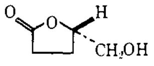
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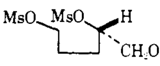
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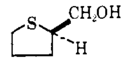
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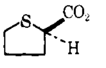
iv

We are greatly indebted to Dr. Yuko Nakahara of this Laboratory for this unambiguous synthesis.

(10) K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Jpn.*, **40**, 2018 (1967); W. Drenth, *Recl. Trav. Chim. Pays-Bas*, **86**, 318 (1967); N. T. Anh, *Chem. Commun.*, 1089 (1968); W. Jefford and U. Burger, *Chimia*, **25**, 297 (1971); C. L. Liotta, *Tetrahedron Lett.*, 523 (1975). A recent suggestion has been made that the S_N2' should be syn with neutral, but anti with anionic, displacing groups (R. L. Yates, N. D. Epiotis, and F. Bernardi, *J. Am. Chem. Soc.*, **97**, 6615 (1975). This is an interesting, but certainly insufficient,[1] suggestion.

(11) There has been considerable discussion whether concerted S_N2' reactions ever occur (F. G. Bordwell, *Acc. Chem. Res.*, **3**, 281 (1970)). They have been said to be "intellectually unreasonable" or "abhorrent" (R. A. Sneen and J. V. Carter, *J. Am. Chem. Soc.*, **94**, 6990 (1972), and footnote 26). These arguments are really concerned with the extent of bond breaking and bond forming at the transition state. It would not be surprising to find that these parameters vary from case to case. See also, in another context, W. H. Saunders, Jr., *Acc. Chem. Res.*, **9**, 9 (1976), and D. J. McLennan, *ibid.*, **9**, 281 (1976).

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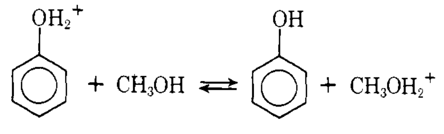
The Proton Affinities of Phenol

Sir:

Phenol and various of its derivatives are known in solution to protonate both at oxygen and on the aromatic ring.[1] The relative extent of protonation at the two sites depends not only on the detailed pattern of substitution, but also on temperature and on the nature of the solvent system. For example, the ratio of oxygen to ring protonation in *p*-cresol varies from 5.5 in pure fluorosulfonic acid to nearly zero in a solution which is 30% by weight SbF_5.[1c] The complex behavior of such systems in solution has seriously hampered attempts at unraveling the electronic structure of either the oxygen or ring protonated ions and has made it difficult to establish the degree to which a phenyl ring influences protonation at oxygen or a hydroxy or alkoxy group affects reaction on the aromatic ring.

In this communication, we describe the results of our combined experimental and theoretical efforts to obtain a quantitative measure of the relative affinities for oxygen and ring protonation of phenol in the gas phase. Our data should enable assessment of both the magnitudes of specific interactions between the phenyl and hydroxy groups and of the influence of solvent on the site of protonation.

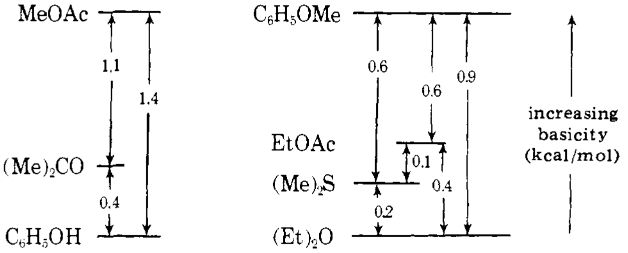
Both the oxygen and ring proton affinities of phenol may be estimated using quantitative molecular orbital calculations. The oxygen proton affinity of phenol may be estimated by biasing the experimental proton affinity of methanol (182.2 kcal/mol[2]) by the calculated energy for the *isodesmic*[3] process,



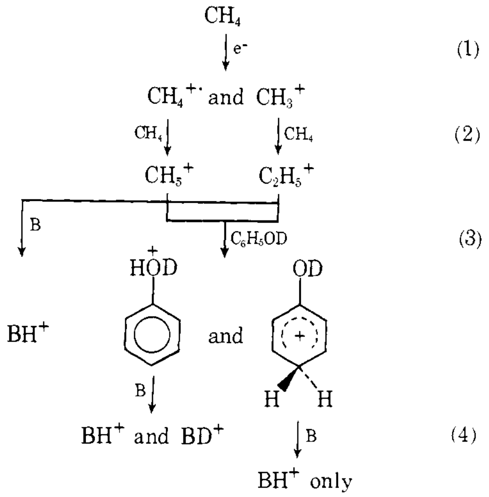
ΔE(STO-3G)[4,5] = −1.0 kcal/mol

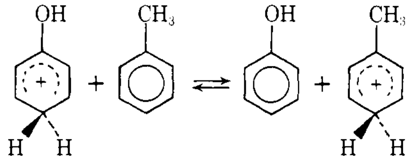
relating the two basicities. The value arrived at in this manner (181.2 kcal/mol) is far smaller than the experimental proton affinity of phenol (195.5 kcal/mol), as determined by pulsed ion cyclotron resonance equilibrium experiments[8] using the method of multiple overlaps[2a] (Scheme I). Such a value is in good accord with a recent determination of the proton affinity of phenol of 195.0 kcal/mol using high pressure mass spectrometry.[9] The theory's estimate for the energy of protonation of phenol on the aromatic ring is obtained by biasing ΔE for the reaction shown below by the experimental proton affinity of toluene (188.7 kcal/mol).[2a,10] This value of 196.1 kcal/mol

Scheme I



Scheme II





ΔE(STO-3G) = 7.4 kcal/mol

is in reasonable agreement with the measured proton affinity of phenol. It appears, therefore, that, in the absence of solvent, phenol protonates on the aromatic ring,[11] and that the energetic preference over oxygen protonation is sizable (~15 kcal/mol).

We have devised a labeling experiment to provide us with a semiquantitative estimate of the enthalpy for protonation of phenol at oxygen. The predominant ion-molecule reactions which take place when a mixture of methane, C_6H_5OD, and a base B of known proton affinity is added to a pulsed ICR spectrometer (in proportions of 100:10:1, respectively) are shown in Scheme II. Electron impact produces CH_4^+ and CH_3^+ predominantly which react rapidly with the methane buffer gas to generate CH_5^+ and $C_2H_5^+$. Both of these ions react exothermically with phenol to produce both the ring and the oxygen protonated forms and with B to produce BH^+. If the proton affinity of the base B is sufficiently high, it is able to deprotonate phenol. The main feature of this experiment for estimating the enthalpy for protonation of phenol at oxygen is that an ion of *m/e* corresponding to BD^+ will be observed only if reaction of B with the oxygen protonated phenol is exothermic, thermoneutral, or slightly (≤1 or 2 kcal/mol) endothermic. Bases with proton affinities significantly lower than phenol protonated at oxygen will not extract deuterium, while bases with equal or greater proton affinities will show BD^+ in their mass spectra. By using a series of bases of increasing strength and by monitoring the onset of production of BD^+, it should, therefore, be possible to determine an ap-

Table I. Determination of the Oxygen Proton Affinity of Phenol

Base	Proton affinity above that of ring protonated phenol (kcal/mol)[a]	Observation of BD^+?
HCO_2Et	3	Yes
HCO_2Me	7	Yes
MeCHO	9	Yes
CF_3CO_2Me	14	Yes
$CH_3CH{=}CH_2$	~15	Yes
HCN	20	No
CO	~56	No
CH_4	~73	No

[a] From ref 2, except: propene, unpublished; CO and CH_4, D. Holtz, J. L. Beauchamp, and S. S. Woodgate, *J. Am. Chem. Soc.*, **92,** 7484 (1970).

proximate enthalpy for protonation of phenol at oxygen. Our data are displayed in Table I. Reference bases methane, carbon monoxide, and hydrogen cyanide do not result in the formation of detectable amounts of BD^+. The proton affinity of HCN, the strongest of these bases, is some 20 kcal/mol below that of phenol (at carbon). On the other hand, deuterium incorporation into propene, methyl trifluoroacetate, acetaldehyde, and methyl- and ethylformates has been observed, implying that the base strengths of these compounds are greater than that of phenol at oxygen. The proton affinity of propene, the weakest of these bases, is about 15 kcal/mol below that of phenol. We conclude, therefore, that the oxygen proton affinity of phenol is some 13-20 kcal/mol less than the enthalpy for reaction on the ring, a value which is in good accord with our theoretical estimate (14.9 kcal/mol).

In aqueous solution protonation of phenol occurs predominantly on oxygen. In view of the present gas phase result regarding the sizable (~15 kcal/mol) preference for protonation on the aromatic ring, it is apparent that the solvent system is a major factor in determining the site of protonation.

References and Notes

(1) For reviews see (a) D. M. Brouwer, E. L. Mackor, and C. MacLean in "Carbonium Ions", Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N.Y., 1970; (b) M. Liler, *Adv. Phys. Org. Chem.*, **11,** 267 (1975); also (c) J. W. Larsen and M. Eckert-Maksic, *J. Am. Chem. Soc.*, **96,** 4311 (1974), and references therein.

(2) (a) J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, in press. The proton affinities presented in the above reference are relative to that of ammonia, and are considered to be accurate to within ±0.2 kcal/mol. The absolute proton affinity of the standard, ammonia, has been assigned a value of 202.3 ± 2 kcal/mol; (b) also 182.1 kcal/mol by high pressure mass spectrometry, R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **98,** 1320 (1976).

(3) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, **92,** 4796 (1970).

(4) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51,** 2657 (1969).

(5) All ab initio calculations reported in this paper have been carried out using the Gaussian 70 series of computer programs.[6] Standard model geometries[7] have been used throughout, except for ring-substituent bond lengths which have been optimized.

(6) Program no. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.

(7) Neutral and substituent protonated molecules: (a) J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89,** 4253 (1967); ring protonated molecules; (b) W. J. Hehre, R. T. McIver, Jr., J. A. Pople, and P. V. R. Schleyer, *ibid.*, **96,** 7162 (1974).

(8) (a) R. T. McIver, Jr., *Rev. Sci. Instrum.*, **41,** 555 (1970); (b) J. D. Baldeschwieler and S. S. Woodgate, *Acc. Chem. Res.*, **4,** 114 (1971); (c) R. T. McIver, Jr., and R. C. Dunbar, *Int. J. Mass Spectrom. Ion Phys.*, **7,** 471 (1971).

(9) Y. Lau and P. Kebarle, *J. Am. Chem. Soc.*, **98,** 7452 (1976).

(10) J. L. Devlin, J. F. Wolf, R. W. Taft, and W. J. Hehre, *J. Am. Chem. Soc.*, **98,** 1990 (1976).

(11) This conclusion has also been reached by Beauchamp and co-workers[12] on the basis of deuterium exchange experiments and by Lau and Kebarle[9] by comparison of their experimental phenol proton affinity with a previously published theoretical value.[13] It is also consistent with the observation that the difference in proton affinities between anisole and phenol (4.8 ± 0.2 kcal/mol from our ICR measurements, see Scheme I, 4.5 kcal/mol from the high pressure mass spectrometry work of Lau and Kebarle[9]) is far smaller than that between typical aliphatic alcohols and the corresponding methyl ethers (7.9 kcal/mol for MeOH vs. $(Me)_2O$; 7.3 kcal/mol for EtOH vs. MeOEt[2]). It is, however, opposite to the conclusion reached by Martinsen and Butrill[14] as a result of their investigation of substituted benzene–water complexes in the gas phase.

(12) B. S. Freiser, R. L. Woodin, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **97,** 6893 (1975).

(13) J. M. McKelvey, S. Alexandratos, A. Streitwieser, Jr., J. L. M. Abboud, and W. J. Hehre, *J. Am. Chem. Soc.*, **98,** 244 (1976).

(14) D. P. Martinsen and S. E. Buttrill, *Org. Mass Spectrom.* **11,** 762 (1976).

(15) (a) University of California Regents Intern Fellow, 1974–1978; (b) Alfred P. Sloan Fellow, 1973–1975; (c) Alfred P. Sloan Fellow, 1974–1976.

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EXAFS: Approximation, Parameterization, and Chemical Transferability of Amplitude Functions

Sir:

Recently, extended x-ray absorption fine structure (EXAFS) spectroscopy using synchrotron radiation has gained wide recognition in providing valuable structural information for large and complex chemical or biological systems.[1-5] Major advances have been made in the understanding of the physics involved,[1,4a,6-10] which result in the improvement of the techniques of data analysis.[1,8-10] Until now, however, attention has been focused on the determination of interatomic distances via Fourier transform technique[1,8] or via curve fitting[9,10] based on the transferability of experimentally determined phase shifts. This article reports: (1) a simple analytical form for the amplitude function; (2) chemical transferability of amplitude functions; (3) the parameterization of theoretical[8b] amplitude curves; and (4) the utilization of these parameters in data analysis. The assumptions of both phase and amplitude function transferabilities in data analysis[1,8-10] greatly enhance the chemical content of EXAFS spectroscopy.

The normalized oscillatory part $\chi(k)$ of the absorption rate (μ) in EXAFS is given by[1,8]

$$\chi(k) = \frac{\mu - \mu_0}{\mu} = \frac{1}{k}\sum_i N_i F_i(k) e^{-2\sigma_i^2 k^2} \times \frac{\sin(2kr_i + \Phi_i(k))}{r_i^2} \qquad (1)$$

where $F_i(k)$ is the backscattering amplitude from each of the N_i neighboring atoms of the ith kind with a Debye-Waller factor σ_i (to account for thermal vibration and static disorder) and at a distance r_i away.[11] The phase shift $\Phi(k)$ has been parameterized with a quadratic function ($\Phi(k) = p_0 + p_1k + p_2k^2$) and shown to be chemically transferable for each pair of atoms by Citrin, Eisenberger, and Kincaid.[10] This allows accurate determination of interatomic distances for single-distance systems. For more complicated molecules with distances less than ca. 0.40 Å apart (which cannot be effectively separated by Fourier transform) more information on the amplitude function $F(k)$ is needed.

We find that, for all practical purposes, the amplitude function $F(k)$ for scatterers with atomic number $Z < 36$ can be approximated by a Lorentzian

$$F(k) = \frac{A}{1 + B^2(k - C)^2} \qquad (2)$$

where A is the peak height, $2/B$ is the width, and C is the peak position in k space. We note that a functional form of $F(k) = C/k^\beta$ ($\beta \approx 2$) has previously been utilized in fitting EXAFS spectra.[9] Our Lorentzian form, however, is preferred for