## The Position of Protonation of Anisole in Concentrated Aqueous Solutions of Strong Acids[1]

*Sir:*

It was recently reported[2] that the 270-mμ ultraviolet absorption band of phenol ethers dissolved in moderately concentrated aqueous $H_2SO_4$ decreases to about one-half its intensity as the acidity of the medium is increased, and that the relationship between absorbance and acidity takes the form of a normal sigmoid titration curve. These observations were interpreted in terms of protonation on ether oxygen, and the p$K_a$'s of a number of phenol ether oxonium ions were calculated. This conclusion, however, has been disputed[3] on the basis that the nmr spectra of anisole in $HSO_3F$ and in $HF-BF_3$ at low temperatures give evidence only of protonation on carbon[4] and that the ultraviolet spectrum of anisole in 100% $H_2SO_4$ shows no absorption at 270 mμ, but does contain bands attributable to C-protonated species at 240 and 285 mμ. It has also been reported[5] that the 270-mμ absorption of anisole dissolved in $HClO_4$ decreases only very gradually with no inflection point over the 8–9 $H_0$ units from pure $H_2O$ to 70% acid, and that a new band then begins to appear at 285 mμ. We wish to report the following information with serves to reconcile these apparently contradictory observations.

The original experiments[2] give −6.8 ($H_0$ scale[6]) as the p$K_a$ of anisole, making it half-protonated on oxygen in 77% $H_2SO_4$. From the carbon basicities of 1,3,5-trimethoxybenzene ("p$K_a$" = −3.7) and 1,3-dimethoxybenzene ("p$K_a$" = −6.5),[7] it can be estimated that anisole would be half-protonated on carbon in *ca.* 92% $H_2SO_4$. It is logical to except the conjugate acid of anisole to change from the O-protonated to the C-protonated species as the acidity of $H_2SO_4$ increases and the activity of free water goes down, for the former can be stabilized by hydrogen bonding to water whereas the latter cannot.[8] In support of this is the fact that the ultraviolet spectrum of anisole dissolved in 93% $H_2SO_4$ shows the band of the C-protonated species at 285 mμ[9] and a weak band of the O-protonated species at 270 mμ as well.

We and others[5,10] have observed that the "p$K_a$'s" of non-Hammett bases are seldom the same in $HClO_4$ and $H_2SO_4$. It seems to be generally true that, whereas bases whose conjugate acids are stabilized by hydrogen bonding to the solvent are considerably less protonated in $HClO_4$ than in $H_2SO_4$ of the same $H_0$ value, the difference is much smaller or perhaps in the opposite sense for cases where such stabilization is not possible. This effect would tend to make the gap between O- and C-protonation of anisole smaller in $HClO_4$ than it is in $H_2SO_4$, and, in $HClO_4$, C-protonation might well begin to occur before O-protonation is half-complete. This, of course, would obscure the inflection point in the titration curve for O-protonation. There is in addition an appreciable medium effect on the intensity of the 270-mμ absorption of phenol ethers in $HClO_4$: in the case of 3,5-dimethylanisole and 3-hydroxyanisole, whose C-basicites are either greater than or roughly comparable to their O-basicities and for which O-protonation should therefore not be observable by ultraviolet methods, the intensity of the 270-mμ band nevertheless drops with increasing acidity to nearly 50% of its value in pure water before C-protonation becomes visible. These two effects can explain the absence of detectable O-protonation of anisole in $HClO_4$.

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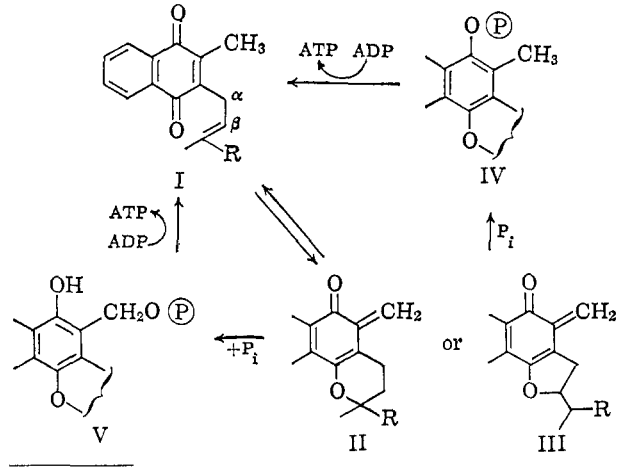
(1) Taken from a thesis submitted by L. E. Hakka to the Illinois Institute of Technology in partial fulfillment of the requirements for the Ph.D. degree.
(2) E. M. Arnett and C. Y. Wu, *J. Am. Chem. Soc.*, **82**, 5660 (1960).
(3) T. Birchall, A. N. Bourns, R. J. Gillespie, and P. J. Smith, *Can. J. Chem.*, **42**, 1433 (1964).
(4) There is now evidence that some O-protonation of anisole occurs along with C-protonation in $HF-BF_3$ solution at very low temperatures: D. M. Brouwer, E. L. Mackor, and C. Maclean, *Rec. Trav. Chim.*, **85**, 109 (1966).
(5) K. Yates and H. Wai, *Can. J. Chem.*, **43**, 2131 (1965).
(6) M. J. Jorgenson and D. R. Hartter, *J. Am. Chem. Soc.*, **85**, 878 (1963).
(7) The symbol "p$K_a$" is used to denote the value of $H_0$ at half-protonation; in the present case this is not equivalent to the negative logarithm of the true thermodynamic acidity constant for neither of these bases follows $H_0$ in its protonation.
(8) A. J. Kresge, G. W. Barry, K. R. Charles, and Y. Chiang, *J. Am. Chem. Soc.*, **84**, 4343 (1962); W. M. Schubert and R. H. Quacchia, *ibid.*, **85**, 1278 (1963); E. M. Arnett and G. W. Mach, *ibid.*, **86**, 2671 (1964).
(9) We have observed that the long-wavelength ultraviolet maxima of protonated polymethoxy- and methyl-substituted aromatic bases, whose nmr spectra indicate that these are C-protonated species, undergo a regular shift to shorter wavelengths as the number of methoxyl groups is decreased; a quantitative correlation of these spectral changes predicts that this absorption maximum occurs at 285 mμ in C-protonated anisole.
(10) E. M. Arnett and G. W. Mach, *J. Am. Chem. Soc.*, **88**, 1177 (1966).

## The Role of the Quinone in Oxidative Phosphorylation in *Mycobacterium phlei*. Evidence against Carbon–Hydrogen Bond Cleavage[1]

*Sir:*

Various mechanisms[2] proposed for the participation of the quinone in oxidative phosphorylation (sum-




(1) Sponsored in part by Grant AI-04888 from the National Institutes of Health, U. S. Public Health Service.
(2) (a) I. Chmielewska, *Biochim. Biophys. Acta*, **29**, 170 (1960); (b) E. Lederer and M. Vilkas, *Experientia*, **18**, 546 (1962); (c) K. Folkers, R. E. Erickson, and A. F. Wagner, *J. Am. Chem. Soc.*, **85**, 1534, 1535 (1963); (d) R. A. Morton, Ed., "Biochemistry of Quinones," Academic Press Inc., New York, N. Y., 1965.