Stabilities of Carbonium Ions in Solution. IV.[1] A Large Baker–Nathan Effect for Alkylbenzenonium Ions[2]

E. M. Arnett and J. W. Larsen

Contribution from the Department of Chemistry,
University of Pittsburgh and Mellon Institute, Pittsburgh, Pennsylvania 15213.
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Abstract: Heats of formation in SbF_5–HSO_3F at −62° are reported for a number of alkyl and polyalkyl benzenonium ions with methyl, ethyl, isopropyl, and *t*-butyl substituents and for two polycyclic systems. Large heats of formation are found which increase in size as a function of the number of groups in the benzene ring. Within experimental error, all results for a given series fall in the Baker–Nathan order (*i.e.*, methyl > ethyl > isopropyl > *t*-butyl), the effects being many-fold larger than those observed previously for series of this type. It appears likely that the enthalpy and free energy differences in this series are equivalent and, hence, correspond to potential energy differences. If this possibility is supported by further studies, it may be taken as evidence that hyperconjugation is an important contributor to the Baker–Nathan order found in this system.

Progressive replacement of hydrogens on a methyl group through the "big four" alkyl series (methyl, ethyl, isopropyl, *t*-butyl) involves a variety of conceivable steric, electronic, and mass effects which may interact with each other and be complicated further by solvent and temperature effects. The influence of structural change in this series generally is determined through some process where an initial state is converted to a secondary state, such as a product, transition state or excited state. The comparison then really involves eight different states considering all initial and secondary ones. The results of structural variation on kinetic, equilibrium, and spectral measurements in this series are frequently rather small; sometimes scarcely outside experimental error. It is, therefore, not surprising, that different orders of reactivity are found, the two most obvious and common ones being the well-known inductive order (*t*-butyl > isopropyl > ethyl > methyl) and its reverse. In view of the many combinations of possible effects on the ground states and secondary states within the series which could cause such ordering, it is not surprising that a variety of explanations for these phenomena have been advanced. Beyond the question of experimental validity of the orders lies the question as to whether they are produced by such potential energy factors as inductive, resonance, or nonbonded steric interactions, which would be found in the motionless molecules at absolute zero in the gas phase, or whether the observed values result from the combined influence of these potential energy terms with solvation and temperature effects,

Direct nonbonded interactions may be removed by placing the substitutent groups at a remote position on a rigid molecular framework such as a benzene or cyclopentadiene ring. It is comparisons of molecules carrying the "big four" series of substituents in reactions where electron demand can be transferred from a sterically unencumbered site to a carbon atom bearing an alkyl group that the reactivity order methyl > ethyl ≥ isopropyl > *t*-butyl (first noted over 30 years ago by Baker and Nathan[3] for an S_N2 reaction) is observed most commonly. Since that time, the search for "anti-inductive" orders has motivated numerous experimental studies which have been accompanied by parallel efforts to justify the effect on theoretical grounds. Most of these results and interpretations are accessible through several reviews of the problem.[4–6]

Until recently, most (if not all) of the energies for processes falling in the Baker–Nathan order involved differences of less than 0.5 kcal/mol between the limits of methyl and *t*-butyl groups. Last year Sorensen[7] reported an elegant study of isomerization equilibria for several series of tri- and tetraalkyl cyclopentadienyl cations in concentrated sulfuric acid. He found that when placed in open competition for stabilizing allylic carbonium ions of this type, a methyl group is favored thermodynamically over a *t*-butyl by about 1.8 kcal/mol in terms of free energy and by about the same amount in enthalpy (obtained through the van't Hoff temperature-coefficient method). The effect of ethyl and isopropyl groups fell in between these limits in the proper Baker–Nathan order. To the best of our knowledge, Sorensen's claim that this is the largest range of energies to fall in this order up to that time is correct.

Our hope of making a contribution to the problem arose when we developed a method for measuring the relative heats of formation of stable carbonium ions[8,9] at high dilution in super acids at temperatures down to −70°. Benzenonium ion formation by protonation of aromatic precursors with Olah's combination of antimony pentafluoride and fluorosulfuric acid (SbF_5–HSO_3F) was chosen for initial effort since considerable spectral information substantiated the clean formation of ions whose structures were known under these conditions.[10]

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[1] Paper III: E. M. Arnett and J. W. Larsen in "Carbonium Ions," G. Olah and P. von R. Schleyer, Ed., Interscience Publishers, New York, N. Y., 1968, p 441.

[2] Supported by National Science Foundation Grant GP-6550X.

[3] J. W. Baker and W. S. Nathan, *J. Chem. Soc.*, 1844 (1935).

[4] F. A. Matsen, W. W. Robertson, and R. L. Chouoke, *Chem. Rev.*, 41, 273 (1947).

[5] Conference on Hyperconjugation, V. J. Shiner, Jr., and E. Campaigne, Co-Chairmen, Pergamon Press, New York, N. Y., 1959.

[6] M. J. S. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962.

[7] T. Sorensen, *J. Am. Chem. Soc.*, 89, 3782, 3794 (1967).

[8] E. M. Arnett and John W. Larsen, *ibid.*, 90, 791 (1968).

[9] E. M. Arnett and John W. Larsen, *ibid.*, 90, 792 (1968).

[10] H. H. Perkampus, *Advan. Phys. Org. Chem.*, 4, 195 (1966).

Table I. Enthalpies of Solution at 25° and of Protonation of Alkylbenzenes in 11.5 Mol % SbF_5–HSO_3F at −65°

Compound	$\Delta \bar{H}_{s\,CCl_4}{}^{25}$	$\Delta \bar{H}_{s\,EtOH}{}^{25}$	$\Delta H_{proton}{}^{65}$ (SbF_5–HSO_3F)	Ref to nmr
Toluene	−0.09 ± 0.04	+0.31 ± 0.03	−5.00 ± 1.13	...
Ethylbenzene	+0.13 ± 0.04	+0.30 ± 0.03	−2.26 ± 0.58	*a*
Isopropylbenzene	+0.21 ± 0.06	+0.34 ± 0.03	−2.49 ± 0.3	*a*
t-Butylbenzene	−0.08 ± 0.03	+0.45 ± 0.07	−1.24 ± 0.3	*a*
Mesitylene	+0.19 ± 0.03	...	−10.3 ± 0.3	*b–d*
1,3,5-Triethylbenzene	−0.20 ± 0.03	...	−2.25 ± 1.04	...
1,3,5-Triisopropylbenzene	−0.27 ± 0.06	...	−1.37 ± 0.40	*a*
Hexamethylbenzene	+4.96 ± 0.13	...	−10.6 ± 0.8	*b, d*
Hexaethylbenzene	+4.55 ± 0.18	...	−4.76 ± 0.31	...
Tritetralin[f]	+5.00 ± 0.35	...	−7.01 ± 1.01	*e*
Trindane[f]	+3.31 ± 0.50	...	−7.15 ± 0.34	*e*

[a] The nmr spectrum of this material was examined at −60° in 15 mol % SbF_5–HSO_3F and was completely consistent with the formation of the expected benzenonium ion. [b] T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **42,** 502 (1964). [c] C. MacLean and E. L. Mackor, *Discussions Faraday Soc.*, **34,** 165 (1962). [d] D. M. Brouwer, E. L. Mackor, and C. MacLean in "Carbonium Ions," Vol. 2, G. A. Olah and P. von R. Schleyer, Ed., Interscience Publishers, New York, N. Y., in press, Chapter 19. [e] G. A. Olah and T. E. Kiovsky, personal communication. The nmr spectrum was completely consistent with the clean formation of the expected benzenonium ion. [f] See Table III for structures.

Beyond this are the advantages of dealing with readily available, simple, planar systems whose geometries are known and in which complications involving leaving groups are absent or at least minimized. Of greatest importance to the present problem was the expectation that the heats of formation would be large and sensitive to variation of the substituent across the "big four" series. These hopes have been realized, and the large observed differences follow the Baker–Nathan order.

Experimental Section

Chemicals. Trindane and tritetralin, prepared by the method of Wallach,[11] were kindly supplied by Robert Smoyer. All other compounds were commercial materials and were either distilled, crystallized, or sublimed until their physical properties agreed with those given in the literature. The solids were dried over P_2O_5 and the liquids were stored over 4 A molecular sieves. The fluorosulfuric acid was Baker and Adamson's Technical Grade. It was flushed with dry N_2 to remove the excess HF and then distilled, bp 162°. Antimony pentafluoride was obtained from both Allied Chemical Co. and Ozark Mahoning, Inc. This material was flushed with dry N_2 until most of the HF was removed and the liquid became quite viscous. It was then distilled (bp 142°) directly into a Teflon bottle, where it was stored until used.

Description of the Apparatus. The calorimeter has been described previously.[8] However, several points not covered in the original communication are treated below. For this work, a clear, unsilvered dewar without spacers was used, the glass exterior of the dewar being covered with adhesive tape. The stirrer was an eight-bladed Teflon propeller, diameter 20 mm, thickness 5 mm, mounted on a shaft of 7 mm glass tubing. Equipped thus, the calorimeter had a useful temperature range of −55 to −65° when filled with 11.5 mol % SbF_5 in HSO_3F.

The sample, either solid or liquid, is introduced using a modified disposable, plastic, 3-cc syringe (Stylex Pharmaseal Laboratories, Glendale, Calif.). These syringes are apparently unaffected by the acid, since they remain constant in both weight and appearance on submersion in the acid at −65°. After such treatment at room temperature, they become brittle and crack.

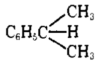
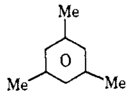
Procedure. The following procedure was followed carefully in all runs. The calorimeter is assembled, the head covered with Dry Ice, and the calorimeter placed in its Dry Ice–acetone bath. While it is cooling, a charge of *ca.* 80 g of SbF_5 and 300 g of HSO_3F is weighed into a 16 oz Teflon bottle. The acid is cooled to *ca.* −70° by placing the bottle in powdered Dry Ice. Because of the violent reaction between the acid and acetone (and most other substances) the use of a Dry Ice–liquid slurry is not recommended for this cooling operation. After the desired temperature is reached (in *ca.* 30 min), the acid is poured into the calorimeter through a funnel. After stirring for 30 min, measurements can be made; however, greater precision will be obtained if a longer time is allowed for equilibration. Most measurements require the use of the 2.5 or 5 mV recorder range for 50–150 mg of sample because of highly exothermic reactions.

While the loaded calorimeter is coming to thermal equilibrium, the samples are prepared for injection. The sample is weighed into the syringe in the space between the plunger and the plug. The syringe is cooled in Dry Ice for at least 0.5 hr before it is positioned in the calorimeter and is allowed to stand there for *ca.* 20 min before injection of the sample. After the syringe has reached thermal equilibrium, a heating curve is run and the sample is injected by depressing the plunger rapidly. The values presented here are based on at least six injections of each sample.

Results

The heats of solution at 25° in CCl_4 and ethanol and of protonation in 11.5 mol % SbF_5–HSO_3F at −65° for the alkylbenzenes studied are shown in Table I. The process represented by $\Delta H_{react}{}^{-65}$ is the conversion of the pure alkylbenzene at −65° into a dilute solution of its benzenonium ion in 11.5 mol % SbF_5–HSO_3F.[8,9] To obtain the relative heats of formation of the benzenonium ions, the energy associated with separating the solute molecules from each other must be accounted for. This is done best by the selection of a standard state in which such interactions are absent. The dilute gas phase at −65° could be ideal for this purpose, however, enough data are available[12] to allow the calculation of $\Delta H_{C^+}{}^{g-l}$ as defined in Figure 1 for only the four compounds shown in Table II. Therefore, as

Table II. Thermodynamic Quantities for Formation of Benzenonium Ions in 11.5 Mol % SbF_5–HSO_3F at −65° from the Gas Phase (kcal/mol)

	$\Delta H_{C^+}{}^{g-l}$	$\Delta H_{react}{}^{-65}$	$C_p{}^l \Delta T^b$	ΔH_{vap}	$C_p{}^g \Delta T^b$
Toluene	−14.34	−5.00	−3.57	+8.00	−2.23
C_6H_5Et	−12.23	−2.39	−4.00	+8.60	−2.76
 $C_6H_5CH(CH_3)_2$	−12.81	−2.70	(−4.4)[a]	+8.97	−3.26
	−21.11	−10.5	−4.51	+9.33	−3.23

[a] Calculated assuming a constant difference between $C_p{}^l$ and $C_p{}^g$. [b] Calculated using the tabulated values for C_p at 273°.[13] $\Delta H_{C}{}^{g-l} = C_p{}^l \Delta T + \Delta H_{react}{}^{-65} - \Delta H_{vap} - C_p{}^l \Delta T$.

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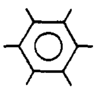
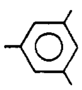
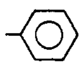
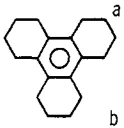
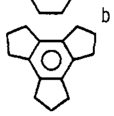
(11) O. Wallach, *Ber.*, 30, 1094 (1897).

(12) Landolt-Bornstein's "Handbuch der Chemie," Springer-Verlag, Berlin, 1961.

we stated in our previous articles,[8,9] the paucity of suitable data has led us to choose carbon tetrachloride at 25° as a more useful standard state than the gas phase. Shown in Table III are the relative enthalpies of carbonium ion formation (ΔH_{C^+}) for the alkylbenzenes using carbon tetrachloride at 25° as the standard state. This heat (ΔH_{C^+}) is the heat of transfer from carbon tetrachloride at 25° to 11.5 mol % SbF_3–HSO_3F at −65°.[8,9] In the four cases where comparison is possible, the differences in ΔH_{C^+} and $\Delta H_{C^+}{}^{g\text{-}l}$ from compound to compound are the same, indicating that the use of carbon tetrachloride as the standard state introduces no change in the relative values of ΔH_{C^+}.

The stabilities of most of the benzenonium ions studied here under these conditions have been well documented.[10] However, several of the alkylbenzenes (shown in Table III) were not stable under our conditions as indicated by a peak in the proton nmr at −4.8 ppm[13] suggesting the presence of the *t*-butyl cation.

Table III. Calorimetrically Determined Relative Heats of Formation of Benzenonium Ions in 11.5 Mol % SbF_5–HSO_3F at −65°

	$\Delta H_{C\oplus}$ −65°C		
			
CH_3-	−15.6 ± 0.9	−10.5 + 0.3	−4.91 ±1.1
CH_3CH_2-	−9.31 ±0.40	−7.05 ±1.05	−2.39 ±0.61
$(CH_3)_2CH-$	−18.6* ± 2.5	−1.10 ±0.41	−2.70 ±0.30
$(CH_3)_3-C-$	Unstable* by n.m.r.	−7.43* +0.60	−1.16 ±0.30
 [a]	−12.0 ± 1.2		
 [b]	−10.5 ± 0.7		

[a] Tritetralin. [b] Trindane. Asterisks indicate ions unstable as shown by appearance of singlet absorption at −4.8 ppm in nmr spectrum corresponding to formation of *t*-butyl cations.[14]

Discussion

The results presented in Table III are principally notable for providing a consistent set of data in which large ionization energies fall in the Baker–Nathan order. The effects are one or two orders of magnitude larger than those upon which previous speculations relating Baker–Nathan order to the concept of hyperconjugation have been based.[5] A few interpretative comments on the matter are, therefore, justified.

$$\begin{tikzcd}
\text{Ar}^{g}, 25^\circ \arrow[rr, "\int_{25}^{-65} C_p{}^{g}\,dT \simeq C_p{}^{g}\Delta T"] & & \text{Ar}^{g}, -65^\circ \arrow[d, "\Delta H_{c^+}{}^{g\text{-}l}"] \\
\text{Ar}^{l}, 25^\circ \arrow[u, "\Delta H_{\text{vap}}"] \arrow[r, "\int_{25}^{-65} C_p{}^{l}\,dT \simeq C_p{}^{l}\Delta T"] & \text{Ar}^{l}, -65 \arrow[r, "\Delta H_{\text{react}}{}^{-65}"] & \text{ArH}^{+}(\text{soln}), -65^\circ
\end{tikzcd}$$

Figure 1. Enthalpy cycle for carbonium ion formation using the dilute gas phase as the standard state. The thermodynamic symbols in the figure have their usual meanings (G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1961); the superscripts g and l refer to the gas and liquid states, respectively.

Hyperconjugation may be defined as the partial delocalization of charge from electrons in a bonding σ orbital to a partially open orbital on an adjacent carbon. There is excellent evidence (*e.g.*, nuclear quadrupole resonance, electron-spin resonance, and nuclear magnetic resonance spectroscopy) for the delocalization of σ electrons from C–H bonds,[7] but there remains a controversy about whether such delocalization gives rise to significant stabilization such as to affect a chemical process. Ideally such a question could be answered by comparing bond angles and lengths in appropriate molecules, ions, and radicals but this approach is practically beyond the scope of present experimental techniques. Thermodynamic and kinetic data of themselves cannot demonstrate or refute such concepts; however, they can show whether or not there is an effect which is of sufficient size to merit careful structural investigation or theoretical examination. Small energy differences in large complex molecular systems are a notoriously fertile field for speculation but contribute little to the isolation of individual factors which might help to develop our sense of reality about molecules. One, therefore, seeks conditions which will maximize the effects.

The generation of a benzenonium ion by protonation of an aromatic hydrocarbon converts a nearly nonpolar neutral species into a carbonium ion. The enormous demand for electrons may be satisfied partially by interaction with electrons inside the molecule through delocalization mechanisms such as resonance (of which hyperconjugation is a special case). It may also be reduced in energy through interaction with electrons from an external source such as the solvent molecules or counterions from autoprotolysis of the solvent.[14] Since our measurements are made at high dilution and the super acids probably have large dielectric constants whose values increase sharply as the temperature decreases,[14] pairing with the counterions produced by protonation of the aromatic should be negligible. Thus the benzenonium ions considered here might be stabilized internally through resonance or inductive effects or externally by interaction with the solvent.

It has been recognized by a number of authors

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(13) G. A. Olah and C. U. Pittman, Jr., *Advan. Phys. Org. Chem.*, **3**, 305 (1966).

(14) R. C. Thompson, J. Barr, R. J. Gillespie, J. B. Milne, and R. A. Rothenbury, *Inorg. Chem.*, 4, 1641 (1965).

(Dewar's comments[6] are most clearly relevant here) that a Baker–Nathan order methyl > ethyl > isopropyl > *t*-butyl may represent a steady increase in the ability of the alkyl group to shield a charge on an adjacent carbon from interaction with the solvent. The ability to provide steric hindrance to solvation parallels exactly the decreasing ability to stabilize charge by delocalization of electrons from adjacent C–H bonds. In the present case, the high acidity of the medium creates the enormous electron demand needed to give a large Baker–Nathan effect. However, this high acidity must also be related closely to the size of the solvent molecules and counterions. Therefore, the same factors which produce the high electron demand required for maximizing hyperconjugation are linked to exactly those factors which will also amplify steric effects. In the absence of structural information at the molecular level about both types of interaction, there is no reliable way to separate internal from external contributions.

The Effect of Solvent on ΔH_{C^+}. It was shown in a previous communication[9] for a series of benzenonium ions (including several shown in Table III) that: (a) the stabilizing effect of progressively adding methyl groups on the ring was reflected to a nearly equal degree in the standard free energy change for ionization ($\Delta G_{C^+}°$ measured in HF–BF$_3$ by Mackor and coworkers),[15,16] and the corresponding enthalpy for the process (ΔH_{C^+}), (b) the effect of structure on ΔH_{C^+} was the same in Mackor's[15] HF–BF$_3$ system at 0° as in SbF$_5$–HSO$_3$F at −60°.

If these observations can be generalized to include the rest of the compounds presented in Table III, they provide an argument (albeit inconclusive) in favor of an internal potential energy factor (presumably hyperconjugation) as the principal source of the Baker–Nathan effect in this system. There is no reason to believe that it may be uncritically extended to others. The case rests on the following reasoning.

1. The first fact (a) indicates that the structural effects on ΔH_{C^+} and ΔG_{C^+} may be equal for the few cases reported in HF–BF$_3$ and therefore represent potential energy differences since they meet the sufficient (but not necessary) requirement that $\delta\Delta S° = 0$.[17] Although steric hindrance to solvation is a reasonable concept, we know of no case where its thermodynamic consequences have been documented unequivocally which could serve as a precedent. Two reasonable models for the kind of specific solvation which should be especially sensitive to steric effects are hydrogen bonding and Lewis acid–base complexes. Both of these 1:1 interactions have entropy terms which are highly sensitive to steric crowding so that $\delta\Delta S° \neq 0$.[18,19]

2. Antimony pentafluoride is a much larger molecule than HF. Gillespie has inferred from nmr and conductance measurements that SbF$_5$ solutions in HSO$_3$F contain large aggregates[14] of both types of molecules, therefore, this system provides the bulky solvent molecules and anions proposed by Dewar[6] to discriminate between hyperconjugation and steric hindrance to solvation. The results for our previous series of aromatics[9] (including toluene, *m*-xylene, *p*-xytene, and mesitylene) showed remarkable independence of $\Delta\Delta H_{C^+}$ both to temperature (over a range of 90°) and to solvent (HF–BF$_3$ *vis à vis* SbF$_5$–HSO$_3$F). Through the series of methyl benzenes cited above, $\Delta\Delta H_{C^+}$ appears to be insensitive to the temperature and bulkiness of the solvent molecules and counterions, both of which facts should affect seric hindrance to solvation.

It must be stressed at this point that we have only enthalpy data (no entropies or free energies) for benzenonium ion in HSO$_3$F–SbF$_5$ at −60°. However if it turns out that the same ΔH–ΔG relationship observed in HF–BF$_3$ applies generally to benzenonium ions, then, by Dewar's arguments, steric hindrance to solvation might be dismissed as the cause of the Baker–Nathan orders seen in Table III. His arguments appear to presuppose that solvation of the cationic carbon operates through specific and geometrically sensitive interactions with surrounding solvent molecules. If, however, the solvent were behaving here in the classical (and often inappropriate) sense of a continuous dielectric, it would not matter what the sizes of the solvent molecules were. The acidic systems being compared here probably both have high dielectric constants,[13] so that in this particular case the classical electrostatic picture might apply and, hence, steric inhibition of solvation might not be very sensitive to the size of the alkyl group.

The Effect of Structure on ΔH_{C^+}. Table III may be approached most profitably by noting a few general trends. We will then discuss particular cases which seem noteworthy.

First and foremost, we note that within each series, the Baker–Nathan order is followed either to the limit of experimental error or to the limit of stability for the resulting benzenonium ion under these conditions. In the monoalkyl series, the effect covers a range of 4 kcal/mol from toluene to *t*-butylbenzene with ethylbenzene and isopropylbenzene being indistinguishable from each other within the rather large range of their combined experimental errors.

In the trisubstituted series, we find larger differences between methyl and ethyl or between ethyl and isopropyl than were encountered in the monosubstituted benzenes. This, of course, is what would be expected if the benzenonium ion is able to enjoy stabilization of two *ortho* and one *para* substituents rather than that of a single *para* alkyl group.

Comparing the mono and tri series in more detail, we note that the trimethyl- and triethylbenzenonium ions are each stabler by about 5 kcal/mol than are their monosubstituted neighbors. However, an anomaly arises when comparison of 1,3,5-triisopropyl- with the monoisopropylbenzenonium ion is attempted in that the former might have been expected to be more stable than it is observed to be, Its heat of formation is actually *less* exothermic than that of the latter. Thus, compared to 1,3,5-triethylbenzene, 1,3,5-triisopropylbenzene gives a large Baker–Nathan decrease in stability. However, compared horizontally with monoisopropylbenzene, the decrease in stability appears to be

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(15) E. L. Mackor, A. Hofstra, and J. H. Vander Waals, *Trans. Faraday Soc.*, **54**, 186 (1958).

(16) Free energy measurements have also been made on this system by McCaulay and Lien [D. A. McCaulay and A. P. Lien, *Tetrahedron*, **5**, 186 (1959)] but they were forced to make an assumption about the solubility of alkylbenzenes in HF–BF$_3$ which, in light of our results, seems highly improbable.

(17) For a thorough discussion of this point see L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp 69–78.

(18) G. Olofsson, *Acta Chem. Scand.*, **22**, 377 (1968).

(19) R. W. Taft, 12th Conference on Reaction Mechanisms, Brandeis University, Waltham, Mass., June 1968.

too large. These relative orders would be hard to explain on the basis of substituent effects and we suggest that they are evidence for steric hindrance to solvation as an important factor which adds its effect to hyperconjugation as congestion around the ring accumulates. This idea is supported by the relatively small difference between ethyl and isopropyl in the mono-substituted series compared with the very large "jump" in the trialkyl series. Unfortunately, the cumulative effects of steric hindrance appear to result in instability of the corresponding tri-*t*-butylbenzenonium ion so that our series is truncated at this point preventing further tests of these speculations.

The effects noted in the mono- and trisubstituted ions are amplified in the first two hexaalkyl ones where hyperconjugation and steric hindrance to solvation are complicated further by many new steric and electronic factors. Instability of the ions prevents our pressing the question further. A peripheral commentary on hyperconjugation is provided by the results for the two polycyclic systems shown at the bottom of the table, namely, tritetralin and trindane.[20] These compounds are cyclic analogs of hexaethylbenzenes. The hydrogens on the α-carbons are held in a position where there may be considerably more favorable overlap with a neighboring positive carbon than might be possible in the hexaethylbenzenonium ion where the ethyl groups might be stacked to relieve steric repulsions with the α-hydrogens in less favorable positions for hyperconjugative interaction. If this were the only factor at work, one might have supposed the benzenonium ions from these two compounds to be especially stable. However, some other factor apparently is counteracting whatever benefits may be contributed by the favorable planarity. Since it is the less planar tritetralin which seems to enjoy the greater stability, compared to trindane, we conclude tentatively that there are unfavorable torsional contributions produced by twisting the ring at the site of protonation so that an already slightly strained planar system is buckled upon rehybridization.

We have pointed out and tried to explain inconsistencies that we see in Table III. However, we hope that the reader will not lose sight of the primary fact that we have found large Baker–Nathan effects in a highly electron-demanding reaction where solvent and temperature effects appear to be generally small and where enthalpy changes may be a direct expression of potential energy differences. Work presently underway in this laboratory on the relative free energies of the benzenonium ions should be able to test this important question.

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(20) Both ions have been observed in SbF_5–HSO_3F and are stable: T. Kiovsky and G. Olah, personal communications.