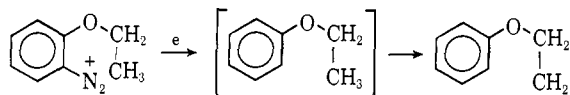dered by the five-membered ring transition state. Nevertheless, the 1–4 or 1–5 hydrogen transfer in *n*-alkyl radicals requires temperature above 200° with $E_A \leq 9$ kcal/mol.[13] Beckwith and Gara[14] demonstrated, however, the occurrence of 1–5 hydrogen transfer of 2-ethoxyphenyl in aqueous solution 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–π^* 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]

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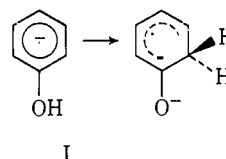
The proton transfer in this case does not involve the crossing of σ and π radical states.

(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 Hydroxypyridines[1]

Paul H. Kasai* and D. McLeod, Jr.

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 –CH₂–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.
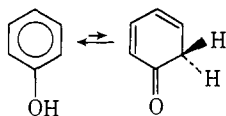
The resonance energy consideration suggests that the enol form is 17 kcal more stable than the keto form.[2] Recently, however, we have found that the anions of phenol generated in argon matrix possess the keto structure depicted below.[3]

(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).
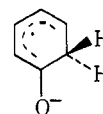
Thus, the negative charge is localized on the electronegative oxygen atom, while the spin density is delocalized over the conjugated section. Phenol has a low-ionization potential ($\sim$8.5 eV) and should behave as an electron donor. On the other hand, a carbonyl group linked to a conjugated system 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-
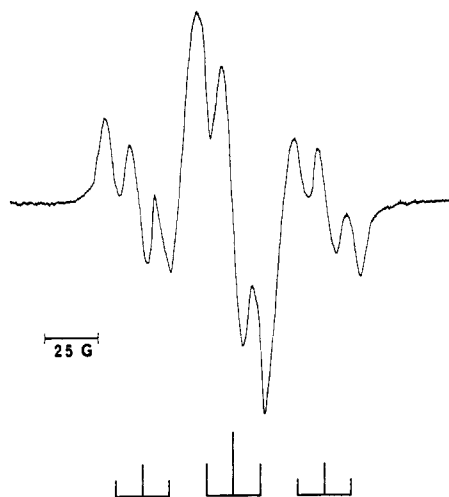
**Figure 1.** Esr spectrum of phenol anions photoinduced in an argon matrix.

droxy-substituted benzenes and pyridines generated in argon matrices. The esr spectrum of phenol anion is recounted, and those obtained from catechol, resorcinol, hydroquinone, and 2-, 3-, and 4-hydroxypyridines are shown, analyzed, and discussed. 2- and 4-hydroxypyridines are of special interest, since the oxamido forms A and B are known to dominate the tautomerism of these molecules in the neutral state.[4]
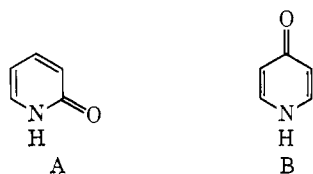
We have found that not only the anion radicals of dihydroxybenzenes but also those of 2- and 4-hydroxypyridines possess the keto structure $-CH_2CO^-$ in their ground states. The 3-hydroxypyridine anion alone was found to maintain the enol structure of the neutral molecule.

Experimental Section

A detailed description of the apparatus and the method which would permit generation of charged species within a rare-gas matrix at $\sim 4\,°K$ and the observation of the esr spectrum of the resulting ion radicals have been reported previously.[5] In the present series of experiments, Na atoms (electron donors) and hydroxy-substituted benzene or pyridine (electron acceptors) were trapped within an argon matrix, the composition being roughly 1:10:1000 for the donors, acceptors, and argon atoms, respectively. The esr spectrum of the resulting matrix was then examined before and after irradiation of the matrix with red light ($\lambda > 580$ nm). A high-pressure mercury lamp (GE, AH-6) equipped with a sharp cut-off filter (Corning, 2-62) was used for this purpose. Prior to the irradiation, the matrix exhibited only the esr signals of Na atoms. The irradiation of the matrix with red light resulted in a decrease of the Na signals and the appearance of a signal consisting of several hyperfine components centered about $g = 2.00$. The photoinduced signals are assigned to the anion radicals produced by the photoelectron transfer process.

$$\text{Na} + \text{A} \xrightarrow{h\nu} \text{Na}^+ + \text{A}^-$$
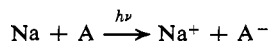
All the esr spectra were obtained while the matrix was maintained

(4) A. R. Katritzky and J. M. Lagowski, *Advan. Heterocycl. Chem.*, 1, 339 (1963).
(5) P. H. Kasai, *Accounts Chem. Res.*, 4, 329 (1971).
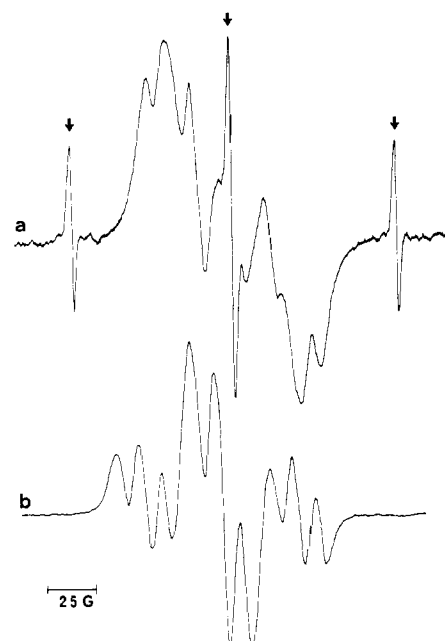
Figure 2. Esr spectra of anions of (a) monodeuterated phenol, Ph–OD, and (b) *p*-deuteriophenol generated in argon matrices. The sharp triplet indicated by the arrows is due to D atoms.

at $\sim 4\,°K$. The frequency of the spectrometer locked to the loaded sample cavity was 9.425 GHz.

Phenol, dihydroxybenzenes, and hydroxypyridines were obtained from Aldrich Chemical Co. and purified further by sublimation. Monodeuterated species Ph–OD and 2-OD–C_5H_5N were prepared by exchange with D_2O. *p*-Deuteriophenol was prepared following the method of Pedersen and Larsen.[6]

Spectra and Assignments

Phenol Anion. The spectrum photoinduced in an argon matrix containing Na and phenol is shown in Figure 1. As indicated, the spectrum has a triplet-of-triplet pattern. The spacing of the larger triplet ($A = 44$ G), however, is clearly too large to be attributed to a π-type radical possessing a planar structure of phenol. The spectrum was therefore attributed to the anion of phenol in its ketonic form I. The larger
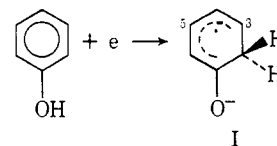

triplet is thus assigned to the two protons at carbon-2, projected above and below the skeletal plane, and the smaller triplet ($A = 12$ G) to the protons at C-3 and C-5. The structural feature of this radical is similar to that of cyclohexadienyl (II). The isotropic coupling
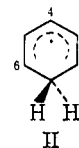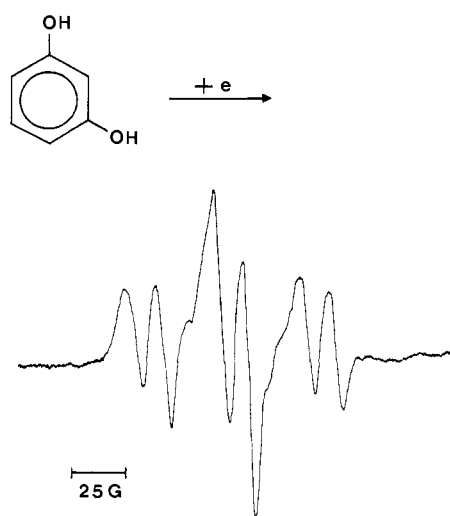

constants of II are reported[7] to be 47.5 G for the methylene protons and 10.4 G for the protons at C-2, C-4, and C-6. The proximity of the coupling constants dis-

(6) T. Pedersen and N. W. Larsen, *J. Label. Compounds*, 5, 195 (1969).
(7) H. Fisher, *J. Chem. Phys.*, 37, 1094 (1962); S. Ohnishi, T. Tanei, and I. Nitta, *ibid.*, 37, 2402 (1962).
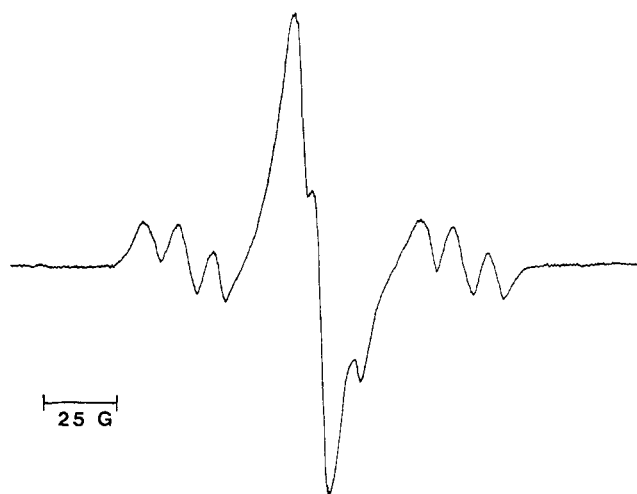
Figure 3. Esr spectrum of catechol anions generated in an argon matrix.


Figure 4. Esr spectrum of anions of resorcinol generated in an argon matrix.

cussed above to those of the corresponding protons of cyclohexadienyl is a strong support for the proposed structure and the assignment.

Figure 2a shows the spectrum obtained when the experiment was repeated with monodeuterated phenol Ph–OD. The doublet-of-triplet pattern observed here is exactly that expected from the proposed assignment. It provides an unequivocal proof for the migration of the hydroxy proton. These patterns, however, could also arise if the proton migration occurs to the para position. Figure 2b is the spectrum obtained using p-deuteriophenol. Other than the slightly improved resolution, it is identical with that obtained with the nondeuterated species, indicating that the proton transfer occurs exclusively to the ortho position.

The proposed keto structure of the anion must result from the intramolecular 1–3 proton transfer of the enol anion since (1) only a mild radiation (λ >580 nm) is necessary for its generation, (2) only a trace amount of atomic hydrogen is detected, and (3) no addition or transfer to the para position occurs.

Catechol Anion. Figure 3 shows the spectrum photo-induced in an argon matrix containing Na and catechol.
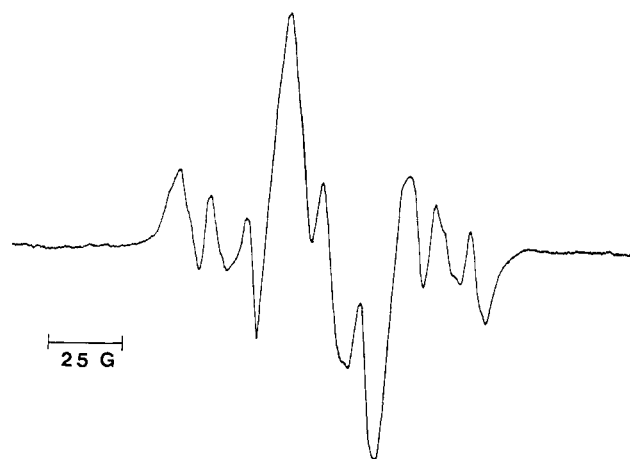

Figure 5. Esr spectrum of hydroquinone anions generated in an argon matrix.

The triplet-of-triplets is attributed to the anion of ketonic form III. Again the negative charge is lo-


III
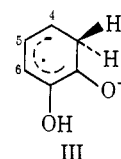
calized on the ketonic oxygen, while the spin density is delocalized over C-4–C-2. The larger triplet (A = 44 G) is thus assigned to the methylene protons at C-3 and the smaller triplet (A = 11 G) to the protons at C-4 and C-6. The proximity of these coupling constants to those of the corresponding protons of phenol anion (I) is remarkable.

Resorcinol Anion. If the anion of resorcinol should also have the ketonic ground state, the following two structures are possible.


IVA   IVB
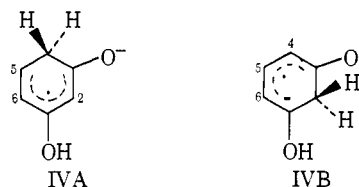
In either structure, the spin density would mostly be at carbons-1, -3, and -5. The spectrum should then possess a triplet-of-doublet pattern, the large triplet arising from the coupling to the methylene protons and the small doublet from the proton at C-5. This was indeed found to be the case. See Figure 4, the spectrum photoinduced in an argon matrix containing Na and resorcinol. The spacings are measured to be 38 and 12 G for the triplet and the doublet, respectively. As expected, these values are very similar to those of the corresponding protons of phenol anion (I). It cannot be determined from this spectrum alone, however, which of the structures IVA and IVB is actually assumed by the anion. Our attempts to prepare selectively deuterated material failed because of a rapid proton exchange at C-2, C-4, and C-6 in an aqueous system.

Hydroquinone Anion. Figure 5 shows the spectrum of the hydroquinone anions generated in an argon matrix. The triplet-of-triplet pattern is quite discerni-
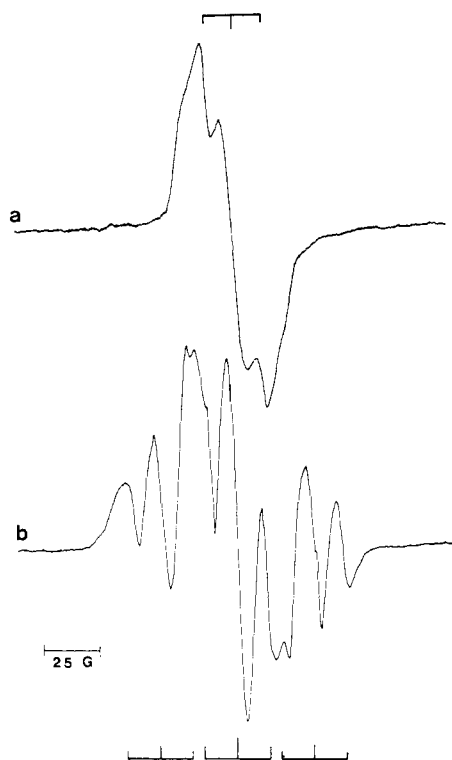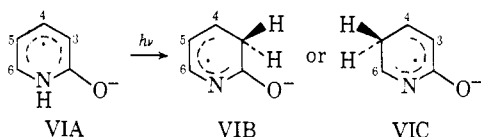
Figure 6. Esr spectra of anions of 2-hydroxypyridine generated in an argon matrix and observed (a) before and (b) after the irradiation of the matrix with yellow light.

ble and is assigned to the anions having the ketonic structure V. Again the essential features of the radical
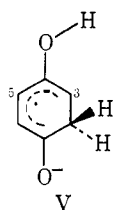

are identical with those of the phenol anion. The larger triplet (the CH_2 coupling) has a spacing of 38 G, while the smaller triplet (the couplings to the protons at C-3 and C-5) has a spacing of 10 G.

2-Hydroxypyridine Anion. Figure 6a is the spectrum photoinduced in an argon matrix containing Na and 2-hydroxypyridine. When the matrix exhibiting this spectrum was subsequently exposed to more energetic yellow light (λ >480 nm) for 10 min, the spectrum changed to that shown in Figure 6b. As discussed earlier, 2-hydroxypyridine exists mostly as 2-pyridone, its oxamido tautomer A. We propose to assign the first spectrum to the anion of 2-pyridone (VIA) and the latter to the anion of ketonic structure VIB or VIC.

The transfer of the N hydrogen in VIA to C-6 upon irradiation is ruled out since the resulting structure is not a possible keto form of the original enol.

The resonance signal in Figure 6a possesses an overall spread of only $\sim$30 G and is consistent with the
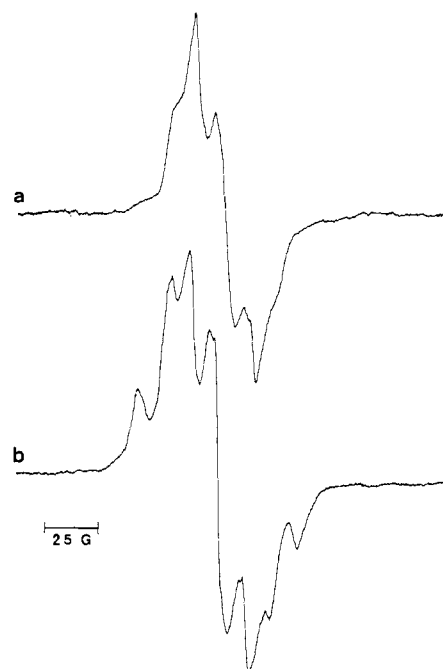
Figure 7. Esr spectra of anions of monodeuterated 2-OD-C_5H_4N observed (a) before and (b) after the irradiation of the matrix with yellow light.

planar π radical VIA. The triplet pattern indicated (A = 11 G) is attributed to the protons at C-4 and C-6.

The spectrum in Figure 6b is an overlapping triplet of triplets. The larger triplet (A = 33 G) is assigned to the methylene protons and the smaller triplet (A = 12 G) to the protons at C-4 and C-6. We believe the structure VIB is responsible for this pattern. The most pertinent resonance structures of VIB must be those in which the negative charge is shared between the oxygen and nitrogen atoms.
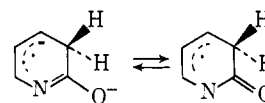
The unusually small coupling constant to the methylene protons thus can be rationalized. From the structure VIC one would expect the methylene coupling of the normal magnitude ($\sim$40 G). The presence of a barrier for the conversion of VIA to VIB can also be appreciated, since the conversion is likely to involve the higher lying enolic state.

Shown in Figures 7a and 7b are the spectra obtained from an argon matrix containing Na and monodeuterated 2-OD-pyridine after successive irradiation with red light and yellow light. Consistently with the assignment proposed above, the deuteration has little effect upon the spectrum of VIA, while it produces a profound change upon the spectrum of VIB. Thus, the migration of the N-H proton is unequivocally supported.

3-Hydroxypyridine Anion. The spectrum photoinduced in an argon matrix containing Na and 3-hydroxypyridine is shown in Figure 8. Subsequent irradiation of the matrix with more energetic light produced no change in the spectrum. The over-all spread of the signal is $\sim$30 G, suggesting that a totally planar π radical is responsible. The spectrum is assigned to
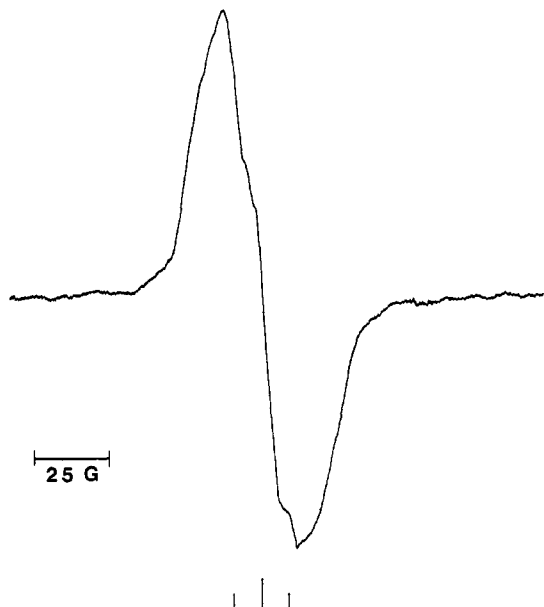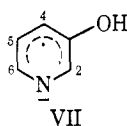
Figure 8. Esr spectrum of anions of 3-hydroxypyridine generated in a argon matrix.

the anion VII. The semiempirical SCF molecular or-

VII

bital calculation, INDO,[8] suggests that the protons at C-2 and C-4 are responsible for the barely resolved triplet pattern indicated in the figure (A = 9 G).

4-Hydroxypyridine Anion. Similarly to 2-hydroxypyridine, 4-hydroxypyridine exists mostly as 4-pyridone, its oxamido tautomer B. Figure 9a is the spectrum photoinduced in an argon matrix containing Na and 4-hydroxypyridine. Subsequent irradiation of the matrix with yellow light changed the narrow signal to a familiar triplet of triplets (Figure 9b). These signals are assigned, respectively, to the anions of the oxamido form VIIIA and the keto form VIIIB. The triplet

VIIIA   VIIIB
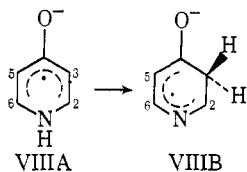
feature (A = 9 G) of Figure 9a is attributed to the protons at C-2 and C-6. The large triplet (A = 41 G) of Figure 9b is assigned to the methylene protons at C-3, while the smaller triplet (A = 11 G) is assigned to the protons at C-2 and C-6.

The transfer of the N proton of VIIIA to C-2 upon irradiation is ruled out, since the resulting structure is not a possible keto form of the original enol.

Summary and Comments

The assignments and observed coupling constants of the anions of phenols and hydroxypyridines presented above are summarized in Table I. The coupling tensors

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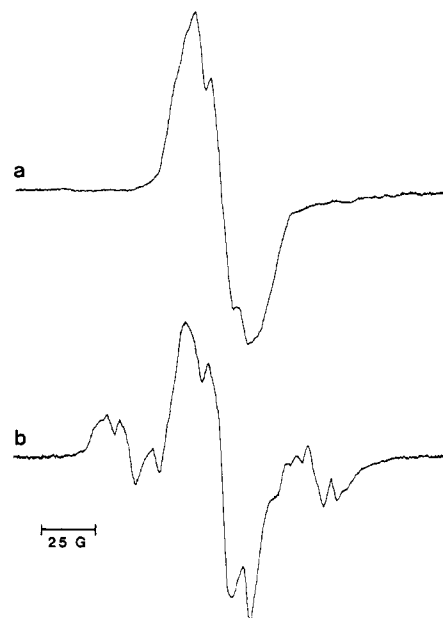

Figure 9. Esr spectra of anions of 4-hydroxypyridine generated in an argon matrix and observed (a) before and (b) after the irradiation of the matrix with yellow light.

**Table I.** Observed Isotropic Coupling Constants (in G) of Anions of Phenols and Hydroxypyridines[a]

Anions (structure)	CH₂	C-2	C-3	C-4	C-5	C-6
Phenol (I)	44		12		12	
Catechol (III)	44			11		11
Resorcinol (IVA or B)	38			12		
Hydroquinone (V)	38	10		10		
2-Hydroxypyridine (VIA)				11		11
(VIB)	33			12		12
3-Hydroxypyridine (VII)		9		9		
4-Hydroxypyridine (VIIIA)		9				9
(VIIIB)	41	11				11

[a] Accuracy ±1 G.

to the methylene protons are expected to be large and dominated by the isotropic term. The coupling tensors to the protons in the conjugated section of these radicals, on the other hand, should possess significant anisotropy. The broadness and often-noticed additional structures of the spectra are due to such anisotropy. The situation is compounded with the fact that the directions of the principal axes of the coupling tensors to different protons are not coincident. The isotropic coupling constants of these protons could still be assessed from the observed spectra since the major pattern of the spectra is dictated by the signal corresponding to the direction perpendicular to the molecular plane, the only direction along which the principal axes of all the π-type protons are coincident, and the contribution of the dipolar part to the coupling element is negligible compared to the isotropic part.

As stated earlier, we proposed to attribute the observed reversal of the enol–keto tautomerism in the anionic state to the better electron-accepting capacity of the keto structure. Depicted in Chart I are the

Chart I
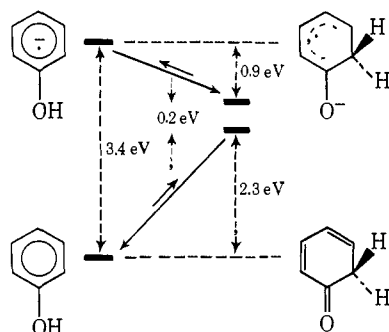
energetic relations between the enol and keto forms of phenol and their anions calculated by INDO molecular orbital theory.[8] The standard bond lengths and angles given in ref 8 were used for the calculation. Because of the uncertainties of the assumed structures, the exact energy differences given above should be viewed with some reservation. Nevertheless, the relative stabilities of the four species predicted by the theory are in excellent agreement with the experimental results.

The photoconversion of the anions of 2- and 4-pyridones (VIA and VIIIA) to their ketonic tautomers (VIB and VIIIB) is an interesting phenomenon since

the –NH– group is isoelectronic to –CH_2–. The greater stability of the keto forms may be attributed to their structural feature where both the oxygen and nitrogen atoms can share the anionic charge.

That 3-hydroxypyridine maintains the enol structure in its anionic state can also be attributed to a structural feature of the possible keto forms.

In these structures the negative charge of the anion cannot be imparted to the nitrogen atom. Perhaps in line with these observations, no significant energy difference (>0.2 eV) was predicted by INDO molecular orbital theory between the anions of the enol form (VII) and those of the keto structures shown above.

Finally, as we have reported earlier, the enamine–imine tautomerism of pyrrole is also reversed in its anionic state.[9]
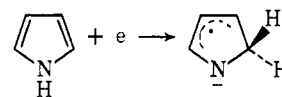
The similarity in the rationale of the reversal of tautomerism of pyrrole, phenols, and hydroxypyridines should be appreciated.

(9) Part II: P. H. Kasai and D. McLeod, Jr., *J. Amer. Chem. Soc.*, **95**, 27 (1973).

Spectral Studies of Monothioacetylacetone and Its Sodium and Potassium Derivatives

Olavi Siiman, James Fresco, and Harry B. Gray*

Contribution No. 4799 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91109, and the Department of Chemistry, McGill University, Montreal, Quebec, Canada. Received July 19, 1973

Abstract: Infrared and Raman spectra of monothioacetylacetone and its dideuterio derivative recorded between 4000 and 200 cm^{-1} establish that the ligand exists predominantly in the thio–enol form. The infrared and Raman spectra of sodium and potassium monothioacetylacetonates, as solids and in solution, have been measured over the range 1700–100 cm^{-1}. A planar-chelated structural model for the alkali metal salts is proposed from vibrational assignments based on normal-coordinate calculations. The proton magnetic resonance spectra of solutions containing the sodium and potassium salts of monothioacetylacetonate show two sets of methyl and γ-proton signals, attributable to cis and trans isomers of monothioacetylacetonate. Conductance data establish that substantial ion pairing occurs in DMSO solutions between Na$^+$ or K$^+$ and monothioacetylacetonate, but because of very fast ligand substitution only a single set of pmr signals is observed for each geometrical isomer.

Although the vibrational and nuclear magnetic resonance spectra[1,2] of acetylacetone and alkali metal derivatives[3–5] of β-diketones have been studied

(1) H. Ogoshi and K. Nakamoto, *J. Chem. Phys.*, **45**, 3113 (1966).
(2) L. W. Reeves, *Can. J. Chem.*, **35**, 1351 (1957).
(3) K. Shobatake and K. Nakamoto, *J. Chem. Phys.*, **49**, 4792 (1968).
(4) E. E. Ernstbrunner, *J. Chem. Soc. A*, 1558 (1970).

fairly extensively, the monothio analogs have not been similarly characterized. We have therefore analyzed the ir and Raman spectra of monothioacetylacetone (TAA) and both solids and solutions of the sodium and potassium salts of TAA$^-$. Nmr spectra have been measured for TAA and solutions containing NaTAA and KTAA. To further characterize the properties of

(5) A. J. Carty, D. G. Tuck, and E. Bullock, *Can. J. Chem.*, **43**, 2559 (1965).