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Alkyl Substituent Effects on the Stability of Protonated Benzene

Sir:

The Baker–Nathan order of alkyl substituent effects (Me > Et > *i*-Pr > *t*-Bu) has engendered much experimental work and controversy.¹ Although the results of theoretical molecular orbital calculations on model systems² seem to support the contention that this reverse inductive ordering is due primarily to a differential inhibition of solvation by the alkyl substituents,³ experimental tests in solution have not led to unambiguous conclusions.¹

Recently Arnett and Larsen^{4a} reported what must be the largest Baker–Nathan effect to date, noting that in superacid media the proton affinity of toluene is nearly 4 kcal/mol greater than that of *tert*-butylbenzene. It is on this observation that we focus our attention in the present communication. We have employed experimental pulsed ion cyclotron resonance techniques⁵ as well as theoretical *ab initio* molecular orbital calculations⁶ to investigate the effect of alkyl substituents on the stability of protonated benzene. As both of our tools provide information on the ions in their isolated—dilute gas—state, comparison of our data with that of Arnett and Larsen should afford a quantitative assessment of the importance of solvation.

Experimental values for the relative basicity of the alkyl benzenes in the gas phase were obtained by measuring equilibrium constants for reaction 1, where A



and B are alkyl benzenes. The pulsed ion cyclotron resonance techniques utilized in this study were identical with those described previously⁷ with the exception that

(1) Reviews: (a) "Conference on Hyperconjugation," *Tetrahedron* **5**, 105 (1959); (b) M. J. S. Dewar, "Hyperconjugation," Ronald Press New York, N. Y., 1962; (c) J. W. Baker, "Hyperconjugation," Oxford University Press, Oxford, 1952. For more recent papers on this subject, see (d) W. M. Schubert and D. F. Gurka, *J. Amer. Chem. Soc.*, **91**, 1443 (1969); (e) A. Himoe and L. M. Stock, *ibid.*, **91**, 1452 (1969); (f) E. M. Arnett and J. W. Larsen, *ibid.*, **91**, 1438 (1969); (g) F. R. Jensen and B. E. Smart, *ibid.*, **91**, 5686 (1969); (h) T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *ibid.*, **93**, 5715 (1971); (i) J. M. Jerkunica and T. G. Traylor, *ibid.*, **93**, 6278 (1971); (j) J. W. Larsen, P. A. Bouis, M. W. Grant, and C. A. Lane, *ibid.*, **93**, 2067 (1971).

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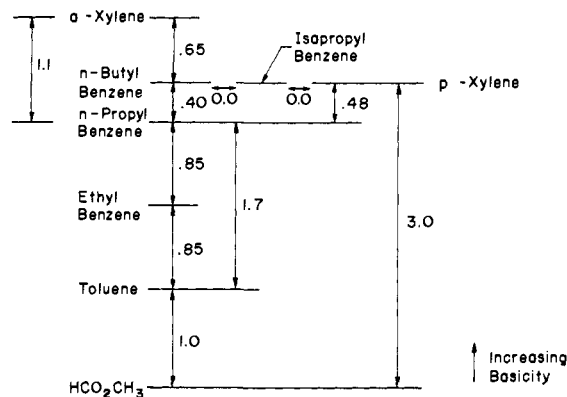
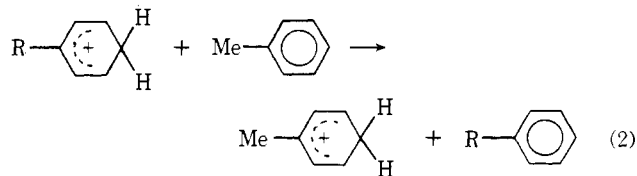


Figure 1. Pulsed ion cyclotron resonance measurements of ΔG°_{298} (kcal/mol) for the proton transfer reactions: $\text{AH}^+ + \text{B} \rightarrow \text{BH}^+ + \text{A}$.

a fivefold excess of phosphine was added to the system as a source of protons since alkyl benzenes self-protonate very slowly. Our experimental data are shown in Figure 1. The multiple overlap method was used to check the data for internal consistency and to confirm that equilibrium was attained. For example, direct measurements of the proton transfer equilibrium between toluene and *n*-propylbenzene gave $\Delta G^\circ = 1.7$ kcal/mol. Separate measurements between toluene and ethylbenzene and between ethylbenzene and *n*-propylbenzene gave $\Delta G^\circ = 0.85 + 0.85 = 1.7$ kcal/mol. Comparisons of this type establish an internal consistency of ± 0.1 kcal/mol. Assuming zero entropy change for the gas-phase reactions (1) our values of ΔG° may be used to calculate the relative proton affinities of the alkyl benzenes and the heats of formation of the protonated alkyl benzenes.

STO-3G energies for the *isodesmic*⁸ processes (eq 2),

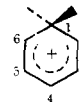


providing a measure of the basicity of an alkyl benzene relative to that of toluene, are presented along with the experimental icr data in Table I.⁹ The agreement is remarkably good! Calculations on all positional isomers confirm experimental results in superacid

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
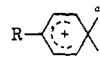
(9) (a) Standard model geometries¹⁰ used throughout. For protonated benzene: $r(\text{C}_1\text{C}_2) = 1.485 \text{ \AA}$, $r(\text{C}_2\text{C}_3) = r(\text{C}_3\text{C}_4) = 1.40 \text{ \AA}$, $r(\text{C}_1\text{H})$



$= 1.09 \text{ \AA}$, $r(\text{C}_2\text{H}) = r(\text{C}_3\text{H}) = r(\text{C}_4\text{H}) = 1.08 \text{ \AA}$; $\angle(\text{C}_6\text{C}_1\text{C}_2) = 109.47^\circ$, $\angle(\text{C}_1\text{C}_2\text{C}_3) = 125.66^\circ$, $\angle(\text{C}_2\text{C}_3\text{C}_4) = \angle(\text{C}_3\text{C}_4\text{C}_5) = 120^\circ$, $\angle(\text{HC}_1\text{H}) = 109.47^\circ$, other hydrogens bisect ring CCC angles. Connecting (ring-substituent) bond lengths set at 1.52 \AA . (b) For the STO-3G geometry optimized structure of protonated benzene, see W. J. Hehre and J. A. Pople, *J. Amer. Chem. Soc.*, **94**, 6901 (1972).

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Table I. Energy Data

R			ΔE^b STO-3G	$\Delta G^{\circ b}$ Exptl (icr)	$\Delta H^{\circ b,c}$ Exptl (soln)
Me	-266.47382	-266.84917	0.0	0.0	0.0
Et ^d	-305.05333	-305.43090	1.4	0.85	-2.74
<i>n</i> -Pr ^{d,e}	-343.63299	-344.01202	2.3	1.7	
<i>i</i> -Pr ^f	-343.63067	-344.00972	2.3	2.1	-2.51
<i>n</i> -Bu ^{d,e}	-382.21248	-382.59221	2.7	2.1	
<i>t</i> -Bu ^f	-382.20297	-382.58329	3.1	2.3 ± 0.5 ^g	-3.76

^a STO-3G total energies (hartrees). ^b ΔE , ΔG°_{298} , or ΔH°_{298} of the isodesmic reaction (eq 2) (kcal/mol). ^c Reference 4a. ^d $C_{\alpha}-C_{\beta}$ bond held perpendicular to ring plane. ^e All trans conformation. ^f Methyl groups symmetrically disposed about ring plane. ^g Upon protonation *tert*-butylbenzene fragments extensively, paralleling its behavior in superacid media (see ref 11a). The ΔG° of reaction quoted corresponds to an apparent proton transfer equilibrium with dimethyl ether. In the gas phase, all of the other alkyl benzenes protonated cleanly without fragmentation.

solution¹¹ that each of the monoalkyl benzenes protonates preferentially para to the substituent. It is assumed that the experimental icr data pertains to protonation at these same sites. Comparison is also made in the table between the relative basicities obtained in the gas phase and in solution, hence providing estimates of differential solvation energies.¹²

The following conclusions deserve special note.

Stabilization of protonated benzene by para positioned alkyl groups follows the sequence (Me < Et < *i*-Pr < *t*-Bu) rather than the Baker-Nathan ordering observed by Arnett and Larsen^{4a} in superacid solution. Whereas Arnett's solution measurements indicate the heat of protonation of toluene to be 3.76 kcal/mol greater than that of *tert*-butylbenzene, our data suggest the opposite ordering in the gas phase. The differential represents an increased shielding to solvation of the larger *t*-butyl group over that of methyl.¹¹

The effects of *n*-propyl and isopropyl substituents in altering the proton affinity of benzene are similar (as are those of *n*-butyl and *tert*-butyl groups) suggesting, that, due to polarizability, the size of the alkyl chain is nearly as important a factor as the degree of branching. Simple carbocations behave similarly in the gas phase,^{2a} but marked attenuation of this polarizability effect is expected in solution.

STO-3G calculated π charges at C₄ (adjacent to the alkyl substituent) in the protonated benzenes show little dependence on the alkyl group, ranging from +0.38 electrons in protonated toluene to +0.39 electrons in protonated *tert*-butylbenzene. This parallels the ¹³C chemical shifts observed by Olah and coworkers^{11a} in superacid media. We note, however, that in this series of compounds charge delocalization does not parallel thermodynamic stability.

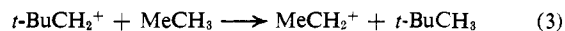
The difference between methyl and *tert*-butyl groups in stabilizing the charge delocalized benzenium cation (3.1 kcal/mol from the theoretical STO-3G calculations) is smaller than the 8.2 kcal/mol differential¹³ (7.5 kcal/

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(12) See also ref 1j.

(13) Experimental thermochemical data (ΔH°_{298}) from J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, National Bureau of Standards, 1969.

mol using theoretical STO-3G data^{2a}) in alkyl group effectiveness when attached to the methyl cation, as measured by the energy of eq 3.



Finally the high level of agreement between experimentally determined and theoretically calculated alkyl substituent effects lends considerable force to the assertion of a classical open structure for the ground state of protonated benzene in the gas phase.

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Theoretical Approaches to Aromatic Electrophilic Substitution Processes. II. Intermediates in Electrophilic Fluorination

Sir:

The current mechanism of electrophilic aromatic substitution centers around the intervention of a stable positively charged adduct between electrophile and aromatic substrate.¹ Direct nmr spectroscopic observations in strong acid media,² and more recently gas phase ion cyclotron resonance techniques³ and theoretical *ab initio* molecular orbital calculations,^{3,4} have concluded that proton addition complexes are better represented in terms of "classical" Wheland or benzenium type structures than as "nonclassical" σ delocalized hydrogen bridged forms. These latter structures appear not to be stable forms; rather they best fit the role of low energy transition states to degenerate hydrogen scrambling.⁵

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(5) Olah and his coworkers report that an activation energy of 10 ± 1 kcal/mol is required for hydrogen scrambling in parent protonated benzene.^{2a} *Ab initio* molecular orbital calculations suggest a larger value (20.6 kcal/mol).^{4a}