91**, 4364 (1969).

(2) P. H. Kasai and D. McLeod, Jr., *J. Amer. Chem. Soc.*, **94**, 720 (1972).

(3) P. H. Kasai, E. B. Whipple, and W. Weltener, Jr., *J. Chem. Phys.*, **44**, 2581 (1966).

(4) L. L. Sparks and R. L. Powell, N.B.S., Boulder, Colorado, PB 175621, Clearing House for Federal Scientific and Technical Information, Springfield, Virginia 22151.

(5) P. H. Kasai, *Accounts Chem. Res.*, **4**, 329 (1971).

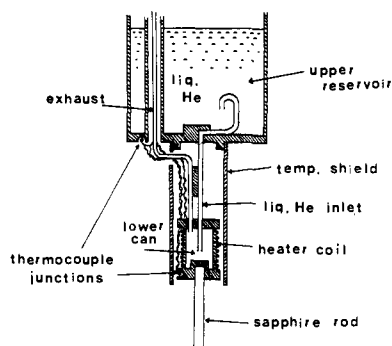
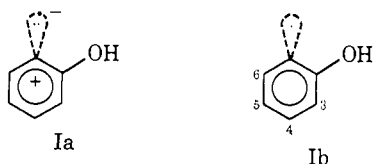


Figure 1. The inner, variable-temperature section of the matrix isolation cryostat for esr study.

with uv. The octet pattern indicated is quite discernible. When the experiment was repeated using mono-deuterated species $\text{IC}_6\text{H}_4\text{OD}$, the identical pattern was observed proving that only the ring protons are responsible for the observed hyperfine structures (hfs). We also note that the components of the octet are of same intensity indicating the three different couplings (20, 10, and 5 G) to three unique protons. The large overall spread (~ 40 G) immediately precludes the possibility that the π radical Ia is responsible for the spectrum.



The spectrum is, therefore, assigned to the 2-hydroxyphenyl radicals of σ state (Ib) with the following coupling constants.

$$A(\text{H}_2) = 10 \pm 1 \text{ G}$$

$$A(\text{H}_4) < 2 \text{ G}$$

$$A(\text{H}_5) = 5 \pm 1 \text{ G}$$

$$A(\text{H}_6) = 20 \pm 1 \text{ G}$$

The observed splittings were assigned to the specific protons indicated by comparison with the known coupling constants of phenyl radicals¹ and those calculated by the semiempirical SCF molecular orbital calculation, INDO.⁶ The signs of all of these isotropic coupling constants are thus decided to be positive. The INDO calculation also predicted the σ ground state for the radical. The calculation was performed assuming the standard bond lengths and angles given in ref 6. The orientation of the hydroxy group (cis or trans to the cleaved bond) made no significant difference upon the calculated total energy of the radical nor on the spin density distribution.

Compared in Table I are the observed and calculated coupling constants of the 2-hydroxyphenyl radicals assigned above and those of the phenyl radicals reported earlier.¹ It is particularly impressive that the INDO theory correctly predicts the effects of the hydroxy group substitution at the 2 position upon all the coupling constants of the remaining protons in phenyl radicals. The most conspicuous is the large difference

(6) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

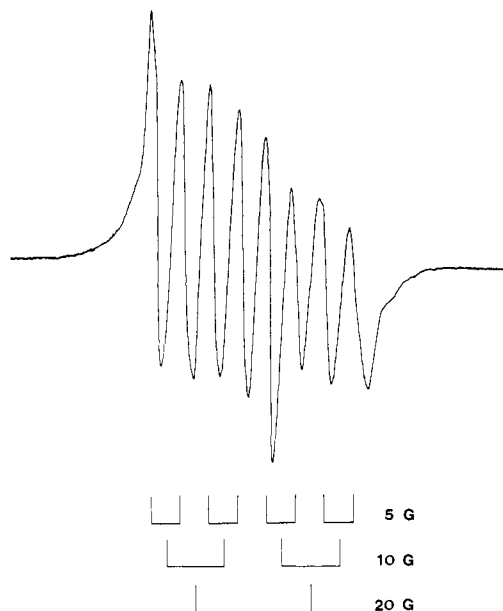


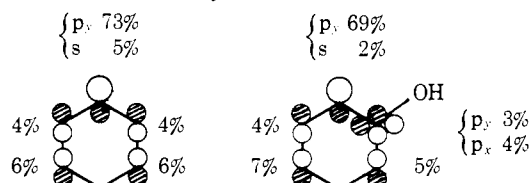
Figure 2. ESR spectrum of 2-hydroxyphenyl generated in an argon matrix by photolysis of 2-iodophenol.

Table I. The Observed and Calculated (INDO) Isotropic Coupling Constants (in G) of 2-Hydroxyphenyl and Phenyl Radicals

Proton	2-Hydroxyphenyl		Phenyl	
	Obsd	Calcd	Obsd	Calcd
H ₂		+1.4 ^a	+17.4	+18.7
H ₃	+10	+9.1	+5.9	+6.1
H ₄	<2	+3.2	+1.9	+3.9
H ₅	+5	+5.7	+5.9	+6.1
H ₆	+20	+22.5	+17.4	+18.7

^a The coupling constant predicted for the OH proton.

between the coupling constants of meta protons $A(\text{H}_3)$ and $A(\text{H}_5)$. Depicted schematically below are the LCAO descriptions of the semifilled orbitals of phenyl and 2-hydroxyphenyl given by the simpler one-electron molecular orbital theory EHT.⁷



Both orbitals are weakly bonding with respect to the in-plane σ bonds of the aromatic ring and place approximately 70% of the spin density at the broken σ orbital of the carbon-1, and $4 \simeq 7\%$ each at the p_y orbitals of the ortho and meta carbons. A notable exception is the involvement of the p_x orbital ($\sim 4\%$) of the carbon-2 in the 2-hydroxyphenyl radical, increasing the bonding nature of the orbital between the carbons-1 and -2. This can be attributed to the inductive effect of the electronegative hydroxy group. The increased coupling to the proton-3 must then result from the direct overlap between the p_x orbital of the carbon-2 and the $1s$ orbital of the hydrogen-3.

The resonance-originated stability of phenoxy radical is well known. An extremely interesting question about

(7) R. Hofmann, *J. Chem. Phys.*, **39**, 1307 (1963).

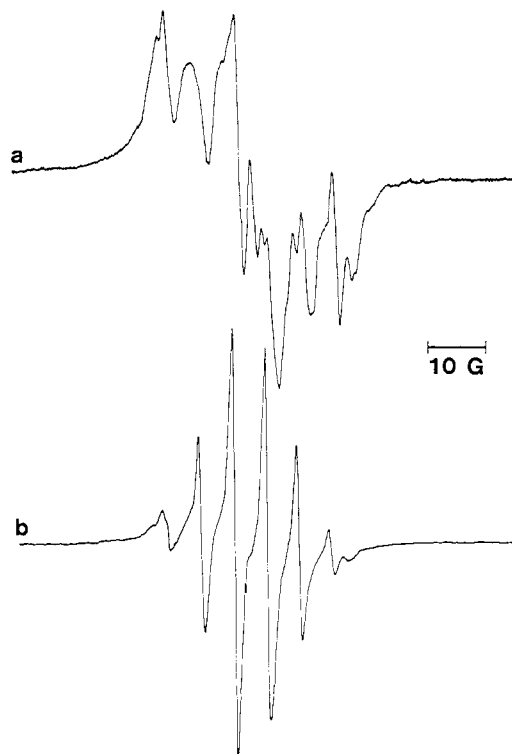
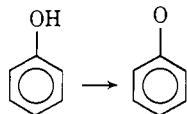


Figure 3. ESR spectra of the pyrolysate (at 700°) of 2-iodophenol trapped in an argon matrix; (a) observed at 4.6°K, (b) observed at 8°K.

2-hydroxyphenyl Ib is whether the intramolecular hydrogen transfer could be induced thus affecting the isomerization to the phenoxy radical. The radical Ib



was found to be stable against further uv irradiation. No change in the spectrum was observed when the matrix was warmed to 20°K. Nor was the change observed when the radicals were generated in nitrogen matrix and warmed to 50°K.

However, when 2-iodophenol was pyrolyzed at 700° and the resulting pyrolysate was trapped in an argon matrix, a completely different spectrum was obtained (Figure 3a). The spectrum was recognized as that of Jahn-Teller distorted, immobilized, and randomly oriented cyclopentadienyl radicals.⁸ On warming the matrix to 8°K, the spectrum changed to a sharp sextet characteristic of the hfs due to five equivalent protons (Figure 3b). The change was found to be completely reversible. The sharp sextet is attributed to cyclopentadienyl with C_5 symmetry, rapidly rotating in plane within the matrix. Lossing and coworkers⁹ reported earlier that the phenoxy radicals decarbonylate at ~900° to yield cyclopentadienyl and carbon monoxide. We therefore concluded the following scheme for the pyrolysis of 2-iodophenol.¹⁰

(8) E. Hedaya, *Accounts Chem. Res.*, **2**, 367 (1969); G. R. Liebling, and H. M. McConnell, *J. Chem. Phys.*, **42**, 3931 (1965).

(9) A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *J. Amer. Chem. Soc.*, **82**, 5593 (1960).

(10) The present experiment showed that the decarbonylation occurs at temperatures lower than that reported in ref 9. This might be due to an experimental artifact or more likely to the exothermic nature of the hydrogen-transfer process.

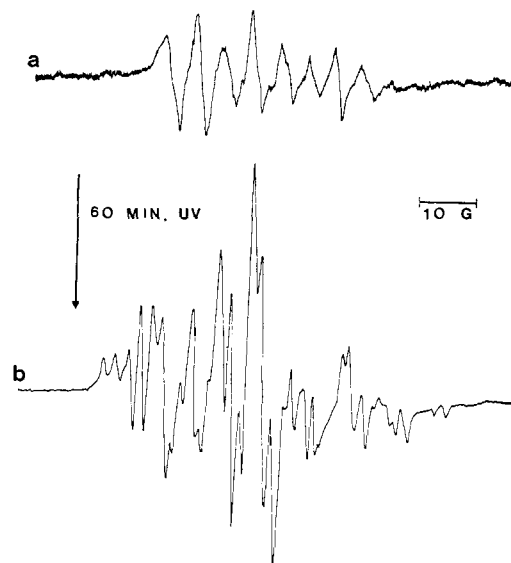
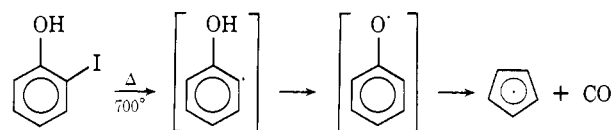
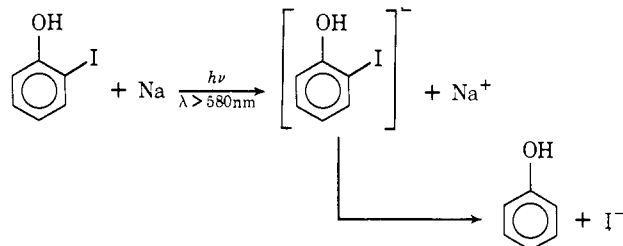


Figure 4. ESR spectra obtained when an argon matrix containing 2-iodoanisole was irradiated with uv (a) for 5 min and (b) for 60 min.



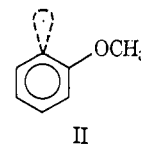
2-Hydroxyphenyl could also be generated by dissociative photoelectron transfer process. The spectrum identical with Figure 2 was obtained when the argon matrix containing 2-iodophenol and Na atoms was irradiated with red light.



When the intensity of Na beam was increased, some hydroxyphenyl was formed through vapor-phase collisions. No phenoxy radical was formed by collisions, however. It is concluded, therefore, that the intramolecular hydrogen transfer of Ib must occur at temperature above 300°.

2-Methoxyphenyl Radicals

The electronegativity of the methoxy group is similar to that of the hydroxy group. The esr spectrum of 2-methoxyphenyl is, therefore, expected to be similar to that of 2-hydroxyphenyl. Figures 4a and 4b are the spectra obtained when an argon matrix containing 2-iodoanisole was irradiated with uv for 5 and 60 min, respectively. The weak octet seen in Figure 4a is indeed very similar to that of 2-hydroxyphenyl. It is hence assigned to the 2-methoxyphenyl radical of σ state II. The spectrum in Figure 4b is most interesting.



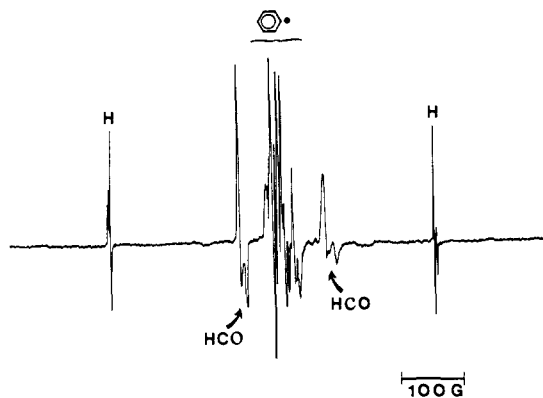
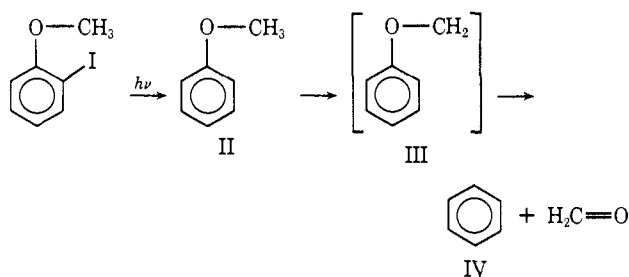


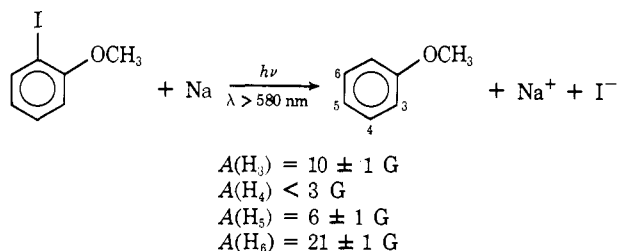
Figure 5. Same as Figure 4b except scanned over 1000 G. Note the signals due to hydrogen atoms and $\text{HC}=\text{O}$ radicals.

It turned out to be that of phenyl radicals observed and analyzed earlier in detail.¹ The sequence of reactions under uv irradiation must be



The formation of formaldehyde along with the phenyl radical is supported by the detection of hydrogen atoms and formyl radicals $\text{HC}=\text{O}$ (Figure 5). The reaction $\text{H}_2\text{C}=\text{O} \rightarrow \text{H}\cdot + \text{HC}=\text{O}$ is known to occur under uv irradiation.¹¹

In the photolysis sequence discussed above, a well-resolved spectrum of the radical II could not be obtained free from the overlapping phenyl signal. However, an excellent spectrum of II was obtained by means of the dissociative photoelectron transfer process (Figure 6a), from which the following coupling constants were assessed.



Again the assignment of the observed splittings to the specific protons was done by comparison with the known coupling constants of phenyl radicals and those predicted by INDO molecular orbital calculation. The proximity of these coupling constants to those of the corresponding protons of 2-hydroxyphenyl is remarkable.

When the temperature of the matrix exhibiting the spectrum in Figure 6a was raised to 14°K, the spectrum changed drastically (Figure 6b). The change was irreversible. The broad triplet pattern can be readily

(11) F. J. Adrian, E. L. Cochran, and V. A. Bowers, *J. Chem. Phys.*, **36**, 1661 (1962).

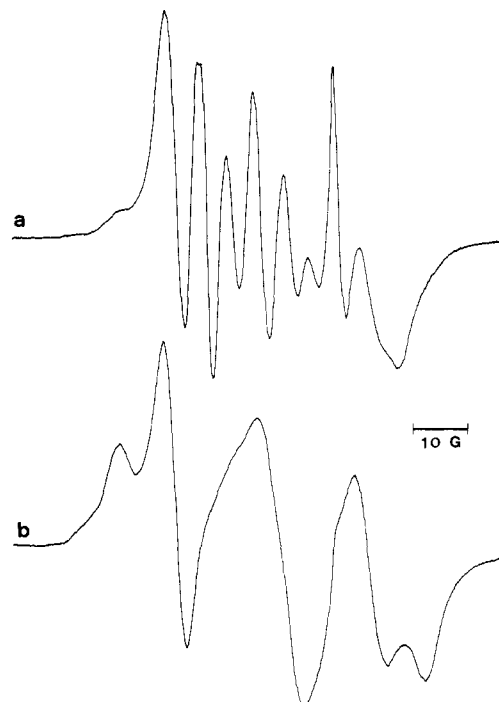
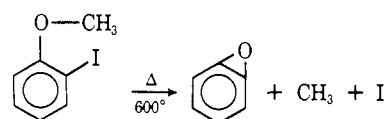


Figure 6. (a) ESR spectrum of 2-methoxyphenyl generated in an argon matrix by the method of dissociative photoelectron transfer process. (b) The spectrum of the above matrix after it had been warmed to 14°K and cooled back to 4.6°K.

recognized as that of monosubstituted methyl radicals immobilized in a matrix.¹² The spectrum is, therefore, assigned to the phenoxyethyl radical III possessing the coupling constants of ~ 22 G to the two α protons. Irradiation of this matrix with uv light resulted in the disappearance of the signal due to phenoxyethyl and the appearance of the signal due to phenyl radicals, as expected. The isomerization and dissociation sequence $\text{II} \rightarrow \text{III} \rightarrow \text{IV}$ is thus firmly established.

When 2-iodoanisole was pyrolyzed, the resulting matrix exhibited an extremely intense signal of methyl radicals only. The formation of epoxybenzynes, for example, could account for the total absence of other radicals.



This suggestion is tentative, however, and will be the subject of future investigation.

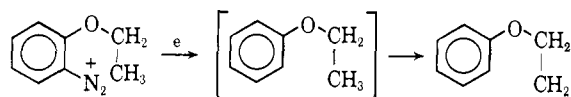
Summary and Comments

We have thus shown that both 2-hydroxyphenyl and 2-methoxyphenyl are σ radicals and that thermal or photoexcitation of these radicals result in the intramolecular hydrogen abstraction from the respective substituent group. It is remarkable, however, that temperature above 300° is needed for this to occur in the case of 2-hydroxyphenyl, while temperature of only 14°K is required for the isomerization of 2-methoxyphenyl to phenoxyethyl.

Generally speaking 1-4 hydrogen transfer is easier than 1-3 transfer because of the steric advantage ren-

(12) See, for example, P. H. Kasai, *J. Amer. Chem. Soc.*, **94**, 5950 (1972).

dered by the five-membered ring transition state. Nevertheless, the 1-4 or 1-5 hydrogen transfer in *n*-alkyl radicals requires temperature above 200° with $E_A \leq 9$ kcal/mol.¹³ Beckwith and Gara¹⁴ demonstrated, however, the occurrence of 1-5 hydrogen transfer of 2-ethoxyphenyl in aqueous solution by reducing 2-ethoxybenzenediazonium ion and detecting by esr the 2-phenoxyethyl radicals.

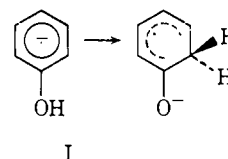


The activation energy for this type of unimolecular rearrangement must be significantly lower for aryl radicals. We must also note that the advantage of the five-membered ring transition state for the isomerization of 2-methoxyphenyl can only be realized when the orientation of the methoxy group is *cis* relative to the radical site. The extremely facile isomerization observed here indicates, at least for those radicals having the *trans* arrangement, an onset of the rotational motion of the methoxy group at a temperature lower than that required for the hydrogen transfer.

(13) See, for example, a review article by A. Fish, *Quart. Rev., Chem. Soc.*, **18**, 243 (1964).

(14) A. L. J. Beckwith and W. B. Gara, *J. Amer. Chem. Soc.*, **91**, 5689 (1969).

Our chemical knowledge portrays that the phenoxy radical is more stable than 2-hydroxyphenyl. An INDO molecular orbital calculation also showed the energy difference of 3.2 eV in favor of the phenoxy radical. The difficulty of the hydrogen transfer in the case of 2-hydroxyphenyl can be attributed to the fact that the O-H bond is stronger than the C-H bond but surely more importantly to the fact that the homolytic cleavage of the O-H bond of phenol leaves the resulting phenoxy radical in its excited state. The phenoxy radical is a π radical in its ground state. The hydrogen transfer in 2-hydroxyphenyl thus can be viewed as a symmetry forbidden process involving a $n-\pi^*$ excited state of the phenoxy radical. The situation may be compared with an extremely facile proton transfer in phenol anions generated within an argon matrix at liquid helium temperature.¹⁵



The proton transfer in this case does not involve the crossing of σ and π radical states.

(15) P. H. Kasai and D. McLeod, Jr., *J. Amer. Chem. Soc.*, **94**, 6872 (1972).

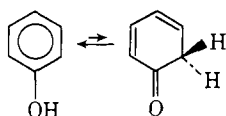
Electron Spin Resonance Study of Heterocycles. IV. Anion Radicals of Phenols and Hydroxypyridines¹

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Contribution from the Union Carbide Corporation, Tarrytown Technical Center, Tarrytown, New York 10591. Received September 25, 1973

Abstract: Anions of phenol, dihydroxybenzenes, and hydroxypyridines were generated in argon matrices and were examined by electron spin resonance spectroscopy. The spectral analyses revealed that not only the anions of phenol and dihydroxybenzenes but also those of 2- and 4-hydroxypyridines possess the ketonic structure $-\text{CH}_2\text{-CO}^-$. The observed reversal of the enol-keto tautomerism in the anionic state is attributed to the better electron-accepting capacity of the keto form. 3-Hydroxypyridine is an exception. Its anion was found to maintain the enol structure of the neutral state.

The enol-keto tautomerism of phenol is known to be dominated by the enol form.

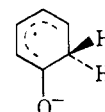


The resonance energy consideration suggests that the enol form is 17 kcal more stable than the keto form.² Recently, however, we have found that the anions of phenol generated in argon matrix possess the keto structure depicted below.³

(1) Part III: P. H. Kasai and D. McLeod, Jr., *J. Amer. Chem. Soc.*, **95**, 4801 (1973).

(2) See, for example, J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. E. Benjamin, New York, N. Y., 1965, p 862.

(3) P. H. Kasai and D. McLeod, Jr., *J. Amer. Chem. Soc.*, **94**, 6872 (1972).



Thus, the negative charge is localized on the electronegative oxygen atom, while the spin density is delocalized over the conjugated section. Phenol has a low-ionization potential (~ 8.5 eV) and should behave as an electron donor. On the other hand, a carbonyl group linked to a conjugated system is known to constitute a good electron trap. We proposed, therefore, that the 1-3 proton transfer of the enol anion, hence the reversal of the enol-keto tautomerism in the anionic state, be attributed to the better electron-accepting capacity of the keto form.

Presented in this report are the results of electron spin resonance (esr) studies of anion radicals of hy-