

cathodically to the cation radical (7) which has a visible spectrum identical with that of 2. A stable solution of 6 could also be prepared by the antimony pentachloride oxidation of 8 in dichloromethane.

The formation of 5 during oxidation of 1 most likely occurs by nucleophilic attack on either 3 or 4 by water or other trace impurities in the solvent-electrolyte system. In neutral media, the deprotonation of 3 would be expected to be rapid compared to nucleophilic attack, and thus the most likely species to undergo demethylation under those conditions is the nitrenium ion 4. On the other hand, in more acidic media 3 is the favored species and would be expected to be more reactive toward nucleophiles than 4. The question then arises, why is 3 stable in strongly acidic media? The function of strong acid in stabilizing 3 must be the deactivation of nucleophilic impurities by protonation. Evidence for the latter effect is that 2 is oxidized irreversibly in acetonitrile containing TFA (1%) but upon addition of TFA anhydride (a very effective nucleophile scavenger) a reversible cyclic voltammogram for oxidation of 2 was observed and the solution still contained 3 (25% yield) after oxidation which required 6.5 min for total conversion of 2.

The present state of knowledge of the chemistry of nitrenium ions is largely due to the investigations of Gassman and coworkers.⁶ The reactions of aryl-nitrenium ions reflect the relative electronegativities of nitrogen and carbon providing a new means of nucleophilic aromatic substitution of anilines.⁷ While it is clear from Gassman's work that nitrenium ions are indeed intermediates in a variety of reactions involving organic nitrogen compounds, the voltammetric observation of 4 in neutral acetonitrile and the isolation of a salt of 3 along with the spectroscopic observation of 3 in strongly acidic media appears to be the first indication of stability of such species.

Protonated aryl-nitrenium ions have been observed during oxidation of several other aromatic amines, for example, di-*p*-tolylamine. The stability of the ions is greatly affected by the substitution on the aryl groups, methoxy groups being very effective stabilizing groups. Details of the anodic and antimony pentachloride oxidation of anilines to aryl-nitrenium ions will appear later.

(6) For a recent review see P. G. Gassman, *Accounts Chem. Res.*, **3**, 26 (1970).

(7) P. G. Gassman, G. A. Campbell, and R. C. Frederick, *J. Amer. Chem. Soc.*, **94**, 3884 (1972).

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Concerning the Separation of Polar and Resonance Effects in the Ionization of 4-Substituted Pyridinium Ions¹

Sir:

According to the field model,² the protonation of 4-substituted pyridines (I) and 4-substituted quinuclidines

(1) This work supported in part by the National Science Foundation.

(2) (a) F. H. Westheimer and J. G. Kirkwood, *J. Phys. Chem.*, **6**, 513 (1938); (b) L. M. Stock, *J. Chem. Educ.*, **49**, 400 (1972).

(II) to good quantitative approximation should be accompanied by (large) equal polar effects of X.



Both experimental and theoretical evidence have been obtained in support of this conclusion in analog systems. The ionization of 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids and the ionization of the para-substituted benzoic acids have been interpreted as having equal polar effects,³ providing the basis for definition of σ_R parameters.⁴ The calculation of F atom σ electron densities by CNDO/2 theory has shown equal polar effects of corresponding 4 substituents in fluorobenzenes and bicyclo[2.2.2]octyl 1-fluorides.⁵

A critical test of the behavior anticipated for I and II is made possible by recent developments. Although the ionization of 4-substituted pyridinium ions in water at 25° is rather poorly fitted by either σ_p or σ_p^+ (SD > 0.30), the data are well fitted by the dual substituent parameter (DSP) eq 1⁶ ($n = 13$; SD = 0.14).

$$\log (K/K_0)_I = 5.15\sigma_I + 2.69\sigma_R^+ \quad (1)$$

The σ_R^+ parameters, which are structurally appropriate for this reaction, are from Ehrenson, *et al.*,⁷ and are based upon independent basis sets.

The ionization constants of 4-substituted quinuclidinium ions in water at 25° have been reported for an extensive series of substituents by Grob and associates.⁸ According to the field model and eq 1, these data should follow eq 2. Figure 1 illustrates that eq 2 is indeed

$$\log (K/K_0)_{II} = 5.15\sigma_I \quad (2)$$

followed. The values of $\log (K/K_0)_{II}$ are shown plotted *vs.* σ_I with a regression slope of 5.15 indicated. The least-squares regression for this correlation is: $\log (K/K_0)_{II} = 4.81\sigma_I + 0.20$; $n = 21$, SD = 0.15, $r = 0.990$. A DSP equation analysis gives: $\log (K/K_0)_{II} = 5.21\sigma_I - 0.24\sigma_R^+$; $n = 13$, SD = 0.13. No significance is attached to the second term. The essential identity of corresponding polar effects in the ionization of I and II appears to provide further support^{3b,c} for the field over the internal inductive model. The different bond transmission modes for I and II probably would not be expected to be equal.⁹

Since polar effects in series I and II are essentially

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(4) (a) R. W. Taft in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13; (b) R. T. C. Brownlee and R. W. Taft, *J. Amer. Chem. Soc.*, **90**, 6537 (1968).

(5) R. T. C. Brownlee and R. W. Taft, *J. Amer. Chem. Soc.*, **92**, 7007 (1970).

(6) P. R. Wells, S. Ehrenson, and R. W. Taft, *Progr. Phys. Org. Chem.*, **6**, 147 (1968).

(7) (a) S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *Progr. Phys. Org. Chem.*, **10**, 1 (1973); *cf.* also S. Dayal, S. Ehrenson, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 9113 (1972).

(8) (a) E. Ceppi, W. Eckhardt, and C. A. Grob, *Tetrahedron Lett.*, 3627 (1973); (b) J. Paleček and J. Hlavatý, *Collect. Czech. Chem. Commun.*, **38**, 1985 (1973). These authors have reported pK_A values for a somewhat more limited series of II bases in three aqueous-organic solvents. They are the first to report satisfactory correlation of $\log (K/K_0)_{II}$ values with σ_I parameters.

(9) This point is by no means certain, however. Recent evidence has indicated that the polarizability of phenyl and cyclohexyl groups are very similar; *cf.* R. W. Taft, M. Taagepera, K. D. Summerhays, and J. Mitsky, *J. Amer. Chem. Soc.*, **95**, 3811 (1973).

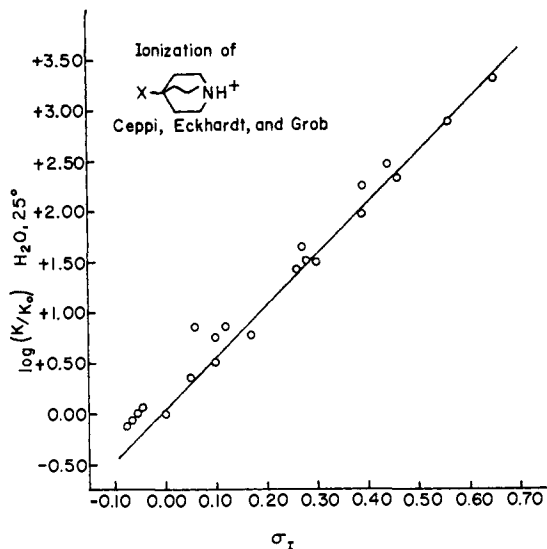
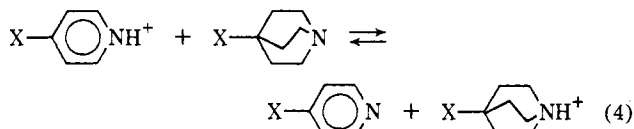


Figure 1. Ionization of acids of II vs. σ_I .

equal, it follows that the difference in $\log(K/K_0)$ values for corresponding 4-X substituents in I and II gives quantitatively resonance or π -electron delocalization effects (R) for the ionization of 4-substituted pyridinium ions, *i.e.*

$$\log(K/K_0)_I - \log(K/K_0)_{II} = R \quad (3)$$

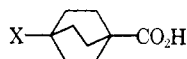
Alternatively stated, it may be readily seen that R is a standard free-energy change measure for the reaction



I.e., $\delta_R \Delta G_4^\circ / -2.303RT = (\Delta G_{X^\circ} - \Delta G_{H^\circ}) / -2.303RT = R$, where ΔG_{H° is the standard free-energy change for reaction 4 with $X = H$. Thus, for the first time, a large standard free-energy change has become available for a reaction involving an extended series of substituted aromatic compounds for which π -electron delocalization effects alone are measured, unencumbered by any polar effect contributions.

Values of R are summarized in Table I, together with values of $\log(K/K_0)_I$, $\log(K/K_0)_{II}$, and σ_I and σ_{R^+} parameters. Figure 2 shows a plot of R vs. σ_{R^+} , which is of sufficient precision in linearity to confirm directly the validity of σ_{R^+} parameters.¹⁰ R values are fitted to substantially poorer precision by any other substituent parameter that has been proposed.¹¹ The least-squares regression for Figure 2 is $R = 2.87\sigma_{R^+} - 0.09$; $n = 17$, $SD = 0.17$, $r = 0.995$. The agreement with eq 1,

(10) A similar confirmation of the $\sigma_{R(BA)}$ scale is provided by $\log(k/k_0)_{III} - \log(k/k_0)_{IV}$ values for 50% (Vol) aqueous EtOH, 25°, where III is *p*-XPhCO₂H (data of B. M. Wepster, private communication) and IV is



(data of ref 3a and b). Best fit to the DSP equation is obtained by the use of $\sigma_{R(BA)}$ values giving the following results: $\rho_R = 1.22$; $\rho_I = 0.01$ (insignificant); $SD = 0.03$; $SD/RMS = 0.100$; $n = 7$.

(11) For example, best linear fits to σ_{R^+} , $\sigma_{R(BA)}$, and R parameters (*cf.* 7a) have $SD \geq 0.40$ and the SD of fits to $\sigma_{(p)}$ or $\sigma_{(p)^+}$ greatly exceed this.

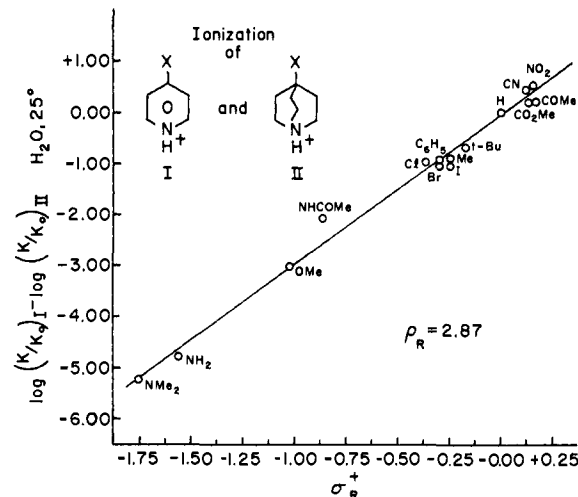


Figure 2. $\log(K/K_0)_I - \log(K/K_0)_{II}$ vs. σ_{R^+} .

Table I. Data Summary

4-X	σ_I^a	$\sigma_{R^+}^a$	Log $(K/K_0)_{II}^e$	Log $(K/K_0)_I^f$	$R = \log(K/K_0)_I - \log(K/K_0)_{II}$
<i>t</i> -Bu	-0.07 ^b	-0.18 ^c	-0.11	-0.82	-0.71
<i>i</i> -Pr	-0.06 ^b	-0.21 ^c	-0.06	-0.85	-0.79
Et	-0.05 ^b	-0.23 ^c	0.01	-0.85	-0.86
Me	-0.04	-0.25	0.08	-0.82	-0.90
H	0.00	0.00	0.00	0.00	0.00
CH=CH ₂	0.05 ^d	<i>g</i>	0.26	-0.42	-0.68 ^g
NMe ₂	0.06	-1.75	0.85	-4.38	-5.23
C ₆ H ₅	0.10	-0.30	0.76	-0.14	-0.90
CH ₂ OH	0.10 ^d		0.51		
NH ₂	0.12	-1.61	0.86	-3.91	-4.77
CH ₂ Cl	0.17 ^d		0.77		
NHCOMe	0.26	-0.86	1.42	-0.66	-2.08
OMe	0.27	-1.02	1.65	-1.37	-3.02
COMe	0.28	0.16	1.51	1.70	0.19
CO ₂ Me	0.30	0.14	1.50	1.72	0.22
OCOMe	0.39 ^d		1.97		
I	0.39	-0.25	2.26	1.20	-1.06
Br	0.44	-0.30	2.47	1.46	-1.01
Cl	0.46	-0.36	2.34	1.38	-0.96
CN	0.56	0.13	2.89	3.35	0.46
NO ₂	0.65	0.15	3.31	3.82	0.51

^a From ref 7 unless otherwise noted. ^b R. W. Taft and I. C. Lewis, *Tetrahedron*, **5**, 210 (1959). ^c Calculated from data of H. C. Brown, J. D. Brady, M. Grayson, and W. H. Bonner, *J. Amer. Chem. Soc.*, **79**, 1897 (1957), using ρ_I and ρ_R values of ref 7. ^d R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *J. Amer. Chem. Soc.*, **85**, 709 (1963). ^e From ref 8. ^f (a) D. D. Perrin, "Discussion Constants of Organic Bases in Aqueous Solution," Butterworths, London, 1965; (b) A. Fischer, W. J. Galloway, and J. Vaughn, *J. Chem. Soc.*, 3591 (1964). ^g Calcd σ_{R^+} value is -0.21.

i.e., $R = 2.69\sigma_{R^+}$, is entirely satisfactory. Indeed, the agreement confirms the power of eq 1 to quantitatively separate composite but independent polar and resonance effects. The method, when properly utilized, is indicated to be a major general tool for this purpose. The use of model systems clearly receives strong support too.

At least some degree of scatter in Figures 1 and 2 may be expected to arise from differential aqueous solvent modification of substituent electronic properties. Work is in progress on the determination of gas-phase base strengths toward H⁺ for both series I and II using pulsed ion cyclotron resonance spectroscopy.

Acknowledgment. We are indebted to Professor J. W. Timberlake for bringing to our attention the correlation of $\log(K/K_0)_{II}$ values with σ_I . Mr. James Fukunaga provided the least-squares fitting results reported herein and useful discussions. We are indebted to Professor B. M. Wepster for communication of unpublished results.

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Cation Radicals of Tetraalkylporphyrins

Sir:

Oxidation of tetraphenyl- and octaethylmetalporphyrins leads to π cation radicals¹⁻³ which fall into two general categories:⁴⁻⁷ (1) radicals where the electron presumably has been removed from the a_{2u} highest occupied orbital leading to a ${}^2A_{2u}$ ground state (D_{4h} symmetry) and (2) those assumed to arise instead from the removal of an electron from the a_{1u} orbital resulting in a ${}^2A_{1u}$ state.^{4,7,9} The radicals possess characteristic optical spectra and exhibit the following esr parameters:^{4,7,10} for ${}^2A_{1u}$, spectra consistent with predicted high spin density at the meso positions, nitrogen hyperfine splitting, metal hyperfine splitting, and, in solvents of low dielectric constants, hyperfine splitting from the gegenion. By comparison, ${}^2A_{1u}$ radicals show small spin densities at the meso positions, and, to date, no nitrogen, metal, or anion splittings have been resolved. This has led to the conclusion⁷ that the α carbons of the pyrroles bear high spin densities in this ground state as theoretically predicted.^{4,9} Recent results on zinc and magnesium tetrapropylporphyrins^{7,11} indicate that their cation radicals fit the ${}^2A_{2u}$ requisites, but the spin densities at the meso positions, deduced from the esr splittings, are considerably smaller than expected on the basis of SCF-MO calculations.⁴

We present here esr data on a series of meso tetraalkylporphyrins which confirm that these radicals fall in the ${}^2A_{2u}$ category. The particularly well-resolved

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(10) A. Forman, D. C. Borg, R. H. Felton, and J. Fajer, *J. Amer. Chem. Soc.*, **93**, 2790 (1971).

(11) Yu. V. Glaskov, P. V. Kuzovkov, and A. M. Shul'ga, *Zh. Prikl. Spektrosk.*, **18**, 320 (1973).

spectrum of zinc tetramethylporphyrin provides a direct probe of the spin density at the meso carbons *via* hyperconjugation and thus permits direct testing of MO calculations for the ${}^2A_{2u}$ state. The apparent disparity between experimental results and theory, observed upon substitution of methyl groups by larger alkyl derivatives, is explained by restricted rotation of the alkyl groups.

Oxidations¹² of the zinc complexes of meso-tetra-methyl-, -tetraethyl-, -tetrapropyl-, -tetrabutyl-, and -tetraoctylporphyrins¹³ yield radicals whose esr spectra are readily analyzed in terms of interactions with four equivalent nitrogens and with four methyl (or methylene) groups (Table I). Experimental spectra and

Table I. Hyperfine Splitting Constants of Zinc Tetraalkylporphyrins in CCl_4 at 0° , $g = 2.0026 (\pm 0.0001)$

Compound	a_N , G	a_H , G	Others
$Zn(CH_3)_4P^{+\cdot}$	1.72	5.90 (CH ₃)	
$Zn(C_2H_5)_4P^{+\cdot}$	} 1.69 ^a	} 2.75 (CH ₂)	0.20 (-CH ₃)
$Zn(C_3H_7)_4P^{+\cdot}$			} Not resolved
$Zn(C_4H_9)_4P^{+\cdot}$			
$Zn(C_8H_{17})_4P^{+\cdot}$			

^a Based on computer simulations.

computer simulations for $Zn(CH_3)_4P^{+\cdot}$ and $Zn(C_4H_9)_4P^{+\cdot}$ are shown in Figures 1 and 2.

The large differences between the methyl splittings observed in $Zn(CH_3)_4P^{+\cdot}$ *vs.* the methylene couplings of the other radicals are not expected on the basis of predicted spin densities.⁴ Similar effects have been observed^{15,16} for alkyl substituted aromatic cations with the ratio of splitting constants $a_{CH_2}/a_{CH_3} \sim 0.46$. The phenomenon is explained by a restricted rotational model;^{15,16} β proton splittings depend on the dihedral angle, θ , between the proton and $2p_z$ orbital of the α carbon to which the methyl (or methylene) group is attached

$$a_{H\beta} = \rho_{C\alpha}(B_0 + B \cos^2 \theta) \quad (1)$$

where B and B_0 are constants with $B \gg B_0$ and ρ is the unpaired spin density of C_α . For a freely rotating methyl group $\cos^2 \theta \sim 1/2$ while, for locked methylene groups, the conformation of lowest energy requires $\theta = 60^\circ$ and $\cos^2 \theta = 1/4$, giving rise to the observed ratio of ~ 0.5 between hindered and free alkyl groups. In this work, as shown in Table I, a_N remains effectively constant when the alkyl groups are changed while $a_{CH_2}/a_{CH_3} = 0.47$. The difference in the splitting constants

(12) Oxidations were carried out in $CHCl_3$ or CH_2Cl_2 chemically using $(FeTPP)_2O^+ClO_4^-$ and Br_2 or electrochemically at a platinum electrode with tetrapropylammonium perchlorate as carrier electrolyte.^{4,6,7,10} We are indebted to Dr. R. H. Felton for a generous supply of the iron compound.

(13) Porphyrins were prepared using methods previously described¹⁴ by condensation of pyrrole with the appropriate aldehyde in xylene containing 0.1 M trifluoroacetic acid. Metalation was performed in dimethylformamide, and the resulting metalloporphyrins were recrystallized from heptane.

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