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Ion Thermochemistry of Low-Volatility Compounds in the Gas Phase. 3. Polycyclic Aromatics: Ionization Energies, Proton and Hydrogen Affinities. Extrapolations to Graphite

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Proton affinities (PA) and ionization energies (ΔH°_i) of polycyclic aromatic hydrocarbons (PAH) were determined to within ± 1 kcal mol^{-1} by using gas-phase ion-equilibrium measurements. PA values (related to PA(NH$_3$) = 207 kcal mol^{-1}) range from 193.2 (naphthalene) to 213.0 (perylene) and 222.0 (azulene) kcal mol^{-1}. Comparison with basicities in anhydrous HF solution shows that the solvent attenuates the basicities of C$_{14}$–C$_{18}$ PAHs by 9 ± 1 kcal mol^{-1} more than of benzene; perylene (C$_{20}$) showed larger and naphthalene (C$_{10}$) shows smaller solvent attenuation. Gas-phase PAs correlate well with rate constants for electrophilic attack (protodetritiation nitration) in solution, as well as with previously published theoretical (CNDO/2) PAs. Hydrogen atom affinities (HA) of the radical ions decrease with increasing molecular size but level off at 64 ± 1 kcal mol^{-1}. This trend is used to estimate HA and PA of an edge-hydrogenated graphite monolayer as 64 and 278 kcal mol^{-1}, respectively. Some results are as follows (ΔH°_i, PA, HA, all in kcal mol^{-1}): naphthalene, 187.7, 193.2, 70; phenanthrene, 183.3, 201.1, 71; fluorene, 183.0, 202.4, 72; chrysene, 175.8, 203.3, 66; pyrene, 173.0, 208.5, 68; picene, 172.6, 205.8, 65; anthracene, 171.9, 209.4, 68; coronene, 170.8, 207.0, 64; 1,12-benzoperylene, 167.4, 210.6, 64; azulene, 171.1, 222.0, 79.

Introduction

Equilibrium studies on ion–molecule exchange reactions yielded an extensive set of data on the intrinsic gas-phase basicities and proton affinities (PA) of organic bases.[1] On the basis of these data, the intrinsic structural effects[2] and the effects of solvents[3] on basicities of nitrogen and oxygen bases could be analyzed in detail. It is desirable that similar measurements will be extended to other classes of organic bases. Especially it is desirable that quantitative gas-phase data will be available for complex molecules which are of theoretical as well as biological or environmental interest. However, many such compounds are refractory solids. We therefore recently developed a technique of direct sample introduction combined with a kinetic measurement of the partial pressures of the low-volatility samples in the ion source. This technique has been used with success to obtain quantitative information on amino acids and nucleic bases, as we reported in preceding papers in this series.[4,5]

In the present work we applied ion-equilibrium methods to measure the gas-phase basicities of polycyclic aromatic hydrocarbons (PAHs). These data are of theoretical interest since the relation between structure and proton affinity of PAHs has been investigated by using several molecular orbital methods.[6-8] However, until now the theoretical results could not be compared directly with experiments since the theoretical calculations predict gas-phase values, but the basicities of PAHs have been measured only in solution under rather special conditions, i.e., in anhydrous HF. Even there, heats of protonation are generally not available. We shall now use the gas-phase results to examine the correlation of the theoretical results with experiment.

The gas-phase data can be used also to establish empirical relations between the ion chemistry of PAHs in the presence of the absence of solvent. Thus, besides the basicities of PAHs in HF, data are also available on the rate constants for electrophilic substitution reactions of PAHs, such as protodetritiation and nitration reactions. It was believed that the rate constants constitute a measure of the relative gas-phase proton affinities.[8] Using the gas-phase data we shall now be able to examine the applicability of solution basicities and rate constants to estimate quantitatively the gas-phase proton affinities.

The gas-phase proton affinities are also of applied interest, since they may be useful in designing specific chemical ionization reactants for selective protonation of components in mixtures of PAHs. Furthermore, on the basis of recent observations of Hunt and co-workers,[9] quantitative data on the proton affinities of PAHs should allow the selection of appropriate chemical ionization reagents for selective H–D exchange with isomeric PAHs.

Ion-equilibrium measurements can be used, in addition to proton affinity deteriminations, also to obtain accurate values of relative ionization energies of gas-phase molecules. Such measurements were applied to substituted benzenes by Meot-Ner and Field[10] and Lias and Ausloos.[11] The relative ionization energies (ΔH_i) measured by the equilibrium method agree with adiabatic IPs from photoionization and photoelectron spectroscopy to within a fraction of 1 kcal mol^{-1}. The equilibrium technique should therefore be used to obtain accurate ionization energies of polycyclic aromatics.

Finally, having measured both PAs and ionization energies, we shall examine the empirical relation between these variables in a series of PAHs of increasing size. The objective is to explore a trend in this relation which may be extrapolated to graphite in order to estimate the proton affinity and hydrogen atom affinity of this macromolecule.

Experimental Section

The present measurements were performed by pulsed ionization high-pressure mass spectrometry, using The Rockefeller University Chemical Physics mass spectrometer. Proton affinity (PA) and ionization energy (ΔH_i) determinations were based on measurements of the equilibria

$$B_1H^+ + B_2 \rightleftharpoons B_2H^+ + B_1 \tag{1}$$

$$B_1^+ + B_2 \rightleftharpoons B_2^+ + B_1 \tag{2}$$
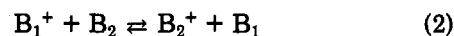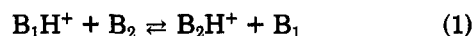
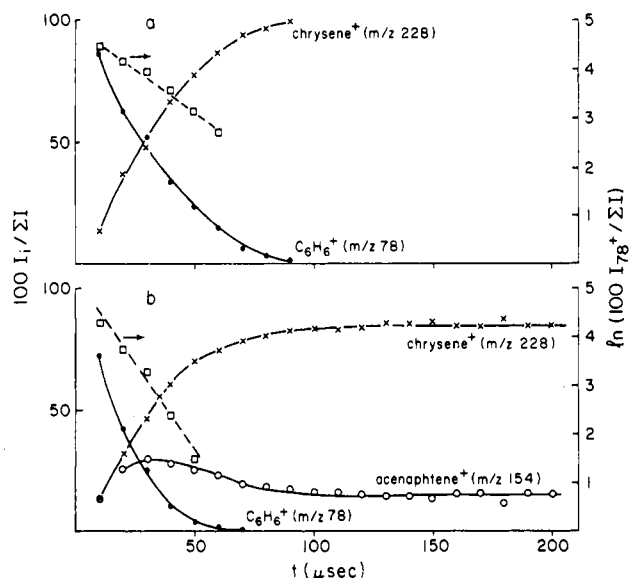respectively, where B_2 is the sample and B_1 is a reference

Figure 1. Ion-intensity distribution in a charge-transfer equilibrium measurement for acenaphthene$^+$ + chrysene $\rightleftarrows$ chrysene$^+$ + acenaphthene: (a) chrysene, introduced via the solids insertion probe, in a reactant gas of 2% benzene in N_2 at 539 K. Rate of disappearance of $C_6H_6^+$, obtained from slope of plot (broken line) of ln $100 I_{78^+}/\sum I$ vs. t, is 3.7×10^4 s^{-1}. Using $k = 1.5 \times 10^{-9}$ cm^3 s^{-1} for $C_6H_6^+$ + chrysene $\rightarrow$ chrysene$^+$ + C_6H_6 yields $N_{chrysene} = 2.5 \times 10^{13}$ cm^{-3}. (b) The reference compound acenaphthene is added to the reactant gas. Total rate of disappearance of $C_6H_6^+$ is now $r_1 + r_2 = 6.9 \times 10^4$ s^{-1}; thus the rate of reaction $C_6H_6^+$ + acenaphthene $\rightarrow$ acenaphthene$^+$ + C_6H_6 is $r_2 = 3.2 \times 10^4$ s^{-1}. Using $k = 1.5 \times 10^{-9}$ yields $N_{acenaphthene} = 2.1 \times 10^{13}$ cm^{-3} and $N_{acenaphthene}/N_{chrysene} = 0.84$. By comparison, the known mixture ratio of acenaphthene in the reactant gas gives $N_{acenaphthene}/N_{chrysene} = 0.76$. The initial ratio of ion intensities yields $N_{acenaphthene}/N_{chrysene} = (I_{154}^+/I_{228}^+)_0 = 1.0$. If one uses the average neutral ratio (0.87), $K_{539} = (I_{228}^+/I_{154}^+)$ equilibrium $\times$ $(N_{acenaphthene}/N_{chrysene}) = (85/15) \times 0.87 = 4.0$, and $\Delta G^{\circ}_{539} = 1.7$ kcal mol^{-1}.

compound whose PA or IP (ionization potential), respectively, is known.

Determination of the equilibrium constants K_1 and K_2 requires the determination of the equilibrium ion ratios $(B_2H^+)/(B_1H^+)$ and $(B_2^+)/(B_1^+)$, respectively. These ratios were obtained by the usual time-resolved methods; an example is given in Figure 1. In addition, the ratios P_{B_1}/P_{B_2} or N_{B_1}/N_{B_2} (N = number density, cm^{-3}) are also required. This causes a difficulty when B_2 is a refractory solid which must be volatilized from a probe directly to the source, since partial pressures $\lesssim 10^{-2}$ torr cannot be measured in the presence of total source pressures of about 1 torr. To overcome this difficulty we employed three indirect methods to measure N_{B_1}/N_{B_2}.

(i) The number density (N_{B_2}) of the sample in the source was determined by measuring the rate r_3 for the reaction between a reactant ion R^+ and the sample B_2, i.e.

$$R^+ + B_2 \rightarrow B_2^+ + R \tag{3}$$

N_{B_2} is then calculated from

$$r_3 = k_{2(R^+,B_2)} N_{B_2} \tag{4}$$

where $k_{2(R^+,B_2)}$ is the theoretical Langevin or average dipole orientation (ADO) collision rate constant of R^+ and B_2; the justification for using this value for k_2 will be discussed presently. Once N_{B_2} was thus determined, a measured amount of the reference compound B_1, mixed with the carrier gas, was added to the ion source. Since we thus knew N_{B_1}, we could then calculate N_{B_1}/N_{B_2}.

(ii) In the second method, N_{B_2} was measured by the kinetic method described in II section i. B_1 was then added

to the carrier gas flow. With both B_1 and B_2 in the source, reaction 3 proceeds in parallel with reaction 5. We can

$$R^+ + B_1 \rightarrow B_1^+ + R \tag{5}$$

thus measure $r_3 + r_5$. Since r_3 was measured above, we can calculate r_5. Using a relation analogous to eq 4, we then obtain N_{B_1}.

(iii) In the third method the ratio N_{B_1}/N_{B_2} was estimated on the basis of initial ion ratios, as follows. B_1^+ and B_2^+ are produced by parallel reactions of R^+ with B_1 and B_2. Thus the initial ratio of B_1^+/B_2^+ is given by eq 6. If the

$$(B_1^+)_0/(B_2^+)_0 = k_{2(R^+,B_1)} N_{B_1}/k_{2(R^+,B_2)} N_{B_2} \tag{6}$$

pursuant reaction between B_1^+ and B_2 is sufficiently slow ($t_{1/2} > 30$ μs), the ratio $(B_1^+)_0/(B_2^+)_0$ may be estimated by extrapolation to time 0 from the ion ratios at later times. The rate constants for the reaction of R^+ and B_1 and B_2, i.e., $k_{2(R^+,B_1)}$ and $k_{2(R^+,B_2)}$, can be calculated from collision theory,[13] and N_{B_1} and N_{B_2} can then be calculated from eq 6. This estimate is independent of the determination of N_{B_1}/N_{B_2} by the previous methods.

In most experiments, the three methods gave values of N_{B_1}/N_{B_2} which were consistent within a factor of 2; if larger discrepancies between the three measured values of N_{B_1}/N_{B_2} were found, the experiment was rejected. An example of ion intensity distributions in an equilibrium measurement, including the various methods of evaluating N_{B_1}/N_{B_2}, is given in Figure 1.

Sample compounds with melting points ≤ 120 °C were introduced to the mass spectrometer through a heated bulb, together with and in a known ratio to the reference compound. The initial ion ratios (method iii) were still used on these known mixtures to confirm the value of N_{B_1}/N_{B_2}.

In charge-transfer equilibria the reactant gas was a mixture of 2–4% benzene in N_2. In this mixture ionization produces mostly N_2^+, which reacts rapidly to produce $C_6H_6^+$ as the major reactant ion. $C_6H_6^+$ then reacts more slowly with B_1 and/or B_2, whose number densities were in the range 0.5×10^{13}–5×10^{13} cm^{-3}. B_1 and B_2 constituted 0.03–0.3% of the overall reaction mixture; $C_6H_6^+$ therefore undergoes 300–3000 collisions with the carrier gas before reacting with B_1 or B_2. We can thus assume that the reacting $C_6H_6^+$ species is the thermalized ion. Charge-transfer reactions from this thermalized $C_6H_6^+$ ion to B_1 and B_2 have the relatively low exothermicities of 15–45 kcal mol^{-1}, which can be distributed in the many degrees of freedom of the present complex molecules; this should hinder structural rearrangements of B_1^+ and B_2^+. The ions B_1^+ and B_2^+ will in turn also collide 300–3000 times with carrier gas molecules before undergoing a reactive collision with B_2 or B_1, respectively. Thus all ionic species in equilibrium 2 should be thermalized at the temperature of the carrier gas which is equal to that of the ion chamber.

Proton-transfer equilibria were handled similarly to charge-transfer equilibria except that the reagent gas in most proton-transfer experiments was C_3H_8, and the proton transfer reagent ion was i-$C_3H_7^+$. However, in the case of some sample molecules with IP < IP(C_3H_7) = 7.5 eV, $C_3H_7^+$ yielded radical ions B_2^+ as well as protonated ions B_2H^+. In these cases the M + 1 isotopes of B_2^+ interfered with the measurement of B_2H^+. We therefore used CH_4 + 2% H_2S as the reagent gas and H_3S^+ as the reagent ion. This technique produced negligible yields of the molecular ion B_2^+.

In the kinetic determination of N_{B_1} and N_{B_2} it is assumed that the reactions of R^+ and B_1 and B_2 proceed at unit collision efficiency; i.e., $k_{(R^+,B_1)}$ and $k_{(R^+,B_2)}$ are equal to the

TABLE I: Rate Constants for the Reactions of i-C$_3$H$_7^+$ + B → BH$^+$ + C$_3$H$_6$^{a} and C$_6$H$_6^+$ + B → B$^+$ + C$_6$H$_6$

reactant		$10^{10} \times k_{exptl}$, ^{b} cm^3 s^{-1}	$10^{10} \times k_{ADO}$, cm s^{-1}
i-C$_3$H$_7^+$ +	fluorene	11	16
	naphthalene	10	17
	indene	12	16
C$_6$H$_6^+$ +	azulene	19	14
	biphenylene	13	15
	9-methyl-anthracene	13	16
	9,10-dihydro-anthracene	17	16

^{a} Under our experimental conditions 60–80% of the reaction yield is BH$^+$ and 20–40% of the yield is the addition product B·C$_3$H$_7^+$. ^{b} On the basis of differences between results of replicate experiments, the precision is ±5 × 10^{-10} cm^3 s^{-1}.

theoretical ADO collision rate constants.[13] To test whether the reactions of C$_6$H$_6^+$ and C$_3$H$_7^+$ with polycyclic aromatics indeed proceed at unit collision efficiency, we measured rate constants of reactions of C$_6$H$_6^+$ and C$_3$H$_7^+$ with several low-melting compounds which could be introduced to the source in known concentrations through a heated bulb. The results (Table I) show that $k_{(R^+,B_2)}$ is always within a factor of 2 of k_{ADO}. It is reasonable to assume that similar rate constants apply for the reaction of R$^+$ with the low-volatility samples which had to be introduced through the probe. We thus used $k_{(R^+,B_2)} = 1.5 \times 10^{-9}$ cm^3/s^{-1} for the reaction of R$^+$ with B$_1$ and B$_2$, except for the highly polar reference compound 3-aminopropionitrile, where the ADO rate constant 2.2 × 10^{-9} cm^3/s^{-1} was used.

The polycyclic compounds used in these measurements were purchased from Aldrich, except biphenylene (Pfaltz and Bauer), octahydroanthracene and octahydrophenanthrene (Chemical Procurement Labs.) and picene (K&K Chemicals). All samples were of nominal purity >98% and were used as purchased. The purity was confirmed by the mass spectrum which showed <2% of impurities. The absence of isomer impurities was confirmed by capillary gas chromatography for all but the involatile compounds perylene, benzoperylene, and coronene. As we noted in a previous paper,[5] impurities on the order of 2% would react too slowly to affect the observed equilibrium constants. Some further details of the experimental technique were discussed in preceding papers in this series.[4,5]

Results and Error Estimates

(a) Proton-Transfer Reactions. The measured free energies $\Delta G^\circ = RT \ln K$ for proton-transfer reactions are summarized in Table II. To evaluate the precision of the measurements, we note that the largest source of experimental error is in the determination of N_{B_1}/N_{B_2}. As stated before, we estimate a maximum uncertainty by a factor of 2 in this ratio, which contributes an uncertainty of ±0.7 kcal mol^{-1} to ΔG° at 550 K. The magnitude of this error is comparable with the precision of measured ΔG° values. Thus, in 34 pairs of duplicate measurements, the average difference between the results was ±0.5 kcal mol^{-1}.

In order to calculate ΔH° from ΔG° for the transfer reactions, one must measure or calculate ΔS°. In previous temperature studies on exchange equilibria in heterocyclic compounds,[5] we found that ΔS° was usually in the range 0 ± 2 kcal mol^{-1}, which is also about the magnitude of the error in entropy measurements. In many reactions in the present study, the practical temperature range would be limited because of volatility problems, thereby further

reducing the accuracy of entropy determinations. For these reasons we must rely on theoretical estimates of ΔS°.

Proton-transfer reactions involving the present compounds are not accompanied by significant structural changes such as hindering of internal rotors or internal solvation. Consequently, the most significant contribution to ΔS° arises from changes in rotational symmetry numbers, i.e., for reaction 1

$$\Delta S^\circ \simeq \Delta S^\circ_{rot. sym} = R \ln (\sigma_{B_1H^+}\sigma_{B_2}/\sigma_{B_2H^+}\sigma_{B_1}) \quad (7)$$

The values of σ_B/σ_{BH^+} that we used are given in Table II.[14]

The use of eq 7 to estimate ΔS° introduces some uncertainty due to the sometimes unknown symmetries of the protonated ions. It also ignores other minor factors that may affect the entropy, as the entropylike term $\Delta S_{intermolecular}$ which was discussed by Ausloos and Lias.[15] Altogether, we estimate that the uncertainty introduced by these factors is <±2 eu, which may contribute an uncertainty of ±1.1 kcal mol^{-1} in deriving ΔH° from ΔG°.

For each sample, ΔH° was derived in this manner from ΔG° values for proton-transfer reactions with two to four different reference bases. From these measurements we constructed the proton affinity scale related to ammonia, i.e., ΔH° for reaction 8. The PA scale is given in Table I, column 3.

$$NH_4^+ + B \rightarrow BH^+ + NH_3 \quad (8)$$
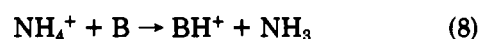
Also in Table II (column 1) we report the gas-phase basicities, related to NH$_3$, i.e., ΔG°_{550} for reaction 8.[16] For only a few of the present compounds were gas-phase basicities reported previously. For example, ΔG° for H$^+$ transfer from NH$_4^+$ to naphthalene was reported by Kebarle and co-workers[17] as 7.6 kcal mol^{-1}, in good agreement with the present 7.2 kcal mol^{-1}. Also, according to our data in the PA of 1,3,5-trimethylbenzene is higher by 18.2 kcal mol^{-1} than the PA of benzene; this is the reasonable agreement with a literature value[18] of 17.0 kcal mol^{-1}.

(b) Charge-Transfer Reactions. Errors in the ionization energy measurement may be evaluated as in the proton-transfer experiments. The uncertainty in N_{B_1}/N_{B_2} causes, as above, an uncertainty of ±0.7 kcal mol^{-1} in ΔG°. The average precision of duplicate measurements of ΔG° for transfer equilibria is ±0.5 kcal mol^{-1}. We assign an error estimate of ±0.7 kcal mol^{-1} to the measured relative free energies of ionization.

To calculate enthalpies of ionization from the equilibrium data, one again needs estimates of ΔS°. Lias and Ausloos[11] showed that in charge-transfer equilibria in many aromatic systems the only significant contributions to ΔS° result from changes in the rotational symmetry numbers upon ionization, due to Jahn–Teller distortions of the radical ions, and from changes in the orbital degeneracies. In most of the present equilibrium systems, these entropy terms will be small because of the low symmetries of the reactants and because of compensating symmetry and degeneracy changes in the reactants. We therefore assume that for charge-transfer reactions $\Delta G^\circ = \Delta H^\circ$. Only in reactions of the high-symmetry species coronene and triphenylene did we apply corrections due to $\Delta S^\circ_{rot. sym}$.

The enthalpy of charge-transfer reactions at 0 K is equal to $\Delta IP_{adiabatic}$ of the reactants. Lias and Ausloos[11] showed that the enthalpy at high temperatures is also close to $\Delta IP_{adiabatic}$. We therefore consider $\Delta G^\circ = \Delta H^\circ \simeq \Delta IP_{adiabatic}$. The validity of these approximations on the present level of energy resolution is tested by comparing our measured ΔG° values with accurate $\Delta IP_{adiabatic}$ values from photoelectron or photoionization spectroscopy. The average difference between our results and the literature values quoted in Table III is 0.8 kcal mol^{-1}, and the
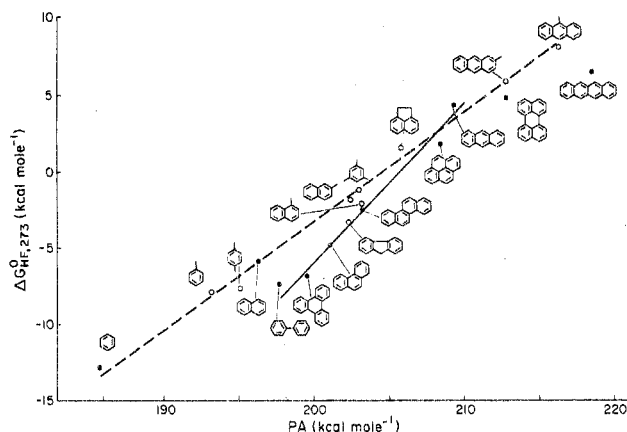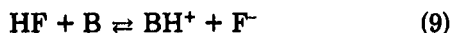
Figure 2. Relation between gas-phase proton affinities and basicities in anhydrous HF; solution basicities are corrected to cancel the entropy contribution of rotational symmetry changes, i.e., $-\Delta G^{\circ}{}_{HF,273} = RT \ln (K(\sigma_{BH}{}^+/\sigma_B))$, where K is the experimental equilibrium constant for B + HF $\rightleftarrows$ BH$^+$ + F (ref 4): (●) unsubstituted compounds; (○) alkyl-substituted compounds. Values of $\sigma_{BH}{}^+/\sigma_B$ are given in Table II. PA of 1,4-dimethylbenzene relative to PA of toluene, taken from ref 18.

agreement in all cases is better than ±2 kcal mol^{-1}.

Discussion

(a) Relation between Gas-Phase and Solution Basicities. Equilibrium constants for the protonation of aromatic hydrocarbons in anhydrous HF (reaction 9) were measured

$$HF + B \rightleftarrows BH^+ + F^- \qquad (9)$$

by Mackor et al.[6,7] From their data it is possible to calculate $\Delta G^{\circ}{}_{HF}$ for reaction 9 in this solvent. The free energies of protonation in solution, corrected for symmetry changes, are compared with relative gas-phase proton affinities in Figure 2.

The solvent-effected attenuation of the basicity of base B, compared with that of benzene, may be defined by eq 10.[19] For example, in going from benzene to triphenylene,

$$\text{attenuation} = (PA(B) - PA(C_6H_6)) - (\Delta G^{\circ}{}_{HF}(B) - \Delta G^{\circ}{}_{HF}(C_6H_6)) \quad (10)$$

the gas-phase proton affinity increases by 14.9 kcal mol^{-1} while the solution basicity increases by only 6.0 kcal mol^{-1}. Therefore solvent effects cause an attenuation of 8.9 kcal mol^{-1} in the basicity of triphenylene relative to that of benzene. Solvent attenuation of a similar magnitude is observed in several other polycyclics of roughly similar molecular size. These compounds lie on the solid correlation line in Figure 2, whose slope is about unity (0.98 ± 0.06), with a standard deviation of the ordinate values of ±0.7 kcal mol^{-1}. The basicity of all of these compounds is attenuated by the solvent relative to benzene by a constant value of 9 ± 1 kcal mol^{-1}. The solvent attenuation of the basicities of these compounds may be due primarily to the less efficient solvation of the large charge-delocalized ions compared with protonated benzene. Indeed, the attenuation in the largest compounds that we measured is further enhanced to an extent that seems to be experimentally meaningful considering the small scatter of the correlation line, i.e., perylene, 10.6 kcal mol^{-1}, and tetracene, 14.6 kcal mol^{-1}. On the other hand, the smallest polycyclic, naphthalene, shows significantly less solvent attenuation, i.e., 4.5 kcal mol^{-1}. Thus there does exist some qualitative relation between solvent attenuation and molecular size, an effect similar to that observed in nitrogen and oxygen bases in aqueous solution.[3] The differential solvent effects are sufficient to invert the relative order of gaseous and solution basicities of naphthalene as compared with biphenylene and triphenylene (Figure 2).

A correlation line with a slope of 0.7 can be drawn through benzene and several substituted methylbenzenes in Figure 2. Naphthalene, 1- and 2-methylnaphthalene, and acenaphthene are connected by a line of similar slope, and so are anthracene and 2- and 9-methylanthracene. These correlations show that variations in intrinsic basicity upon methyl substitution are attenuated by ~30% because of solvent effects in HF. The solvent attenuation upon adding one methyl group to benzene is 3.5 kcal mol^{-1}, and upon adding two methyl groups, as in 1,4-dimethylbenzene, is 5.2 kcal mol^{-1}. The former approach and the latter are comparable to the solvent attenuation upon adding a fused ring substituent, which is 4.5 kcal mol^{-1}. Interestingly, the solvent attenuation upon adding a fused ring or two methyl substituents to ions of aromatic compounds is also comparable in the case of pyridine derivatives in aqueous solution,[5] despite the difference between the bases and the solvents here and in the pyridine systems.

The activation energies of electrophilic substitution reactions of PAHs in solution are believed to be related to the intrinsic proton affinities. For example, log k for the protodetritiation of a series of PAHs and for nitration by NO$_2{}^+$ was correlated with theoretical localization energies or proton affinities.[8] We can examine the correlation between these rate constants and experimental gas-phase proton affinities. Thus we examine the correlation between PA and log k for protodetritiation of the most active carbon in a series of 11 polycyclics: benzene, naphthalene, triphenylene, phenanthrene, fluoranthene, chrysene, biphenylene, pyrene, anthracene, perylene, and fluorene. We find a correlation coefficient of 0.95 and a standard deviation of PA values about the correlation line of 2.3 kcal mol^{-1}. In fact, only one of the 11 compounds, anthracene, shows a deviation from the correlation line which is experimentally significant. We also examine the correlation between PA and log k for the nitration of the most active carbon in a set of PAHs as given by Dewar et al.[20,21] We found a correlation coefficient of 0.94, with a standard deviation of 2.7 kcal mol^{-1} of the PA values about the correlation line.

The gas-phase measurements therefore support the use of relative rate constants for electrophilic substitution reactions to estimate the relative PAs, but only within an accuracy of about ±4 kcal mol^{-1}.

(b) Relation between Experimental and Theoretical Proton Affinities. The proton affinities of PAHs were calculated by several authors using a variety of molecular orbital methods.[6,8] In the absence of gas-phase PA data, these results were tested against experimental solution data such as those discussed in the preceding section. Since the theoretical results predict gas-phase values, it is of interest now to compare the theoretical results with the experimental PAs.

In an early effort, Mackor et al.[6,7] applied Huckel molecular-orbital methods to calculate localization energies involved in localizing two π electrons in a C-H σ bond upon protonation of a series of polycyclic aromatics. More recently, Streitwieser et al.[8] used a variety of MO calculations to calculate localization energies and also used the CNDO/2 method to calculate proton affinities of PAHs. In Figure 3 we examine the correlation of the localization energies of Mackor et al.[6,7] and of the CNDO/2 proton affinities of Streitwieser et al.[8] with the experimental PAs. The localization energies exhibit a correlation coefficient of 0.95, while the CNDO/2 values, for all the PAHs in Figure 3 except biphenylene, yield a correlation coefficient

of 0.99. Thus, although the simple HMO method gives good results, the more advanced CNDO/2 method constitutes considerable improvement in the predictive value of the theory. However, the CNDO/2 calculations underestimate the PA of the sterically strained biphenylene, as was already noted by Streitwieser et al.[8] It should also be noted that the absolute CNDO/2 values are significantly higher than the experimental PAs, and the slope of the correlation line (Figure 3) is much larger than unity.

(c) Relation between Ionization Energies and Proton Affinities. The correlation between decreasing ionization energies and increasing proton affinities has been noted in a series of organic bases such as alkylamines.[2] Such a relation is expected also in polycyclic aromatics, since both ionization and protonation involve the removal of electrons from the π system. Indeed, a correlation between IPs and solution basicities has been noted for PAHs.[22]

The relation between ΔH°_i and PA for several sets of carbon bases is shown in Figure 4. In a previous paper we noted that a PA–IP diagram tends to divide compounds according to structural type and may serve as an indictor of the protonation site. Here we note again that the correlation diagram divides the carbon bases according to structural type. Peri-condensed PAHs, linear acenes, benzene, alkylbenzenes, and dienes fall on clearly distinct correlation lines. Indene and azulene clearly fall on the correlation line which also contains cyclopentadiene and butadiene; this suggests that all are protonated on the diene function. Biphenyl, which contains two benzene rings which are however not condensed, falls in fact in the region between substituted benzenes and the condensed PAHs. One exception to this regularity of division by structure is pyrene, which deviates from the peri-condensed group and in fact falls on the correlation line of the linear acenes.

Quantitatively, ionization energies and proton affinities

TABLE II: Enthalpies and Free Energies of Proton Transfer^a for $NH_4^+ + B \rightarrow BH^+ + NH_3$; Proton Affinities of B and Hydrogen Atom Affinities of B^+

B	σ_B / σ_{BH}^+	$\Delta G^{\circ b}$	$\Delta H^{\circ b}$	PA(B)^c	HA(B^+)^d
t-$C_4H_9NH_2$	1,3^e	-16.9	-16.5	223.5	
pyridine	1	-17.3	-15.8	222.8	
azulene	2	-17.3	-15.0	222.0	79
tetracene	4	-14.8	-11.7	218.7	65
$C_2H_5NH_2$	1/3^e	-12.0	-11.7	218.7	
3-chloro-pyridine	1	-11.5	-10.0	217.0	
2-chloro-pyridine	1	-11.0	-9.5	216.5	
9-methylanthracene	1^f	-10.9	-9.4	216.4	72
perylene	4	-9.1	-6.0	213.0	64
2-methylanthracene	1	-7.3	-5.8	212.8	70
aniline	1/3^e	-5.8	-5.5	212.5	
1,12-benzoperylene	2	-5.9	-3.6	210.6	64
anthracene	2^f	-4.7	-2.4	209.4	68
$H_2NCH_2CH_2CN$	1/3^e	-2.4	-2.1	209.1	
pyrene	4	-4.6	-1.5	208.5	68
coronene	12	-4.3	0.0	207.0	64
NH_3	1/4	(0.0)	(0.0)	(207)	
acenaphthene	2	-1.2	+1.2	205.9	71
picene	2	-1.1	1.1	205.8	65
1,2,3,4,5,6,7,8-octahydrophenanthrene	2	+0.1	2.4	204.6	74
1,2,3,4,5,6,7,8-octahydroanthracene	2^f	0.4	2.7	204.3	73
$CH_3COOC_3H_7$	1	2.3	3.8	203.2	

Thermochemical interconnection values (arrows in table):
3.0(1.1,546); 2.6(1.3,455); 0.0(-0.7,537); 4.8(2.5,460); -0.6(1.7,460); 1.6(0.4,585); 3.8(3.1,508); 0.7(0.7,608); 2.6(1.4,550); 0.9(0.9,588); 2.8(1.4,520); 2.6(2.6,544); -1.0(0.1,544); -0.3(2.3,525); 1.9(0.0,508); 6.1(4.2,531); 2.5(0.8,482); 4.1(1.5,514); 0.3(1.5,482); 1.4(3.3,526); 0.3(-2.3,549); 4.3(1.6,545); 2.9(-1.1,548); 5.3(1.6,547); 1.2(-1.0,535); 3.2(1.3,540); 2.4(0.2,523); 4.1(2.2,537); 2.8(0.6,519); 1.3(2.0,526); 1.2(1.9,521); 2.7(3.4,540)

biphenylene

TABLE II (*Continued*):

B	σ_B/σ_{BH^+}	$H_2NCH_2CH_2CN$ (diagram values)	$\Delta G^{\circ b}$	$\Delta H^{\circ b}$	PA(B)[c]	HA(B$^+$)[d]
NH$_3$	0.25		(0.0)	(0.0)	(207.0)	
biphenylene	4	4.3(1.6,545) 1.4(-1.7,554)	-1.1	2.2	204.8	66
chrysene	2	-0.4(1.1,558) -0.1(0.6,549)	1.4	3.7	203.3	66
C$_3$H$_7$COOCH$_3$	1	0.8(1.5,470) 0.2(0.9,470)	2.3	3.8	203.2	
1-methylnaphthalene	1	0.0(0.0,572) 3.8(1.2,523)	2.3	3.8	203.2	73
1,3,5-trimethylbenzene	3	0.5(-0.6,526)	1.4	4.0	203.0	83
2-methylnaphthalene	1	1.0(0.3,537) 0.2(0.2,537)	3.0	4.5	202.5	72
fluorene	2	0.2(0.2,537) 4.7(2.5,540)	2.3	4.6	202.4	72
benzaldehyde	1	1.8(1.1,540)	3.2	4.7	202.3	
cyclopentadiene	2		2.7	5.0	202.0	86
fluoranthene	2	1.9(1.2,553) -0.2(-0.9,572)	3.0	5.3	201.7	68
phenanthrene	2	2.2(1.5,550) 1.6(0.9,550)	3.6	5.9	201.1	71
triphenylene	6	3.0(1.1,530) 2.2(2.9,547) 4.1(4.8,548)	3.8	7.3	199.7	67
CH$_3$COCH$_3$	1[g]	0.6(2.5,530)	6.9	8.4	198.6	
phenol	1	4.3(4.3,492) 0.1(-0.6,537)	6.3	8.8	198.2	
biphenyl	2	2.1(0.7,537) 1.5(0.8,526)	6.9	9.2	197.8	74
1,2,3,4-tetrahydronaphthalene	2		7.5	9.8	197.2	79
naphthalene	4	1.7(1.0,539) 2.3(0.1,537)	7.6	10.7	196.3	70
1,2-dimethylbenzene	2	0.4(1.1,494) 1.4(1.4,526)	8.8	11.1	195.9	80
toluene	1	1.7(3.1,494) 1.5(2.2,492)	11.0	12.5	194.5	84
benzene	6		18.9	22.4	184.8[h]	84

[a] All values in kcal mol^{-1}. Numbers in the parentheses indicate the measured ΔG° and the temperature of measurement (K). [b] ΔG°_{550} for NH$_4^+$ + B → BH$^+$ + NH$_4$ calculated from $\Delta G^{\circ}_{550} = \Delta H^{\circ} - 550R \ln (\sigma_{NH_4^+}\sigma_B/\sigma_{BH^+}\sigma_{NH_3})$. ΔH° for samples from this work; for reference compounds taken from ref 1a, but adjusted to PA(NH$_3$) = 207 kcal mol^{-1}. In this table reference compounds are all nitrogen and oxygen bases, and also toluene and 1,2-dimethylbenzene. Also see ref 16. [c] Absolute proton affinties related to PA(NH$_3$) = 207 kcal mol^{-1}. [d] HA = PA + IP − IP(H·) = PA + IP − 313.6 kcal mol^{-1}. Ionization energies were taken from Table III; for compounds not included in Table III, from ref 12. [e] Protonation of the amine group increases σ associated with the internal rotation of this group from 1 to 3. [f] Protonation on the carbon in position 10 assumed. [g] Experimental results (ref 15) indicate that protonation of acetone involves an entropy change of 0 eu. [h] From ref 18, but referred to PA(NH$_3$) = 207 kcal mol^{-1}.

are related by the hypothetical processes:

$$B^+ + H \rightarrow BH^+ \qquad (11)$$
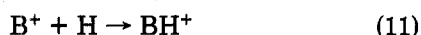
The exothermicity of reaction 11 is accounted for by the hydrogen atom affinity (HA) of the radical ion B$^+$. Using reaction 11, one easily obtains the following relation:

$$HA(B^+) = PA(B) + \Delta H^{\circ}_i(B) - \Delta H^{\circ}_i(H\cdot) \qquad (12)$$

Since reaction 11 transforms the ion from a radical to an even-electron species, the hydrogen affinity expresses the relation between the relative stabilities of the radical ion B$^+$ and the even-electron ion BH$^+$.

Increasingly large π systems of the larger unsaturated compounds permit increasing delocalization of the charge in both radical and protonated ions. However, in the radical ions increasing delocalization of the spin density also becomes possible. Therefore the ionization energy may decrease with increasing size faster than the proton affinity increases. By eq 12 this means that the hydrogen affinity of B$^+$ will decrease with increasingly extensive conjugated π systems. Indeed, using eq 12 we obtain for cyclic dienes HAs of 80–84 kcal mol^{-1}, for alkylbenzenes 76–82 kcal mol^{-1}, and for polycyclic aromatics only 64–70 kcal mol^{-1}. Within the polycyclic series itself the HA also decreases with increasing size (Figure 5). Similar trends for decreasing HA with increasing molecular size were observed also in other series of compounds such as alkylamines.[2]

(d) *Extrapolations to Graphite.* We noted in Figure 5 that the HA of polycylics decreases with increasing size

TABLE III: Free Energies for Charge Transfer: $B_1^+ + B_2 \rightleftarrows B_2^+ + B_1$, and Ionization Energies of Polycyclic Aromatics[a]

B		$\Delta H^{\circ}_{ionization}$	IP(III)
1,12-benzoperylene		167.4	168.8[c]
9-methyl anthracene	1.6(560) 3.9(560)	169.1	
2-methyl anthracene	2.0(553) 0.5(553)	170.2	
coronene	0.9(554)	170.8[d]	169.3[e]
azulene	4.6(550) 1.2(555)	(171.1)[b,f]	171.1[f]
anthracene	1.0(502) 3.1(572)	171.9	171.6[e]
picene	1.5(540)	172.6	173.9[c]
pyrene	1.9(520)	173.0	171.3[e]
biphenylene	1.8(540) 2.7(502) 1.3(491)	174.2	174.5[e]
chrysene	0.8(539)	175.8	175.5[e]
acenaphthene	1.9(539)	178.5	178.3[f]
triphenylene	3.8(482)	181.1[g]	181.0[e]
1,2,3,4,5,6,7,8-octahydroanthracene	4.8(549) 4.2(540)	182.1	
fluorene	0.5(462)	183.0	182.9[d]
1,2,3,4,5,6,7,8-octahydrophenanthrene	4.9(542) 0.2(535)	183.0	
phenanthrene	4.9(549) 0.4(530)	183.3	182.2[e]
naphthalene	3.9(572) 5.7(548) 3.9(535)	(187.7)[b,f]	187.7[f]
1,2,3,4-tetra-hydronaphthalene		195.6[h]	194.4[e]

[a] All values in kcal mol^{-1}. Numbers in parentheses denote temperature of the equilibrium measurement. Positive ΔG° values in the charge-transfer ladder indicate positive value of ΔG° for $B_1^+ + B_2 \rightarrow B_2^+ + B_1$, when B_1 is the upper and B_2 is the lower reactant in the ladder. [b] For the primary reference compounds naphthalene and azulene the ionization energies given in this column are the preferred literature IP values as selected by Rosenstock et al.[12] For other compounds, ΔH°_i is derived from the ladder. For all compounds except coronene and triphenylene we assume $\Delta H^{\circ}_i \approx \Delta G^{\circ}_i \approx$ IP$_{adiabatic}$. [c] R. Boschi, E. Clar, and W. Schmidt, J. Chem. Phys., 60, 4406 (1974). [d] For B = coronene ΔH_i was taken as $\Delta H^{\circ}_i + RT \ln (\sigma_B/\sigma_{B^+}) = \Delta G^{\circ}_i + RT \ln (12/4)$. This correction is made to account for the presumed change in rotational symmetry number due to Jahn-Teller distortion of coronene$^+$, by analogy with benzene$^+$.[11] [e] Average of photoionization and photoelectron spectroscopic values listed in H. M. Rosenstock, D. Sims, S. S. Shroyer, and W. J. Webb, Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.), part I, No. 66 (1980). [f] Preferred literature values as selected by Rosenstock et al.[12] [g] For B = triphenylene, a correction was applied in the sense $\Delta H^{\circ}_i = \Delta G^{\circ}_i + RT \ln (6/4)$ (see footnote d). [h] Measured against 1,2-dimethylbenzene (IP = 197.5) and 1,3,5-trimethylbenzene (IP = 193.7) (not shown in the table).

and reaches a constant value of 64 ± 1 kcal mol^{-1} in perylene, 1,12-benzoperylene, and coronene. HA in the series phenanthrene–chrysene–picene and in the series naphthalene–anthracene–tetracene also reaches a similarly low limiting value. These trends suggest that further increases in molecular size, up to graphite, will not further reduce the HA; i.e., further increase in molecular size would not be accompanied by further excess stabilization of the radical vs. protonated ion.

Observations on dimer ions of polycyclic aromatics also support the conclusion that the incremental stabilization of the unpaired electron levels off in the large radical ions. Thus, in the dimer ions we obtained[23] a measure of the intermolecular resonance stabilization of the unpaired electron by comparing the excess dissociation energies of radical dimer ions B_2^+ vs. protonated dimers B_2H^+. We observed that in the benzene dimer delocalization of the unpaired electron between the two rings increased the
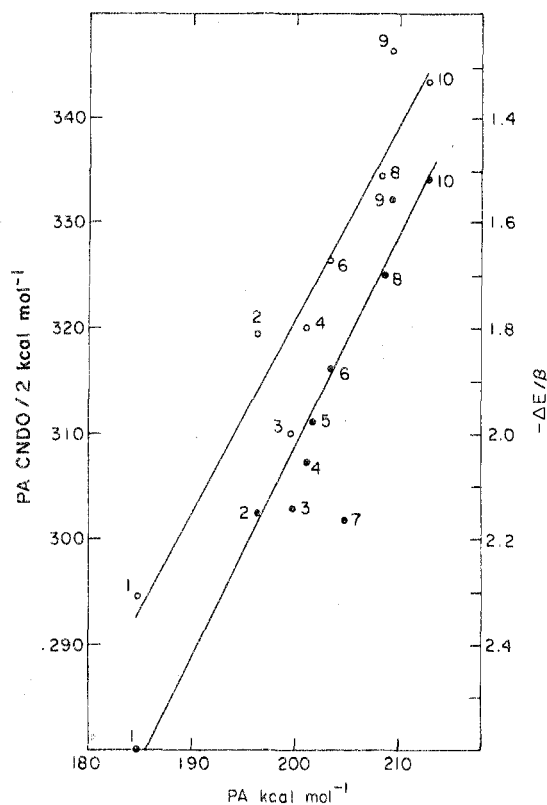

Figure 3. Relation between theoretical and experimental results: (O) localization energies, Mackor et al.;[16] (●) CNDO/2 PAs, Streitwieser et al.[8] (1) benzene; (2) naphthalene; (3) triphenylene; (4) phenanthrene; (5) fluoroanthene; (6) chrysene; (7) biphenylene; (8) pyrene; (9) anthracene; (10) perylene.
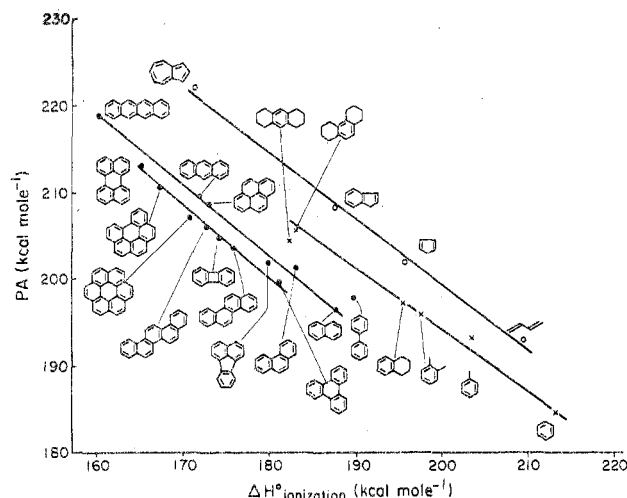

Figure 4. Relation between PA and IP for carbon bases: (O) olefins and azulene; (X) benzene and substituted benzenes; (●) polycyclic aromatics. PAs and IPs from Tables II and III, and ref 12. PA of indene from M. Meot-Ner (Mautner), unpublished results. PA for butadiene from ref 1b.

bonding in B_2^+ vs. BH^+ by ca. 6 kcal mol^{-1}. However, with increasing size the bonding in B_2^+ and B_2H^+ became increasingly comparable. In the same large ions where HA levels off to a constant value, i.e., anthracene, benzoperylene, and chrysene, the excess stabilization of the radical vs. protonated dimers becomes negligible. In other words, the addition to these large ions of either *intramolecular or intermolecular* sites for further delocalization of the spin density does not seem to render further excess stabilization to the radical vs. protonated ion.

Extrapolating from the trends observed in the polycyclic aromatics, we therefore estimate the HA of a singly ionized
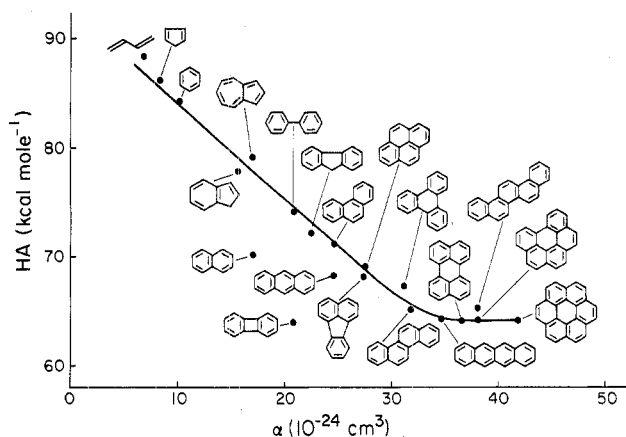
Figure 5. Relation between hydrogen affinity (HA) of B^+ and the polarizability (α) of B: α calculated from refraction indexes for benzene, naphthalene, and phenanthrene. Other values estimated by using 1.7 $\times$ 10^{-24} cm^{-3} per carbon atom, as obtained from the polarizabilities of benzene, naphthalene, and phenanthrene.

graphite monolayer as 64 ± 1 kcal mol^{-1}. We can use this value and eq 12 to estimate the PA of a graphite monolayer. For this purpose we use the ionization potential of graphite as 101 kcal mol^{-1}, as obtained from thermionic emission measurements.[24] This value is interpreted as the IP of a monolayer and is close to a theoretical IP of 98 kcal mol^{-1}.[26] We then calculate the PA of a graphite monolayer as 278 kcal mol^{-1}. Since this value is obtained from the PAH series where protonation occurs on an sp^2 carbon atom bonded to hydrogen, it is only applicable to a graphite layer where the edge carbons are similarly hydrogenated. This restriction also applied to the estimated HA value.

The above HA and PA estimates are strictly applicable only to a monolayer, since in graphite crystal interlayer ion-neutral interactions could effect in principle the values of IP, PA, and HA. However, trends in the bonding energies of dimer ions[23] show that the specifically ionic intermolecular interactions, i.e., resonance charge-transfer and ion-induced dipole interactions, decrease with increasing size and should become negligible in graphite. This is true even in gas-phase dimers which are free to assume optimal geometry for ion-neutral interactions; therefore, it must be also true in a crystal with a more constrained structure. Therefore the above values of HA $\simeq$ 64 kcal mol^{-1} and PA $\simeq$ 278 kcal mol^{-1} should also be applicable for a graphite crystal.

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