carbon of the ketone triplet. It is the competition between the formation of this species and $O_2(^1\Delta_g)$ which leads to S_Δ values of less than unity. Observation of the second-order effect will be dependent on the subsequent fate of the initially produced biradical. Further work on these and related systems is in progress.

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Anionic Homoaromaticity: A Gas-Phase Experimental Study

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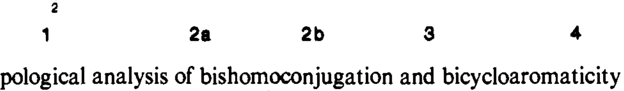
Abstract: The gas-phase acidities of several bicyclic and monocyclic alkenes and dienes have been measured in a model study of anionic homoaromaticity. Bicyclo[3.2.1]octa-2,6-diene (**1**), the precursor for what is considered to be a prototype bishomoaromatic carbanion, is found to have an acidity close to that of ethanol ($\Delta H_{\text{acid}}(\mathbf{1}) = 379.6 \pm 1.0$ kcal/mol). The model compounds bicyclo[3.2.1]oct-2-ene (**3**) and 5-methylene-2-norbornene (**12**) yield allylic carbanions that are incapable of homoaromatic stabilization and are found to be nearly 10 kcal/mol less acidic than **1**, with measured gas-phase acidities of 389.1 ± 1.0 and 389 ± 2 kcal/mol, respectively. A maximal 3–4 kcal/mol contribution to the enhanced acidity of **1** can be ascribed to an inductive effect of the remote C6–C7 double bond since the vinyl C–H acidities measured for norbornene and norbornadiene differ by only 3.1 kcal/mol. Kinetic measurements and experimentally derived acidity estimates for the related hydrocarbons cyclohexene, cyclooctene, 1,3-cyclohexadiene, and the cyclooctadienes are also presented which show that homoconjugation can be an important stabilizing influence in carbanions.

A long-standing problem in physical organic chemistry, one which continues to incite controversy even today, involves the viability of homoconjugative stabilization in carbanions. Alternatively termed "extensive" and "elusive", this unusual electronic delocalization mechanism which is, in principle, available to certain cyclic and polycyclic carbanions has traditionally proven difficult to establish unambiguously by both experiment and theory. The colorful history of anionic homoconjugation clearly illustrates its fluctuant status. The initial discovery by Brown and Occolowitz[1] of the 30000-fold rate enhancement for base-catalyzed H/D exchange of diene **1** relative to olefin **3** was followed by a general topological analysis of bishomoconjugation and bicycloaromaticity by Goldstein and Hoffmann.[2] Carbanion **2** was cited as but one example of a larger class of neutral, cationic, and anionic compounds in which transannular interactions between proximally held polyene "ribbons" may lead to extra stability or unstability, depending upon the symmetries and occupancies of the fragment molecular orbitals involved. Thus, facile H/D exchange in **1** was attributed to the bishomoaromatic character of the intermediate carbanion **2b**.[3] Direct observation of the ^{1}H NMR spectrum of ion **2**[3,4] provided additional support for homoconjugative charge delocalization, as extraordinarily high-field shifts for the C6, C7, and C8 protons were found which could be attributed to weak diamagnetic ring currents. The qualitative appeal of homoconjugation,[5] its successful applications in carbonium ion chemistry,[6] and mounting reports of its existence in other anionic systems[4,7] led to a relatively comfortable status for the idea by the early 1970's. However, questions were raised concerning the interpretation of the earlier NMR experiments when Trimitsis and Tuncay demonstrated in 1976[8] that the 2,4-diphenyl derivative of **1** exhibited only a weak kinetic acidity enhancement over the corresponding derivative of **3**, yet showed upfield shifts in the C6, C7, and C8 protons which were comparable to those found for **2**. Subsequently, a detailed analysis of the ^{1}H and ^{13}C NMR spectra, computed geometries, and electronic structures of cyclohexadienyl anions appeared[9] in which it was concluded that homoaromaticity was absent in these ions. The general failure of homoaromaticity in neutral, closed-shell π-systems was convincingly demonstrated by Houk and Paquette;[10] in fact, compelling arguments were put forth for a *destabilizing* effect of homoconjungation in such systems. The status of anionic homoaromaticity reached its nadir in 1981 when Grutzner and Jorgensen[11] and Kaufmann, Mayr, Chandrasekhar, and Schleyer[12] presented combined semiempirical and ab initio MO results for



1 2a 2b 3 4

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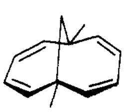
ion **2** and related bicyclic polyene anions which showed that the necessary transannular HOMO–LUMO interactions were essentially absent. The consensus opinion reached in both studies, based on minimal basis set (STO-3G) wave functions using MNDO and MINDO/3 geometries, was that the energy gap between filled and empty π orbitals in the alleged homoaromatic anions was too large to permit significant mixing. This could be clearly seen in the appropriate orbital diagrams and MO plots for each ion.[11-13] The enhanced acidity determined experimentally and computationally for diene **1** relative to the model compound **3** was attributed to inductive effects of the proximate double bond. A counter-claim by Brown quickly appeared[14] in which it was pointed out that a failure to adequately describe anions with the necessary diffuse basis functions[15] could readily account for the absence of orbital mixings, geometry changes, and stabilization commensurate with homoaromaticity which was reported by Grutzner and Jorgensen,[11] and Kaufmann et al.[12] The controversy was further rekindled with two brief communications which provided new experimental evidence for anionic bishomoaromaticity. Huber and co-workers synthesized tetraene **5** and its dianion **6** and found the latter to exhibit features in its ^1H and ^{13}C NMR spectra which were suggestive of a substantial diatropic ring current.[16] Furthermore, the parent tetraene **5** yielded dianion **6** electrochemically with a striking anodic shift in the second reduction potential (i.e., $E_1° \approx -2.1$ V; $E_2° \approx -1.8$ V). Cristl and co-workers[17] carried out isotopic perturbation of resonance[18] experiments with deuterium-labeled derivatives of ion **2** which lent strong support for a fully delocalized form **2b**, as opposed to a rapidly equilibrating mixture of classical allylic, tricyclic, and tetracyclic forms. In the most recent episode, Washburn[19] determined the equilibrium pK_a's of hydrocarbons **1** and **3** in cyclohexylamine/cesium cyclohexylamide solutions to be 31.4 ± 0.3 and >40.5, respectively, corresponding to a substantial 12.2 kcal/mol acidity increase for **1** due to the C6–C7 double bond. While attempted modelling of the inductive effect of two sp^2 carbons by pK_a measurements for **7** met with failure, the small acidity difference measured between 3-cyclopentenecarbonitrile and cyclopentanecarbonitrile (4.1 kcal/mol) suggested that such effects were minor in comparison to homoaromaticity.



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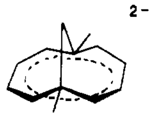

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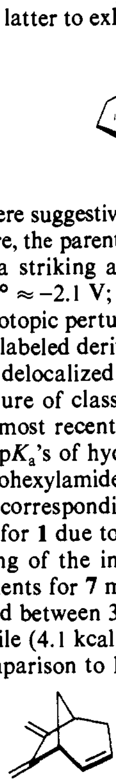

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In his recent review of carbanion chemistry, Staley remarks that "gas phase proton affinities for **2** and analogous systems would be of considerable interest and would put these ideas [about anionic bishomoaromaticity] on a more quantitative footing."[20] Starting about 3 years ago, we began a program of measurements of gas-phase acidities for compounds **1**, **3**, and related hydrocarbons using the flowing afterglow technique. Our specific aim was the determination of thermodynamic data for isolated carbanions which were relevant to the question of anionic homoconjugation and were free of possible complications from solvation and ion-pairing. Our belief was that gas-phase experiments would provide a more reliable means to assess the intrinsic magnitude and origins of homoaromatic stabilization, should it exist, while at the same time providing a much-needed calibration for previous theoretical treatments. In this paper we present the results of our measurements of gas-phase acidities for diene **1** and several model hydrocarbons which show that bishomoaromaticity can be a significant stabilizing influence in carbanions.

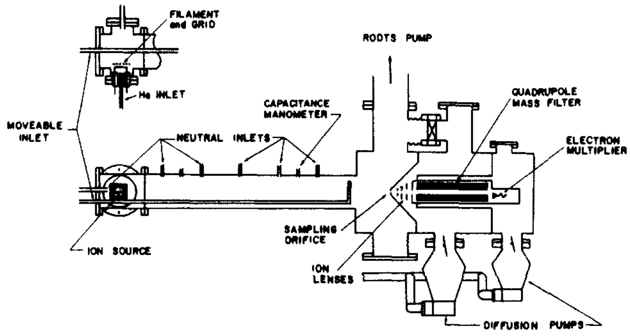

Figure 1. Schematic diagram of the flowing afterglow apparatus.

Experimental Section

All experiments were carried out at 298 ± 2 K with use of a flowing afterglow apparatus which has been described in detail previously.[21] A simplified schematic of the system is shown in Figure 1. Primary reagent ions are produced by electron impact ionization of neutral precursor gases added past an electron gun located in the upstream end of the instrument. A fast flow of purified helium buffer gas (150–250 STP $cm^3\ s^{-1}$) also enters the system in this region and carries the plasma the length of a 100 cm × 7.3 cm i.d. flow reactor. The bulk flow velocity (ca. 10^4 cm s^{-1}) and flow tube pressure (0.2–0.9 Torr) are maintained by a mass flow controller and a 750 L s^{-1} Roots blower. Rapid thermalization of primary reagent ions is achieved in the upstream quarter of the flow tube by ca. 10^7 collisions s^{-1} with helium. Introduction of neutral reagents into the ion stream through fixed or moveable inlets located along the length of the tube permits execution of spatially and temporally resolved ion–molecule reaction sequences. The plasma is sampled at a nosecone, and ions of selected charge are focussed into a quadrupole mass spectrometer which is coupled with a microcomputer controlled data system. The steady-state ion composition in the flow tube is monitored over a mass range of 1–500 amu with an optimal resolution of 1200 at 131 amu. Mass discrimination by the quadrupole is normally minimized by operating at as low a resolution as is practical. For the present experiments, the following standard conditions were employed: $P(\mathrm{He}) = 0.40$ Torr; $\nu(\mathrm{He}) = 9400$ cm s^{-1}; $F(\mathrm{He}) = 190$ STP $cm^3\ s^{-1}$. These conditions correspond to an average ion residence time in the flow reactor of up to 10 ms.

Bimolecular ion–molecule reaction rate coefficients were determined according to standard procedures[22] from semilog plots of the reactant ion intensity vs. either the neutral reagent flow rate or the total reaction time. The latter parameter is simply related to the total reaction distance in the flow tube and is easily varied with the moveable neutral injector over a range of 70 cm (ca. 7 ms). Neutral flow rates ranging from 10^{-4} to 1.0 STP $cm^3\ s^{-1}$ were measured by diverting the flow into a calibrated volume and monitoring the pressure increase with time. Two such flow rates could be measured concurrently for a given experiment with our present instrument configuration. Each of the rate coefficients in the present study represents an average of at least three separate kinetic determinations employing different neutral concentrations (flow rates). The precision is normally better than 5%, and the estimated accuracy is approximately 20%.[22c]

Equilibrium constants for proton transfer reactions were determined either by direct assay or by measurement of forward and reverse reaction rates under conditions where the corresponding back reactions were minimized.[23] For direct assay, a sufficient quantity of a neutral acid

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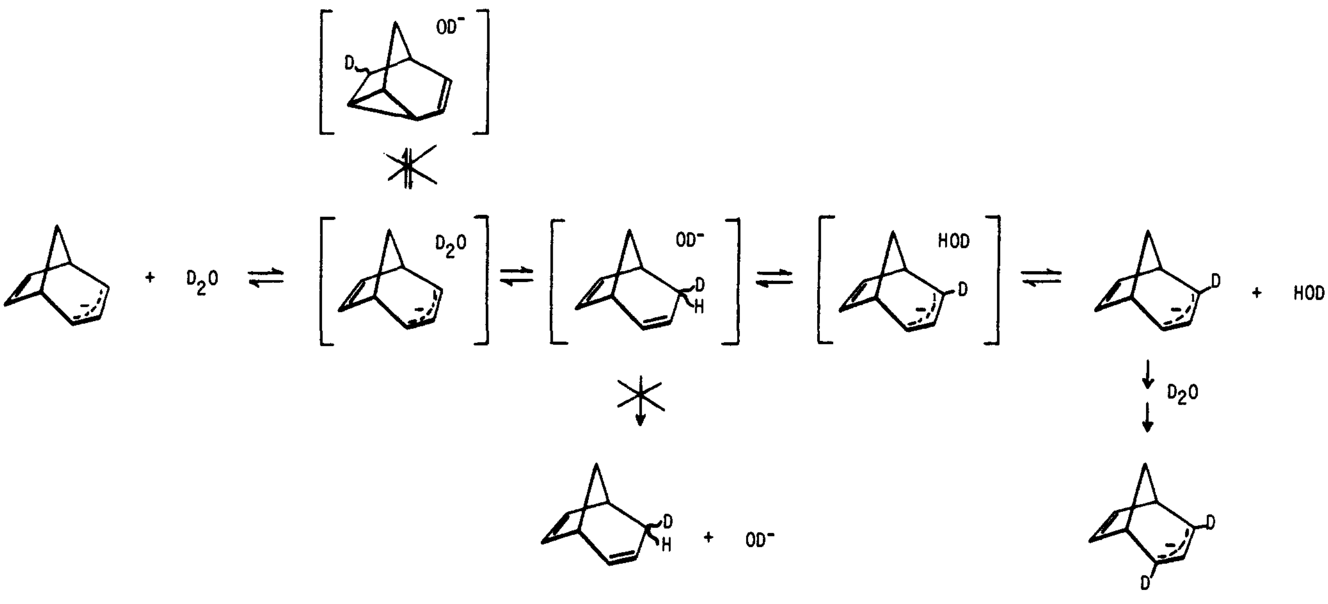
Scheme I



component of the equilibrium was added through an upstream inlet to completely react away a precursor base such as NH_2^- or OH^-. The second acid was then added through the moveable injector with increasing flow rate until variation in the injector position (10–50 cm from nosecone) produced no further changes in the conjugate base anion intensity ratio. Measurement of the two neutral flow rates and the ion intensity ratio then permitted calculation of an equilibrium constant. Equilibrium constants determined by the alternative kinetic procedure (k_f/k_r) are believed to be more reliable since they do not suffer from the potential error arising from mass discrimination in the ion signal intensity ratio measurements.[23,24]

Hydroxide ion was generated at the ion source by electron impact on a mixture of N_2O and CH_4. Amide ions from ammonia, ethylamine, propylamine, and dimethylamine were produced from dissociative electron capture by each amine added at the ion source. Methoxide and ethoxide ions were generated by amide induced elimination from 2,2-dimethoxypropane and electron impact on ethanol, respectively. Hydride ion was produced by electron impact on reduced flow rates of ammonia added at the source. Variable amounts of hydroxide ion (30–50%) were also present when hydride or amide ions were produced owing to adventitious water in the system.

Materials. Most all of the liquid samples used in this study were obtained from commercial sources and were subjected to simple distillation prior to use. A high level of purity was shown for each sample by gas chromatography and/or infrared and ^1H NMR spectra. Each sample was degassed just prior to use by multiple freeze–pump–thaw cycles. Lithium aluminum hydride was also occasionally added to hydrocarbon samples as an additional safeguard against acidic impurities. Bicyclo[3.2.1]octa-2,6-diene (**1**) was prepared from norbornadiene according to the methods described by Brown[1] and Meinwald.[25] Initial purification by flash chromatography followed by fractional distillation gave a product boiling at 65 °C (115 mmHg) exhibiting infrared and NMR spectra which were identical with those previously reported.[1,3] Bicyclo[3.2.1]oct-2-ene (**3**) is a waxy, sublimable solid which was obtained from Wiley chemicals and used as supplied. 2-Methylenenorbornane was prepared by diimide reduction[26] of 5-methylene-2-norbornene followed by fractional distillation. D_2O (99.8 mol % *d*) and CH_3OD (99.5 mol % *d*) were obtained commercially, and CH_3CH_2OD was prepared by hydrolysis of $(CH_3CH_2O)_4Si$ with D_2O.[27] Gas purities were as follows: He (99.995%), CH_4 (99.0%), N_2O (99.0%), NH_3 (anhydrous, 99.5%), ND_3 (99.1 mol % *d*).

Results

The observed reactivity and measured gas-phase acidities for a series of eleven selected hydrocarbons are described in the following sections. Subsequently, we present a detailed discussion of these results in the context of homoconjugation effects in certain of the carbanions.

Bicyclo[3.2.1]octa-2,6-diene. Compound **1** rapidly reacts by proton transfer with both NH_2^- (PA = 403.6 kcal/mol)[28] and OH^- (PA = 390.7 kcal/mol)[28] and more slowly with CH_3O^- (PA = 381.4 kcal/mol)[29] to yield a single carbanion product at *m/z* 105. In each reaction the absolute carbanion yields are quite low (ca. 10%), i.e., at 100% reactant ion conversion the observed intensity of *m/z* 105 is significantly less than the initial intensity of the reactant ion. It can be shown that this effect is not due to mass discrimination by the quadrupole, and it is believed to have its origins in the loss of carbanion **2** through electron detachment. This is probably an example of a phenomenon originally reported by DePuy and co-workers[30] wherein allylic carbanions bearing secondary or tertiary termini such as cyclopentenyl, cyclohexenyl, and 3-hexenyl have consistently proven difficult to observe under flowing afterglow conditions, most likely due to their low electron binding energies. Carbanion **2** undergoes a maximum of two hydrogen–deuterium exchanges[31] without detectable neutralization when D_2O is added to the reactor through a downstream inlet, as illustrated in Figure 2. The appearance of only two H/D exchanges provides indirect evidence for initial ionization at the allylic (C4) position in **1**, while at the same time contraindicating reversible protonation of the carbanion **2** by D_2O at C6 and C7, as might be expected for the fully delocalized ion structure **2b** (Scheme I). This behavior is not surprising since the resulting tricyclic and tetracyclic intermediates[3] are likely to be too high in energy to be formed in the course of a single gas-phase collision between **2** and D_2O.[32] Ion **2** undergoes a somewhat slower exchange of two hydrogens for deuterium in the presence of CH_3OD,[31] with accompanying formation of CH_3O^- by proton transfer. Nearly complete neutralization occurs with the more acidic reagent CH_3CH_2OD, with only traces of H/D exchange appearing in the mass spectrum at low reactant ion conversions. These qualitative observations suggest that the acidity of **1** lies

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[32] A possible alternative explanation for the observation of only two exchanges is that deuteration does occur at the C6 and C7 positions of **2** but, for steric reasons, only removal of this same deuteron may take place. Related reports of stereoselectivity in acid quenching of **2** can be found in the following: Brown, J. M.; Cain, E. N. *J. Am. Chem. Soc.* **1970**, *92*, 3821.

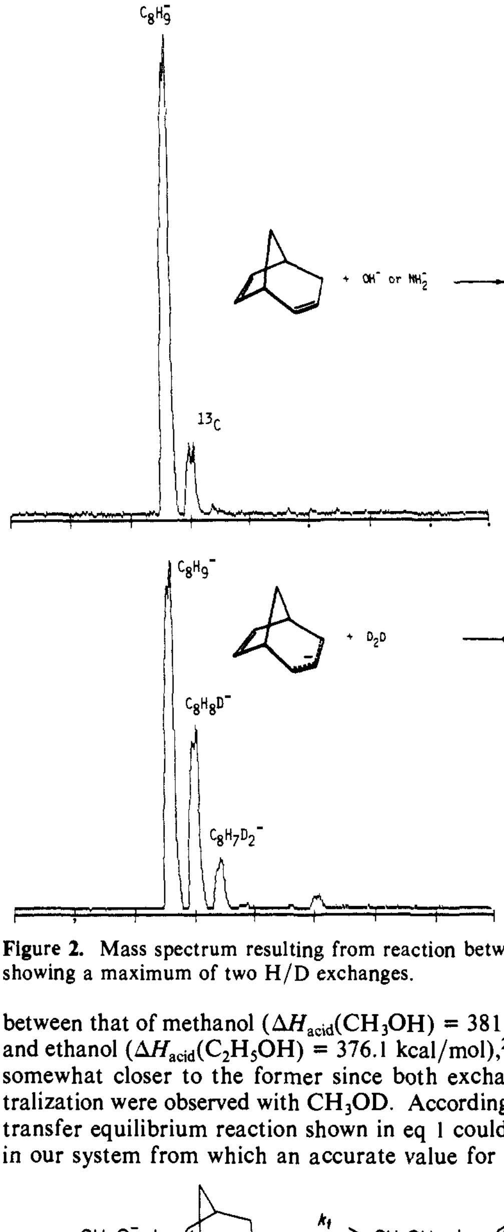
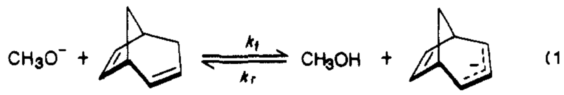


Figure 2. Mass spectrum resulting from reaction between **2** and D_2O showing a maximum of two H/D exchanges.

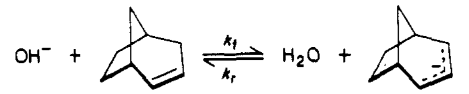
between that of methanol ($\Delta H_{acid}(CH_3OH)$ = 381.4 kcal/mol)[29] and ethanol ($\Delta H_{acid}(C_2H_5OH)$ = 376.1 kcal/mol),[28] with a value somewhat closer to the former since both exchange and neutralization were observed with CH_3OD. Accordingly, the proton transfer equilibrium reaction shown in eq 1 could be identified in our system from which an accurate value for the gas-phase



(1)

acidity of **1** could be determined. The nonconservation of total ion intensity in this reaction due to the factors mentioned previously precluded direct measurement of the equilibrium constant. However, measurements of the forward and reverse reaction rates for eq 1 could be carried out under conditions where the corresponding back reactions were negligible, as shown by reproducibly linear kinetic decay plots for either reactant ion.[23] Four measurements of either rate coefficient with use of a range of neutral reactant concentrations (flow rates) provided the average values: $k_f = 6.5 \pm 0.1 \times 10^{-10}$ $cm^3\ s^{-1}$ and $k_r = 6.4 \pm 1.2 \times 10^{-11}$ $cm^3\ s^{-1}$. The ratio k_f/k_r yields a value for the equilibrium constant $K(1)$ of 10.1 ± 1.8, which corresponds to a free energy change $\Delta G(1)$ at 298 K of −1.4 ± 0.3 kcal/mol. The total entropy change for eq 1 can be reasonably estimated from a sum of the translational and rotational entropy contributions, as given by standard statistical formulae.[28] Assuming C_s symmetry for **2** and C_1 symmetry for **1** leads to $\Delta S(1) = -1.3$ eu, which combines with the measured $\Delta G(1)$ to yield $\Delta H(1) = -1.8$ kcal/mol. Adding this quantity to the known acidity of methanol produces a final value for $\Delta H_{acid}(\mathbf{1})$ of 379.6 ± 1.0 kcal/mol.

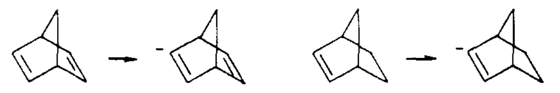
Bicyclo[3.2.1]oct-2-ene. Olefin **3** yields a carbanion product at *m/z* 107 from reaction with either NH_2^- or OH^-. As with **2**, low absolute ion yields are also evident. No reaction occurs with CH_3O^-, implying an acidity for **3** somewhat less than that of methanol. Accordingly, carbanion **4** is completely neutralized by CH_3OD without H/D exchange, but it undergoes two exchanges in the presence of D_2O with accompanying production of traces of OD^- (PA = 392.9 kcal/mol).[28] This latter observation is indicative of an acidity for **3** which is close to that of H_2O. The



(2)

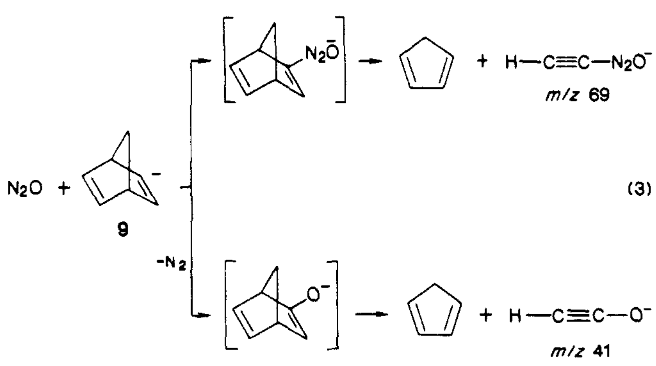
acid–base equilibrium reaction shown above could be identified and was quantitated by measurements of the forward and reverse rate coefficients (eq 2). Average values based on four determinations are $k_f = 1.3 \pm 0.1 \times 10^{-9}$ $cm^3\ s^{-1}$ and $k_r = 3.1 \pm 0.1 \times 10^{-10}$ $cm^3\ s^{-1}$, corresponding to an equilibrium constant $K(2)$ = 4.1 ± 0.2 and free energy difference $\Delta G(2)$ at 298 K of 0.83 ± 0.03 kcal/mol. Evaluation of the entropy change for eq 2 with statistical mechanics leads to $\Delta S(2) = -2.6$ eu and a corresponding final value for $\Delta H(2)$ at 298 K of −1.6 kcal/mol. Combining this with the gas-phase acidity of H_2O leads to $\Delta H_{acid}(\mathbf{3})$ = 389.1 ± 1.0 kcal/mol.

Norbornadiene and Norbornene. We have examined the acid–base behavior of norbornadiene (**8**) and norbornene (**10**) in order to model the influence of a remote double bond on hydrocarbon



8 **9** **10** **11**

acidity. Norbornadiene and its conjugate base carbanion **9** have been the subjects of previous flowing afterglow[33] and ion cyclotron resonance studies. Beauchamp and Wight[34] reported a bracketed acidity for **8** of 402 ± 5 kcal/mol based on its observed deprotonation by NH_2^-, but not H^- (PA = 400.4 kcal/mol).[28] In our system, a good yield of a carbanion product is observed from reaction between **8** and NH_2^-, with a measured bimolecular rate coefficient of $8.3 \pm 1.1 \times 10^{-10}$ $cm^3\ s^{-1}$. Proton abstraction from **8** does not occur with OH^- nor with other anions of lower basicity, and only neutralization is observed when **9** is allowed to react with either D_2O or CH_3OD. A vinylic carbanion structure is indicated by the observed reactivity of **9**. Thus, a maximum of three H/D exchanges is observed when ND_3 is added to the flow tube, and **9** reacts with N_2O to produce, inter alia, a pair of two-carbon product ions which are rationalized most economically by reaction at the vinyl position followed by retro-Diels–Alder fragmentation (eq 3). In solution, the preference for kinetic vinyl deprotonation in norbornadiene is clearly shown by the base-catalyzed H/D exchange studies reported by Streitwieser.[35]



(3)

A refined value for the gas-phase acidity of **8** derives from its proton transfer reactions with alkyl amide ions. Proton abstraction is observed with $CH_3CH_2NH^-$ (PA = 399.4 kcal/mol),[28] $CH_3CH_2CH_2NH^-$ (PA = 398.4 kcal/mol),[28] and $(CH_3)_2CHNH^-$ (PA = 397.3 kcal/mol)[28] and in trace amounts with $(CH_3)_2N^-$ (PA

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(33) Grabowski, J. J.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1983**, *105*, 2565.

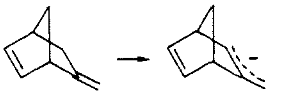
(34) Wight, C. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6499.

(35) Streitwieser, A.; Caldwell, R. A. *J. Org. Chem.* **1962**, *27*, 3360.

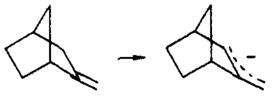
= 396.4 kcal/mol).[28] Furthermore, carbanion **9** proton abstracts from $(CH_3)_2NH$ and $CH_3CH_2CH_2NH_2$, but it does not do so from either $CH_3CH_2NH_2$ or NH_3. Given the tight acidity bracketing by these reference compounds, we did not determine an equilibrium acidity for **8** directly but rather assigned a final value of 398.0 ± 1.5 kcal/mol.

Norbornene (**10**) proton transfers to NH_2^- to yield a vinylic carbanion (**11**) which undergoes a single H/D exchange with added ND_3 and rapidly neutralizes in the presence of D_2O and CH_3OD. Proton abstraction also occurs with H^-, but not with $CH_3CH_2NH^-$ or $CH_3CH_2CH_2NH^-$. Furthermore, **11** slowly proton abstracts from $CH_3CH_2NH_2$. From these reactions we assign ΔH_{acid}(**10**) to be 401.0 ± 1.0 kcal/mol.

5-Methylene-2-norbornene and 2-Methylenenorbornane. Compound **12** is an isomer of **1** which can yield an allylic carbanion (**13**) that is incapable of bishomoconjugation with the remote double bond. Proton abstraction from **12** occurs with NH_2^- (k = 1.8 ± 0.1 × 10^{-9} cm³ s⁻¹) and OH^- (k = 1.0 ± 0.1 × 10^{-9} cm³ s⁻¹), but not with CH_3O^-. Furthermore, the resulting carbanion is completely neutralized by methanol and reacts with H_2O to yield OH^- with an overall rate coefficient of 2.1 ± 0.2 × 10^{-10} cm³ s⁻¹. The site of protonation in carbanion **13** cannot be unambiguously assigned in these experiments. However, the thermodynamic basicities at either end of the unsymmetrical allylic system are expected to be similar since the heats of formation of **12** and its tautomer 2-methylnorbornadiene differ only slightly (ca. 2.0 kcal/mol).[36] Hydrogen-deuterium exchange between D_2O and the carbanion derived from **12** is anomalous. As reported earlier,[37] a total of seven exchanges is observed in the mass spectrum at high flows of added D_2O, with a signal intensity profile suggesting five rapid exchanges accompanied by two slower exchanges. This was originally attributed to exchange within the intact bicyclic ion structure **13**.[37] However, subsequent reactivity studies with **12** and the ions derived from it in our laboratory have led us to conclude that proton abstraction by NH_2^- or OH^- produces a mixture of ions, with the main component being **13** and the minor component being one or more of the xylenyl anion isomers, $CH_3C_6H_4CH_2^-$, derived from a deep-seated skeletal rearrangement. Moreover, reaction between **13** and either water or D_2O appears to slowly catalyze the rearrangement. While this complicates the acidity measurements for **12** somewhat, we can reasonably conclude that it must lie close to that of water since proton transfer in both directions was observed with the OH^-/H_2O reactions. On the basis of the forward and reverse rates presented earlier we can calculate a phenomenological equilibrium constant for **12** + OH^- of 5.0. The corresponding free energy, estimated entropy, and resulting enthalpy changes are −0.95 kcal/mol, −1.2 eu, and −1.3 kcal/mol, respectively. A final value for the gas-phase acidity of **12** is thus estimated to be 389 ± 2 kcal/mol. The 2 kcal/mol uncertainty interval takes into account the ambiguity regarding protonation site in **13** and the error in the kinetics measurements arising from rearrangement.



12 **13**



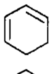
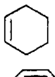
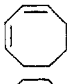
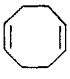
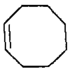
14 **15**

2-Methylene norbornane proton transfers to both NH_2^- and OH^- to yield a carbanion **15** which shows a maximum of three H/D exchanges in the presence of D_2O. Proton abstraction by CH_3O^- does not occur, implying an acidity for **14** between that of H_2O and CH_3OH. The acid-base equilibrium reaction shown below could be established in our system (eq 4), and measurements of the forward and reverse reaction rates were performed: k_f = 1.1 ± 0.2 × 10^{-9} cm³ s⁻¹; k_r = 5 ± 3 × 10^{-11} cm³ s⁻¹.

$$\mathbf{14} + OH^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathbf{15} + H_2O \qquad (4)$$

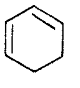
Again, the site of protonation in **15** is not established but the energy difference between tautomers is not large.[36] Indeed, the occurrence of complete exchange in the unsymmetrical allylic moiety shows that protonation at either terminus does occur. On the basis of the kinetics, a phenomenological equilibrium constant $K(4)$ = 21 may be computed, which corresponds to $\Delta G(4)$ = −1.8 kcal/mol. The corresponding entropy and enthalpy changes for eq 4 are −1.2 eu and −2.2 kcal/mol, respectively, which lead to an estimated acidity for **14** of 389 ± 2 kcal/mol.

Table I. Gas-Phase Acidities and H/D Exchange Behavior of Cycloalkenes

compound	bracketing results	ΔH_{acid}[a]	H/D exchange[b]
 **16**	$SiH_4 < x <$ *t*-BuOH	372 ± 2	D_2O (0) CH_3OD (7)
 **17**	$H_2O < x < CH_3OH$	>387	
 **18**	EtOH $< x <$ *n*-PrOH	375 ± 2	D_2O (2) CH_3OD (2)
 **19**	EtOH $< x <$ *n*-PrOH	(375 ± 2)[c]	D_2O (6) CH_3OD (2)
 **20**	$H_2O < x < CH_3OH$	<386	D_2O (13)

[a] Assigned gas-phase acidity in kcal/mol. [b] Maximum number of exchanges observed with high concentrations of exchange agent indicated in parentheses. [c] Isomerization to a conjugated dienyl anion occurs during proton abstraction, see text.

Monocyclic Hydrocarbons. In order to provide a better perspective for interpreting the results obtained with the bicyclic compounds, we have characterized the acid-base behavior of the C_6 and C_8 cycloalkenes and dienes shown below (**16**–**20**). Cyclohexadiene (**16**) is of particular interest as a precursor for the potentially homoaromatic cyclohexadienyl anion,[9,38,39] and 1,5-cyclooctadiene (**19**) is notable for the extraordinary facility with which it undergoes base-catalyzed isomerization to the conjugated isomer **18** in solution.[40] Each hydrocarbon and its derived carbanion has been allowed to react with a series of reference base anions and neutral acids, respectively, with the results outlined in Table I. The assigned acidities are based on either the observed occurrence of both forward and reverse proton transfers with the indicated reference species in a self-consistent manner or on thermochemical cycles involving literature data. For instance, 1,3-cyclohexadiene yields a conjugate base carbanion (m/z 79) with NH_2^-, OH^-, CH_3O^-, and *t*-BuO⁻ (PA = 373.3 kcal/mol),[28] but not with $CF_3CH_2O^-$ (PA = 364.4 kcal/mol)[28] nor $CH_3CH_2S^-$ (PA = 357.4 kcal/mol).[28] Furthermore, this carbanion is neutralized by CF_3CH_2OH and SiH_4 (ΔH_{acid} = 371.5 kcal/mol)[28] but not by C_2H_2 (ΔH_{acid} = 375.4 kcal/mol). Protonation undoubtedly occurs at both the terminal and central positions of the dienyl system in these latter experiments since the energy difference between isomeric dienes is only 0.4 kcal/mol.[36] A bracketed acidity for **16** of 372 ± 2 kcal/mol is derived from the above results. This is in good agreement with a lower limit of 370 kcal/mol which can be deduced from the 1,3-cyclohexadiene C–H bond energy (73 ± 5 kcal/mol)[41] and the upper limit for



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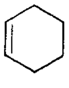

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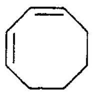

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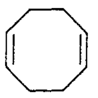

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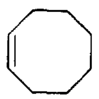

20

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[36] Pedley, J. B.; Rylance, J. Sussex-NPL Computer Analyzed Thermochemical Data, University of Sussex, 1977.

[37] Squires, R. R.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1981**, *103*, 4256.

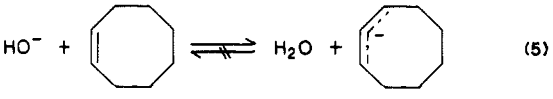
[38] Bates, R. B.; Brenner, S.; Cole, C. M.; Davidson, E. W.; Forsythe, G. D.; McCombs, D. A.; Roth, A. S. *J. Am. Chem. Soc.* **1973**, *95*, 926.

[39] (a) Haddon, R. C. *Tetrahedron Lett.* **1974**, 2797. (b) Haddon, R. C. *J. Am. Chem. Soc.* **1975**, *97*, 3608.

[40] Devaprabhakara, D.; Gardenas, C. G.; Gardner, P. D. *J. Am. Chem. Soc.* **1963**, *85*, 1553.

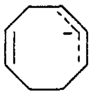
the cyclohexadienyl radical electron affinity (16.2 kcal/mol) which we reported recently.[42] In accordance with previous reports,[31] we observe the cyclohexadienyl anion to undergo complete exchange of all seven hydrogens in the presence of CH_3OD, but no exchange with D_2O.

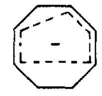
Cyclohexene (**17**) appears to be reactive with both NH_2^- and OH^-, but not with CH_3O^-. As originally reported by DePuy and co-workers,[30] no conjugate base carbanion can be detected from cyclohexene under flowing afterglow conditions, presumably due to its fast electron autodetachment arising from a low electron affinity for the cyclohexenyl radical. However, we can estimate an acidity for cyclohexene from an appropriate thermochemical cycle involving physical data from the literature. Since the parent allyl anion ($C_3H_5^-$) has a low electron binding energy of 8.3 kcal/mol,[43] yet can be readily observed in a flowing afterglow,[44] then cyclohexenyl radical probably has an electron affinity somewhat less than 8.3 kcal/mol. Furthermore, if we assume that the allylic C–H bond energy in cyclohexene is the same as the measured value for cyclopentene (82.3 ± 1.0 kcal/mol),[41] then a lower limit for ΔH_{acid}(**18**) may be calculated from $D[R-H] - EA(R) + IP(H) = 82.3 - 8.3 + 313.6 = 387.6$ kcal/mol. This estimate is consistent with the proton abstraction results. Interestingly, the larger ring cyclooctenyl anion *can* be observed in our system by proton abstraction from cyclooctene **20** with either NH_2^- or OH^-, albeit in low yield. The overall disappearance rate coefficient for OH^- is measured to be $5.4 \pm 0.4 \times 10^{-10}$ cm^3 s^{-1}. The back reaction with H_2O (eq 5) is immeasurably slow ($k < 2 \times 10^{-13}$ cm^3 s^{-1}), which sets an upper limit to $K(5)$ of approximately 2700. This corresponds to $\Delta G(5) \leq -4.6$ kcal/mol at 298 K which, in turn, provides an upper limit for ΔH_{acid}(**20**) of 386 kcal/mol (assuming $\Delta G(5) \approx \Delta H(5)$). Further refinement of this value by proton transfer experiments with other compounds is precluded since reference acids with established acidities in this range are not presently available. The cyclooctenyl anion exhibits complete exchange of all 13 hydrogens for deuterium with added D_2O, clearly illustrating the ease with which double-bond isomerization occurs within the intermediate cyclooctenyl anion–D_2O collision complex. The extensive exchange also indicates that, unlike cyclohexenyl anion, cyclooctenyl is sufficiently stable with respect to electron detachment to survive several milliseconds in the flow reactor during which time it suffers dozens of reactive collisions with D_2O.

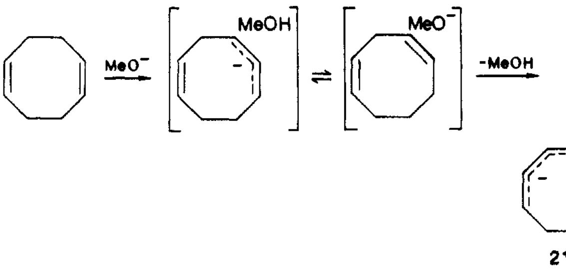


(5)

The conjugated 1,3-cyclooctadiene (**18**) yields an $(M - H)^-$ ion at m/z 107 from reaction with $CH_3CH_2O^-$ and anions of greater basicity but does not proton transfer to $CH_3CH_2CH_2O^-$ (PA = 374.7 kcal/mol)[28] or weaker bases. Furthermore, the resulting carbanion is rapidly neutralized by both $CH_3CH_2CH_2OH$ and *t*-BuOH. A gas-phase acidity for **18** of 375 ± 2 kcal/mol is indicated by these results. H/D exchange between D_2O and 1,3-cyclooctadienyl anion is quite slow, with two exchanges just barely discernable in the mass spectrum at the highest obtainable flows of D_2O. CH_3OD affects exchange more rapidly, but a maximum of only two are observed. This latter behavior makes an interesting contrast to the seven exchanges observed with cyclohexadienyl anion under similar conditions. The origins of this difference are presently under investigation.[45] The deconjugated isomer **19** gives an apparent acidity which is identical with **18** based on the occurrence of carbanion formation with $CH_3CH_2O^-$ but not $CH_3CH_2CH_2O^-$. While it is conceivable that the apparent acidity enhancement for **19** relative to cyclooctene could be due to bishomoconjugation in the carbanion (i.e., **21b**), it is more likely that the initially formed allylic ion is suffering isomerization to a conjugated dienyl anion within the initial energy-rich collision complex through multiple proton transfers (eq 6).[31,37] As a result, weaker bases than would be required to produce **21a** are observed to react with **19** to yield a carbanion product, in this case **21c**. That isomerization may occur is clearly illustrated by the observed H/D exchange behavior of **21**. Proton abstraction from **19** by an NH_2^-/OH^- mixture yields a carbanion product which shows a maximum of six H/D exchanges with added D_2O. This is distinct behavior from that of 1,3-cyclooctadienyl anion under similar conditions, showing that at least part of the initial population of ions have structure **21a**. However, if isomerization were not occurring then, in principle, all eleven hydrogens in **21** would exchange (cf. cyclooctenyl anion). Similar reasoning has been used to rationalize the observed exchange behavior of acyclic 1,5-dienes.[31b]


21a


21b



(6)

21c

Discussion

Table II summarizes the gas-phase acidities of the eleven hydrocarbons examined in this work, and Figure 3 illustrates the pertinent acidity differences in the form of a partial gas-phase acidity scale. It is immediately evident from these data that compound **1** possesses an extraordinarily high gas-phase acidity (low ΔH_{acid}) for an allylic hydrocarbon. Indeed, its acidity is more nearly like that of normally conjugated dienes than model alkenes such as **3** and propylene ($\Delta H_{acid} = 391.3 \pm 0.5$ kcal/mol).[44a] The 9.5 ± 2.0 kcal/mol acidity difference between **1** and **3** is substantial, considering the full range of known hydrocarbon acidities (ca. 60 kcal/mol),[28] and agrees reasonably well with the 12.2-kcal/mol difference measured in cyclohexylamine solution by Washburn.[19,46]

The origin of the acidity enhancement for **1** remains the key issue. Substituent effects on gas-phase acidities traditionally have been divided into four main categories, each of which may play a role in determining the absolute and relative acidities for **1** and **3**: polarizability effects, hybridization/geometry effects, field/inductive effects, and resonance effects.[28,47,48] A systematic evaluation of the influence of these factors on the acidity of **1** in terms of the model compounds illustrated in Table II and Figure 3 follows.

Polarizability effects derive from the electrostatic stabilization of a charged site in an ion through charge–induced dipole interactions involving proximate bonding and nonbonding electrons.[47,48] A familiar manifestation of this effect is the increasing

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[41] McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

[42] Lane, K. R.; Sallans, L.; Squires, R. R. *J. Am. Chem. Soc.*, in press.

[43] Oakes, J. M.; Ellison, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 7734.

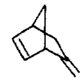
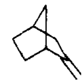
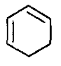
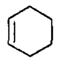
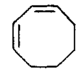
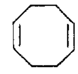
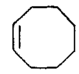
[44] (a) Mackay, G. I.; Lien, M. H.; Hopkinson, A. C.; Bohme, D. K. *Can. J. Chem.* **1978**, *56*, 131. (b) Bohme, D. K.; Lee-Ruff, E.; Young, L. B. *J. Am. Chem. Soc.* **1972**, *94*, 5153.

[45] Exchange exclusively at the end positions of acyclic dienyl anions has been reported by DePuy and co-workers (ref 31b). The absence of additional exchange in cyclooctadienyl anion indicates that isomerization of the diene moiety around the ring does not occur.

[46] In this context we note that new experimental and computational data have recently become available which indicate a significant contribution to the total stabilization of carbanion 2 in solution from η^5-bonding (C6-C7 π-chelation) by the Li^+ gegenion on the endo face of the ion. See: Hertkorn, N.; Köhler, F. H.; Müller, G.; Reber, G. *Angew. Chem.*, in press. Lindh, R.; Roos, B. O.; Jonsall, G.; Ahlberg, P. *J. Am. Chem. Soc.*, in press. Schleyer, P. v. R.; Kaufmann, E.; Kos, A. J.; Mayr, H.; Chandrasekhar, J. *Chem. Commun.*, in press. We thank Professor Schleyer for bringing these new results to our attention.

[47] Taft, R. W. *Progr. Phys. Org. Chem.* **1983**, *14*, 247.

Table II. Measured Gas-Phase Acidities for Selected Hydrocarbons, 298 ± 2K

compound	entry	ΔH_{acid} (kcal/mol)
	**1**	379.6 ± 1.0
	**3**	389.1 ± 1.0
	**8**	398.0 ± 1.5
	**10**	401.1 ± 1.0
	**12**	389 ± 2
	**14**	389 ± 2
	**16**	372 ± 2
	**17**	≥387
	**18**	375 ± 2
	**19**	375 ± 2
	**20**	≤386

gas-phase acidities of the aliphatic alcohols with increasing molecular size[49] (i.e., di-*tert*-butylcarbinol is 14 kcal/mol more acidic than methanol[28]). In considering the influence of polarization in ions **2** and **4**, we note that the unsaturated C6–C7 bridge in **2** is a *less* polarizable "substituent" than the saturated bridge in **4** simply because there are fewer electrons present. Accordingly, stabilizing polarizability effects should operate in **4** to a greater extent than in **2**. As a crude measure of the differential effect, we can apply the simple electrostatic potential below (eq 7) where α is the bulk apolarizability, q is the electron charge, and r is the

$$V(r) = -(\alpha q^2/2r^4) \qquad (7)$$

distance between a hypothetical point charge and point polarization center. Using $CH_2{=}CH_2$ (α = 4.26 Å^3)[50] and CH_3CH_3 (α = 4.44 Å^3)[50] as models for the unsaturated and saturated C6–C7 bridges in **2** and **4**, respectively, at distances of 2–3 Å from a unit charge gives vanishingly small electrostatic energy differences of −1.8 to −0.4 kcal/mol in favor of CH_3CH_3. Thus, polarizability differences are not expected to contribute significantly to the enhanced acidity of **1**.

Molecular geometry or, more specifically, C–H bond hybridization effects can have a pronounced influence on hydrocarbon acidities as shown, for example, by the measured gas-phase acidities for CH_4 (416.6 kcal/mol),[28] $CH_2{=}CH_2$ (408 kcal/mol),[51] and $HC{\equiv}CH$ (375.4 kcal/mol).[28] While the corresponding gas-phase data are presently unavailable, the enhanced kinetic acidities of small-ring compounds in solution are likewise attributed to the increased s-character in peripheral C–H bonds which may accompany severe skeletal distortions.[52] Since the geometries for the pairs of compounds **1** and **3**, and their conjugate base carbanions **2** and **4** should be quite similar,[11,12] C–H bond hybridization effects on their relative energies will tend to cancel. However, it is instructive to consider to what extent angular distortions in the allylic bridges of **1** and **3** may influence the *absolute* acidities. That such effects are operative is suggested by the >3 kcal/mol acidity increase for the approximately strain-free cyclooctene (**20**) relative to bicyclooctene (**3**). A useful quantitative model is given by Boerth and Streitwieser, who examined computationally the effect of CCC angular distortions on the acidity of propene.[53] Here, the main effect appears in the allylic carbanion where destabilization of the antisymmetric HOMO occurs at CCC angles less than the ca. 132° optimum.[54] Plots of the allyl anion proton affinity vs. the CCC angle are provided in this study which can be combined with the computed geometries for ions **2** and **4** to estimate the C2–C3–C4 angular distortion effects on their proton affinities. For both **2** and **4**, the calculated optimum C2–C3–C4 angles is 123°.[11,12] Using 132° as the ideal angle for a fully relaxed allylic anion[54] leads to a 9° distortion which, in turn, corresponds to a 3.1 kcal/mol proton affinity increase according to the graphical relationship presented by Boerth and Streitwieser.[53] A strain effect of this magnitude is nicely consistent with the observed acidity difference between **3** and **20**. Angle strain may also destabilize the dienyl anion **2** somewhat; however, at the same time the raised energy of the allylic HOMO at contracted C2–C3–C4 angles could also result in enhanced homoconjugative interaction with the C6–C7 double bond since the fragment orbital energy gap would be less.[55]

Inductive/field effects were claimed by Grutzner and Jorgensen[11] and Kaufmann et al.[12] to be a likely alternative for homoconjugation as the cause of the increased acidity of **1** relative to **3**. Here, the two electronegative sp^2 carbons in the C6–C7 bridge of **2** could conceivably exert a stabilizing $-I$ effect on the partially charged termini of the allylic anion moiety. While electron-withdrawing effects of a vinyl group on ionization reactions taking place in solution are generally quite small (σ_I = 0.02),[56] polar substituent effects are often found to be strongly amplified in the analogous gas-phase processes since only intramolecular stabilization (or destabilization) is available.[47] Thus, if inductive effects are operative in **1**, then they would be expected to exert a greater influence on its gas-phase acidity than on its solution pK_a. In this context it is interesting to note that, while the magnitude is small and subject to error, the measured acidity difference between **1** and **3** is, in fact, *larger* in solution19 than it is in the gas phase.[46]

We have chosen to model the inductive component of the total effect of the C6–C7 double bond in **1** with the measured acidity difference between norbornadiene (**8**) and norbornene (**10**). Here, direct homoconjugation in the conjugate base vinyl carbanion **9** is effectively prevented since the σ lone pair at C2 lies roughly in the nodal plane of the C5–C6 double bond.

9

Moreover, the (nearly) full negative charge at C2 is in a position to experience the inductive influence of only one sp^2 carbon (C6). This is formally analogous to the situation with **2**, where two approximately half-charges experience the influence of two sp^2 carbons. The experimental **8**/**10** acidity difference, 3.1 ± 2.5

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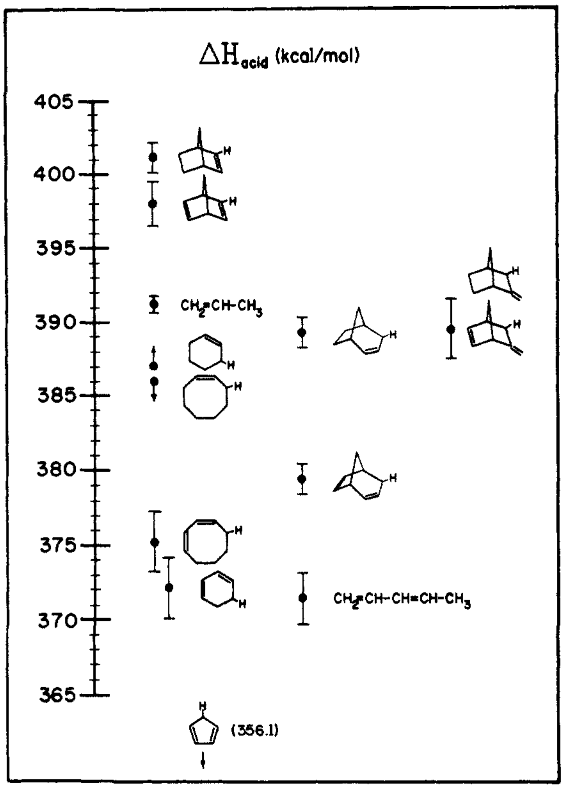
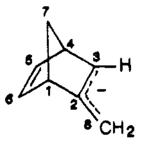


Figure 3. Partial gas-phase acidity scale constructed from data in Table II. Acidities for $CH_2{=}CH{-}CH_3$, $CH_2{=}CH{-}CH{=}CH{-}CH_3$, and c-$C_5H_6$ taken from ref 28.

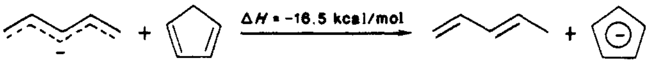
kcal/mol, is only a third to a half of the difference between compounds **1** and **3**. The magnitude of the inductive effect measured with this model should be considered an upper limit to that operating in **2** for the following reasons. It is frequently true that strongly basic species with localized charge (such as vinyl carbanions) exhibit more pronounced substituent effects than weakly basic, delocalized species (such as allylic ions). This interrelationship underlies so-called "saturation effects" of multiple substitutions on certain reactions and physical properties,[57] and provides a basis for the familiar "tool of increasing electron demand" which has found successful applications in carbonium ion chemistry.[58] In the present system, an sp^2 carbon in a remote double bond should respond to a larger extent to the more basic, localized charge in **9** than the less basic, fully delocalized charge in **2**. Therefore, a larger inductive effect on the **8**/**10** acidity difference would be expected.

A second model system in which bishomoconjugation is prevented but induction may still operate involves the relative acidities of **12** and **14**. Deprotonation of **12** produces an ion, **13**, in which only one of the allylic termini can interact with the remote C5–C6 double bond. The estimated acidity for **12** is substantially reduced relative to **1** and does not differ from that of the corresponding monoolefin **14**. Several factors are likely to be responsible. In addition to the absence of bishomoconjugative stabilization, any inductive effects in ion **13** would be substantially diminished relative to **2** since electron withdrawal by only one sp^2 carbon on only one (approximately) half-charge at C3 is possible. Furthermore, normal allylic conjugation is probably reduced in **13** compared to **2** as a result of poor overlap imposed by strain in the [2.2.1] ring system. That is, the reduced C2–C3–C4 bond angle (ca. 100°) and unfavorable torsional interactions with the C4 hydrogen[59] should result in pyramidalization at C3 (cf. cyclopropyl anion)[54b] and a concomitant decrease in resonance interaction between the lone pair and the C2–C8 double bond. As a result, the basicity of **13** should increase.



13

We conclude from the foregoing analysis that bishomoconjugation is the main effect responsible for the extraordinary gas phase acidity enhancement exhibited by compound **1**. By subtracting 3.1 kcal/mol from the total 9.5 kcal/mol acidity difference between **1** and **3** as a maximum contribution from induction, we are left with a 6.4 kcal/mol enhancement due to "homoaromaticity". This may be compared with the 16.5 kcal/mol acidity enhancement attending full aromaticity in cyclopentadienyl anion, as given by the computed enthalpy for the hypothetical gas phase proton transfer reaction shown below (eq 8). The corrsponding acidity increase for cyclopentadiene relative to cyclopentene ($\Delta H_{\text{acid}} \approx$ 388 kcal/mol) is approximately twice this amount (ca. 32 kcal/mol). An additional useful benchmark with which to gauge the magnitude of the resonance effect in ion **2** derives from an MO treatment of hydrocarbon acidities originally developed by Streitwieser[60] and later adopted for gas-phase acidities by Bartmess and McIver.[28] Equation 9 describes the empirical relationship between gas-phase acidities for *planar* hydrocarbon acids, the Hückel π-electron energy difference between each acid and its conjugate base (ΔM),[60] and the bulk molecular polarizabilities (α, Å^3). As described by Bartmess and McIver,[28] regression analysis using a series of hydrocarbons with experimentally established gas-phase acidities leads to $\beta = 23.7$, $A = 1.2$, and $\Delta H_0 = 414.1$. If we make the rough assumption that the acidity of **1** is applicable to eq 9 and use $\alpha(\mathbf{1}) = 13.6$ Å^3,[50] then we obtain $\Delta M(\mathbf{1} \text{-} \mathbf{2}) = 0.8$. Thus, deprotonation of **1** leads to an increase in π-electron energy of 0.8β—an amount nearly equal to that for toluene (0.7β) and roughly one third that for cyclopentadiene (2β).



(8)

$$\Delta H_{\text{acid}} = -\beta\Delta M - \mathrm{A}\alpha + \Delta H_0 \text{ (kcal/mol)} \qquad (9)$$

To keep these results in perspective, it is worthwhile to point out that the energy benefit attending homoconjugation in **2** is small in comparison to the documented homoconjugation energies in carbonium ions.[6,61] For instance, the 7-norbornadienyl cation possesses an estimated 20 kcal/mol stabilization energy relative to the fully saturated ion, resulting in 10^{12}–10^{14} rate enhancement factors for its formation in solvolytic reactions.[62] Similarly, cyclobutenyl and homotropilium cations exhibit homoconjugation energies of ca. 10–15 kcal/mol.[9,61] The attenuation in the homoconjugative energy benefit for **2** is most likely due to the destabilizing repulsive interactions which may accrue with close approach of the allylic and olefinic bridges. Counter-balancing effects of this kind are absent in carbonium ions, so more pronounced geometry distortions and larger stabilization energies attend cationic homoconjugation.

In view of the apparent significance of bishomoconjugation in ion **2**, one might wonder why monohomoconjugation does not appear in the cyclohexadienyl anion. The two cyclic conjugated dienes (**16** and **18**) and the one acyclic diene illustrated in Figure 3 possess essentially identical acidities, at least within the indicated error limits. In a definitive experimental and theoretical study of cyclohexadienyl anions, Olah, Mayr, and Schleyer demonstrated that planar structures are favored, although the ring-puckering potential is quite flat within 20° of planarity.[9] More recently, Tolbert has reached the same conclusions from an analysis of the

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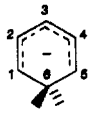
NMR spectra of phenyl derivatives.[63] In the planar form, the C1–C5 distance is approximately 2.5 Å, and the π interaction between the ends of the dienylic system is negligible. Puckering may increase overlap by virtue of the accompanying canting of the C1,C5 p-orbitals toward one another, but it does so only at the expense of a favorable π-interaction between the dienylic HOMO and the $\pi^*(CH_2)$ fragment orbital at C6. Thus, mononohomoconjugation in this carbanion is unimportant. Interestingly, the C2–C7 and C4–C6 distances in ion **2** are also on the order of 2.5 Å,[11,12] yet bishomoconjugative interactions are evident. The key difference is that the rigid, bicyclic framework in **2** effects a canting of the two π-systems toward one another on the endo face of the molecule in such a way that good overlap can be achieved. The apparent stabilization exhibited by homoaromatic dianion **6**[16] also serves to illustrate this geometric criterion, since it has been shown recently that the potentially monohomoconjugated planar analogue **22** is, in fact, substantially *destabilized* relative to cyclooctatetraenyl dianion.[64] In view of this trend, it is useful to envisage other compounds which might possess similar structural features as **2** and **6**. An excellent candidate for "tetrakishomoaromaticity" is carbanion **23**, the conjugate base of dicyclopentadiene. Simple models show that the C3–C9 and C5–C8 distances are nearly the same as the C2–C7 and C4–C6 in **2** but, more importantly, that the p-orbitals in the allylic and olefinic fragments are oriented almost directly at one another, with nearly perfect σ symmetry. We are presently attempting to generate carbanion **23** in the gas phase by proton abstraction from dicyclopentadiene, although its low volatility possesses somewhat of a practical problem for flowing afterglow experiments. In this context, it is interesting to note that one of the canonical forms for a fully delocalized tetrakishomoaromatic ion **23** corresponds to bishomocubyl anion **23b**. Thus, proton abstraction from bishomocubane may provide an alternate entry to **23**.



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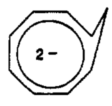

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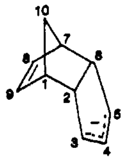
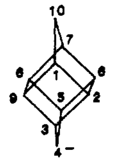


23a



23b

Conclusion

Bishomoaromaticity in the conjugate base carbanion is the main cause of the unusually high gas-phase acidity of bicyclo[3.2.1]-octa-2,6-diene. Of the total 9.5 kcal/mol measured acidity enhancement relative to bicyclo[3.2.1]oct-2-ene, roughly a third of this amount can be attributed to field/inductive effects of the remote C6–C7 double bond, as modelled by the 3.1 kcal/mol acidity increase measured for norbornadiene over norbornene. The polarizability difference between these two hydrocarbons makes a negligible contribution, while angle strain in the allylic bridge of **3** reduces its acidity by approximately 3 kcal/mol. We must conclude from our results that the failure to detect bishomoconjugative interactions in **2** in the earlier theoretical studies[11,12] was an artifact of the inadequacies of the basis sets and the molecular geometries which were employed. At the time of these studies, adoption of a lower level of theory to examine the problem was dictated by the large size of the bicyclic alkenes and carbanions involved. Given the computational advances that have become available since then, it would seem that a reexamination is warranted. We anticipate that calculation of the electronic and geometric structures of **2** with use of basis sets which are properly augmented with diffuse functions[15] will expose the sought-after homoaromatic interactions.

Acknowledgment. We are most grateful to Professors Grutzner, Jorgensen, Schleyer, and Chandrasekhar for many helpful and stimulating discussions on this problem. Dr. Pirjo Vainiotalo is gratefully acknowledged for providing us with samples of 2-methylenenorbornane. We also thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, Research Corporation, and the National Science Foundation (CHE-8502515) for their support of this research.

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Gas-Phase Photodissociation of Organometallic Ions: Bond Energy and Structure Determinations

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Abstract: The photodissociation of a variety of gas-phase organometallic ions was investigated with Fourier transform mass spectrometry in order to obtain spectroscopic and thermodynamic information on these complexes. The results indicate that these ionic complexes absorb broadly and photodissociate readily in the ultraviolet and visible spectral regions, with cross sections for λ_{max} ranging from 0.02 to 0.30 Å^2. Because of this broad absorption, photodissociation thresholds are attributed to thermodynamic and not spectroscopic factors. Bond energies and heats of formation obtained by monitoring photodissociation onsets show good agreement with those obtained by other techniques. Interestingly, product ions generated by photodissociation are found to differ significantly in a number of instances from those produced by collision-induced dissociation. Finally, differentiation of two $FeC_4H_6^+$ and four $NiC_4H_8^+$ isomers is demonstrated by observing differences in cross sections, spectral band positions, and neutral losses.

Gas-phase organometallic ion chemistry has become an active area in recent years with the arsenal of experimental techniques employed constantly growing.[1-4] Delineating reaction mechanisms has been a major focus, drawing heavily on results from exper-

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