

In order for ESE spectroscopy to reach its full potential, both instrumental and theoretical problems need to be resolved. The major instrumental difficulties were outlined above as well as possible means for their resolution. The primary theoretical problem is with the use of ESE methods for the study of slow rotational motions of spin probes. We have previously presented an exact stochastic Liouville treatment of this problem but the computational time for its solution is prohibitively expensive. Simplification may be possible by making use of the Wiener-Khintchine theorem.^{77,78} Some novel pulse sequences used

in NMR may also prove useful. Additional information about very slow motions may be obtained by studying the magnetic field dependence of the phase memory time T_M .

ESE spectroscopy is already a useful technique for the study of dynamics in liquids and biological membranes. We anticipate that with its great potential and the growing interest the remaining theoretical and experimental problems will soon be resolved.

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ARTICLES

Resonance Energies of π Cations and Proton Affinities of Conjugated π Hydrocarbons

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The proton affinities of organic π bases can be correlated with the differences in resonance energy (RE) between the π hydrocarbon precursors (B) and the obtained cations (BH^+). An empirical valence bond approach that makes use of the algorithm $RE = a_1 \ln SC$ (a_1 , constant; SC, structure count) is used to calculate the resonance energies. For the cations, the principal resonance structures are assumed to include hyperconjugation-type structures. The SC ratio $[SC(BH^+)/SC(B)]$ allows the facile identification of pairs of compounds with widely different structural features that should have identical proton affinities.

Parameterized empirical valence bond calculations¹ (structure-resonance theory) give sensible and precise correlations of calculated resonance energies with experimental properties for neutral π hydrocarbons,²⁻⁸ radicals,⁹⁻¹⁰ anions,¹¹ cations,^{11,12} and radical cations.¹³ In all of these cases the algorithm $\ln SC$, where SC is the number of principal resonance structures, is a linear function of the calculated resonance energies,¹⁴ and graph-theoretical procedures for counting resonance structures help to

provide an extremely simple computational procedure.^{15,16} In general, the obtained numerical results go beyond the Hückel MO or perturbational MO methods. In this work, the resonance energy correlations are extended to gas-phase proton affinity data^{17,18} for a wide selection of conjugated olefinic and aromatic hydrocarbons.

The proton affinity of a compound B is defined as $PA(B) = -\Delta H_{298}$ for reaction 1. To a first approximation, it is



assumed that the proton affinity is a linear function of the difference in resonance energies between BH^+ and B. This approximation should be reasonable based on the principle of additive bond contributions to the heats of atomization for species B and BH^+ .¹⁹ It is further assumed that the cations are stabilized by both π resonance and hyperconjugation as depicted in I for cations derived from butadiene ($SC = 3$) and benzene ($SC = 5$). Experimental and the-

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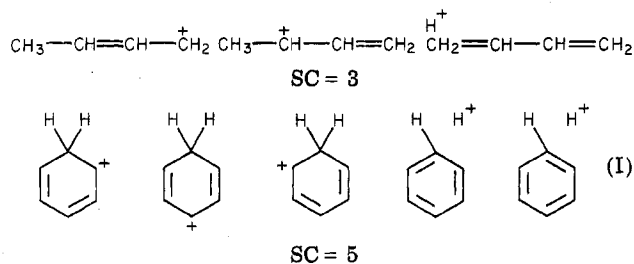
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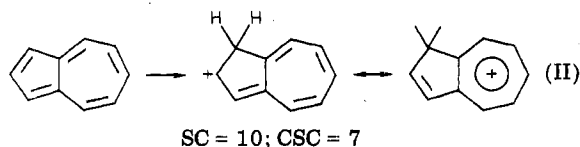
oretical evidence for hyperconjugative stabilization of cationic centers has been discussed by Hehre and co-workers.^{20,21} Finally, experimental proton affinities should correlate with eq 2, where ΔRE is the resonance energy

$$\text{PA} = a_0 + \Delta\text{RE} = a_0 + a_1 \ln [\text{SC}(\text{BH}^+)] - \text{RE}(\text{B}) \quad (2)$$

change for reaction 1, and the resonance energy for the cation is approximated by $a_1 \ln [\text{SC}(\text{BH}^+)]$.

Proton affinity data (through early 1978) for conjugated unsaturated hydrocarbons have been summarized by Aue and Bowers,¹⁷ and several values for alkylbenzene derivatives and polycyclic aromatic species have been recently determined by Meot-Ner.¹⁸ Resonance energies of aromatic hydrocarbons are given by Herndon and Ellzey.² These data, calculated proton affinities from regression analysis, SC's for BH^+ and B, and derived resonance energies of cations, are listed in Table I. All proton affinities are referred to $\text{PA}(\text{NH}_3) = 207.0 \text{ kcal.}^{22}$ The proton affinities in the last column are calculated from the least-squares regression analysis $a_0 = 166.50$ and $a_1 = 27.39$. The correlation coefficient for eq 1 is 0.997, and the average deviation of experimental and calculated proton affinities is $\pm 1.5 \text{ kcal.}$ This uncertainty is of the order of experimental differences for duplicate values determined in different laboratories.

The cation resonance energies are calculated by means of eq 1, the tabulated $\text{RE}(\text{B})$, and the experimental proton affinities. No regularities or structural effects are apparent except for a general increase in resonance energy with molecular size. The last three compounds in Table I, fluoranthene, biphenylene, and azulene, were omitted from the regression analysis because each of these compounds gives ions where the total number of canonical principal resonance structures²³ is smaller than the actual number of resonance structures. The only significant result if found in the azulene system. If the canonical structure count (CSC) is used, protonated azulene would have a calculated resonance energy of 53.3 kcal, compared with 63.3 kcal obtained by use of the experimental proton affinity. The difference could be attributed to extra resonance stabilization associated with the cycloheptatrienyl cation structure (II). Whether or not this viewpoint is



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(22) A theoretical determination gives $\text{PA}(\text{NH}_3) = 205.6 \text{ kcal.}$ See R. A. Eades, K. Scanlon, M. R. Ellenberger, D. A. Dixon, and D. S. Marynick, *J. Phys. Chem.*, **84**, 2840-2 (1980). A recent experimental value of $207.1 \pm 1.7 \text{ kcal}$ has been given by S. G. Lias, D. M. Shold, and P. Ausloos, *J. Am. Chem. Soc.*, **102**, 2540-8 (1980).

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Chart I

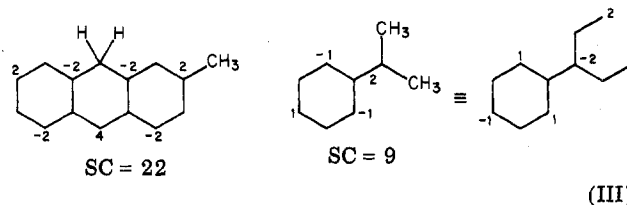
	$\text{H}_2\text{C}=\text{CH}_2$	$\text{CH}_3\text{CH}=\text{CH}_2$	$(\text{CH}_3)_2\text{C}=\text{CH}_2$
PA(expt)	165.5	186.6	198.9
SC(BH^+)	2	3	4
PA(calcd)	196.6	196.6	204.4

Chart II

	$\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$	$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$	$(\text{CH}_3)_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$	$(\text{CH}_3)_6\text{C}_6\text{H}_6$
PA(expt)	207.7	212.6	218.1	210.6
SC(BH^+)	4	6	6	8
PA(calcd)	204.5	215.6	215.6	204.1

valid, it is interesting that the value of the obtained extra resonance energy (10.0 kcal) is practically identical with that derived from photoelectron spectra and molecular orbital calculations on cycloheptatrienone (10.8 kcal).²⁴

The SC of BH^+ given in Table I is chosen for the ion with the maximum number of resonance structures. The SC's are found by using the coefficients of formally non-bonding π MO's. The number of π resonance structures is equal to the sum of the absolute values of the (unnormalized) coefficients,²⁵ and the number of hyperconjugation structures is given by the coefficients at sites adjacent to saturated alkyl moieties (III). An alternative procedure



for counting structures that gives the same total SC is to model the alkyl group (CH_3 or CH_2) as equivalent to a vinyl substituent.

The data in Table I have been restricted to conjugated polyolefinic and aromatic species. Application of eq 2 to ethylene, propene, and isobutylene gives the results shown in Chart I, which demonstrate that the hyperconjugation effects are not properly accounted for in the cations derived from monoolefins. Also not included are some examples of highly alkylated dienes and hexamethylbenzene (Chart II). A referee has pointed out that the discrepancies in these cases show that steric effects and a stabilizing effect of methyl group at the central carbon of the allyl cation are not rationalized by this exceedingly simple theoretical approach. These results, of course, illustrate limitations of structure-resonance theory, but do not detract from the correlations demonstrated in Table I. A possible use of theory in this regard could be to delineate where neglected steric and/or electronic effects are manifested.

An intriguing aspect of the proton affinity data in Table I is the very similar proton affinities that are found for several pairs of compounds which are structurally highly dissimilar. The structure count ratio, defined as $[\text{SC}(\text{BH}^+)]/\text{SC}(\text{B})$ allows one to recognize such pairs of compounds at a glance, since two compounds with identical SC ratios also possess identical ΔRE 's to a very good approximation (structure-resonance theory resonance energies² are given¹⁴ by the equation $\text{RE}(\text{B}) = 27.34 \ln [\text{SC}(\text{B})]$,

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TABLE I: Proton Affinities, Resonance Energies, and SC's for π Hydrocarbons and Cations (Energies in kcal)


























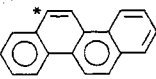
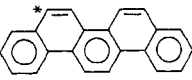

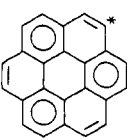
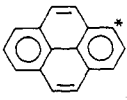
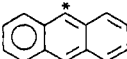
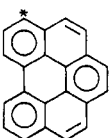
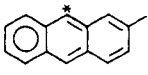
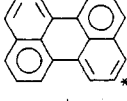
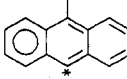
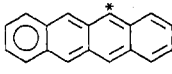
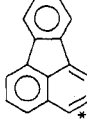
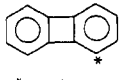

hydrocarbon (B) ^a	SC(B)	SC(BH ⁺)	RE(B) ^b	RE(BH ⁺) ^c	PA(B)	
					expt ^d	calcd
	1	3	0.0	28.5	195.0	196.6
	1	4	0.0	35.9	202.4	204.5
	1	4	0.0	37.3	203.8	204.5
	1	4	0.0	35.5	202.0	204.5
	1	5	0.0	43.4	209.9	210.6
	1	6	0.0	48.6	215.1	215.6
	2	5	19.4	40.7	187.8	191.2
	2	6	19.4	47.7	195.0, 194.5	196.2
	2	6	19.4	49.5	197.3, 195.9	196.2
	2	6	19.4	49.1	196.2	196.2
	2	6	19.4	50.1	197.2	196.2
	2	7	19.4	53.8	200.9	200.4
	2	7	19.4	57.2	204.3	200.4
	2	7	19.4	57.5	204.6	200.4
	2	7	19.4	57.3	204.4	200.4
	2	8	19.4	56.8	204.8, 203.0	204.1
	2	9	19.4	63.1	210.2	207.3
	4	13	38.8	70.1	197.8	198.0
	4	20	38.8	86.6	214.3	209.8
	3	10	31.1	60.9	196.3	198.5
	9	32	61.1	94.3	199.7	200.3
	5	18	45.0	79.6	201.1	200.7
	4	14	38.8	74.7	202.4	200.0
	3	12	31.1	67.1	202.5	203.5
	3	12	31.1	67.8	203.2	203.5

TABLE I (Continued)

hydrocarbon (B) ^a	SC(B)	SC(BH ⁺)	RE(B) ^b	RE(BH ⁺) ^c	PA(B)	
					expt ^d	calcd
	8	34	58.1	94.9	203.3	205.0
	13	58	70.7	110.0	205.8	207.0
	3	13	31.1	70.5	205.9	205.7
	20	88	80.7	121.2	207.0	208.4
	6	27	49.1	91.1	208.5	207.7
	4	20	36.9	79.8	209.4	211.7
	14	70	72.7	116.8	210.6	210.2
	4	22	36.9	83.2	212.8	214.3
	9	49	62.1	108.6	213.0	211.0
	4	24	36.9	86.8	215.4	216.7
	5	32	40.4	92.6	218.7	221.0
	6	26 ^e	50.5	85.7	201.7	205.2
	3 ^e	12 ^e	30.0	68.3	204.8	204.6
	2	7 ^e	7.8	63.3	222.0	212.1

^a The position of protonation is indicated by an asterisk. ^b From ref 2. ^c $RE(BH^+) = PA(expt) + RE(B) - 166.50$.

^d From ref 17 and 18. ^e Canonical SC, see text.

cf. eq 2 where $RE(BH^+) = 27.39 \ln [SC(BH^+)]$. Examples are 1,3-butadiene and toluene (SC ratio = 3.0, $\Delta PA = 0.0$ kcal); 1,3,5-trimethylbenzene and 1-methylnaphthalene (SC ratio = 4.8, $\Delta PA = 0.2$ kcal); and 2,4-dimethyl-1,3-pentadiene and 9-methylanthracene (SC ratio = 6.0, $\Delta PA = 0.7$ kcal). The worst case lies in the group 2-methyl-1,3-pentadiene, 1,1-diphenylethylene, anthracene, and 1,12-benzoperylene, all with SC ratio = 5, where the proton affinity of 1,1-diphenylethylene differs from those of the other three compounds by an average ± 4.4 kcal. This may point to the limitations of the correlation, or may indicate possible experimental errors in the proton affinity data.

In recent kinetic and theoretical studies of the cyclo-

addition reactions of aromatic hydrocarbons, Biermann and Schmidt^{7,8} have shown that structure-resonance theory leads to the discovery of homologous "isocanonical" series in which corresponding members have the same theoretical reactivity indices (SC ratio) and the same experimental rate constants, despite widely differing structures. The pairs of compounds with identical SC ratios for proton addition should therefore be called isocanonical pairs, to correspond with the Biermann and Schmidt terminology. The possibility of identifying such previously unsuspected congruencies and relationships in reactivities or thermodynamic properties is one of the useful aspects of the empirical structure-resonance theory approach.²⁶

The resonance energies in Table I can be used for several purposes, two of which are under current investigation. First, in analogy to the previous studies on ΔH atomization for aromatic hydrocarbons⁴ and boron hydrides,²⁷ an additive bond energy scheme for hydrocarbon cations is being devised. Second, the resonance energies allow one to parameterize²⁸ a more complete valence bond theory for

(26) A concept of "conformal set" additivities in aromatic systems involves matching of pairs of compounds with other pairs and is dissimilar to the idea of isocanonical pairs. See R. A. Marcus, *J. Chem. Phys.*, **43**, 2643-54 (1965).

(27) W. C. Herndon and M. L. Ellzey, Jr., *Inorg. Nucl. Chem. Lett.*, **16**, 361-6 (1980).

carbocations that will presumably give results for calculated properties in better agreement with experiment than those reported here. The results of these investigations will be reported in a full, detailed paper.

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(28) W. C. Herndon and M. L. Ellzey, Jr., *Chem. Phys. Lett.*, **60**, 510-4 (1979).

Positive Ions in Alkane and Mixed Alkane Glasses

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Alkane and mixed alkane glasses have been studied by pulse radiolysis. The spectrum for squalane (SQ) was found to be made up of contributions from both the trapped electron and the primary positive ion of squalane (SQ^+). Charge transfer between the solvent positive ion and solute has been directly observed for the first time in mixed alkane glasses. In an N_2O -bubbled 3-methyloctane (3MO) glass containing 1 vol % SQ, absorption due to SQ^+ was seen to grow, concomitant with the decay of $3MO^+$. Growth of SQ^+ was also observed in an N_2O -saturated glass of 3-methylpentane containing 2 vol % SQ.

Introduction

Much of the early work examining positive ions in hydrocarbon glasses was carried out by Hamill and co-workers.¹ Louwrier and Hamill^{2,3} found that radical ions (RH^+) of higher alkanes were trapped in 3-methylpentane (3MP) matrixes containing both the higher alkane and an electron scavenger, when γ -irradiated at 77 K. They measured the optical absorption spectra of many such alkane cations. The absorption maximum (λ_{max}) of RH^+ was found to increase with increasing carbon number, being 645 nm for *n*-octane and ~ 1200 nm for squalane (SQ), a $C_{30}H_{62}$ alkane. However, in neat alkane glasses containing an electron scavenger, Louwrier and Hamill were not able to observe RH^+ . Mehnert, Brede, Böz, and Naumann⁴⁻⁶ have studied radical cations and positive charge transfer to aromatic solutes in liquid alkanes near room temperature.

In our laboratory, pulse radiolysis was used to measure the absorption spectrum of the 3-methyloctane cation ($3MO^+$) in liquid 3-methyloctane (3MO) at low temperatures⁷ and in glassy 3MO at 6 and 77 K.⁸ We now report

the spectra of the primary cation, SQ^+ , and the trapped electron, e_t^- , in SQ glass. We also report for the first time observation of the charge transfer reaction between RH^+ and an alkane solute in mixed alkane glasses. We measured both the growth of the SQ cation (SQ^+) and the concomitant decay of $3MO^+$ in a 3MO/SQ glass following pulse radiolysis at 72 K. The growth of SQ^+ in a 3MP/SQ glass was also observed.

Experimental Section

Squalane (95% pure), 3-methylpentane (99.9%) and 3-methyloctane (99%) were obtained from Chemical Samples Co. The 3MO was treated with silica gel and molecular sieve before using. The SQ and 3MP were used without further treatment. Triethylamine (TEA) from Matheson, Coleman and Bell was used as a scavenger of RH^+ .⁹ Samples were deaerated by bubbling with argon before sealing in Suprasil cells of 5-mm optical path length. Alternatively, samples were bubbled with N_2O when an electron scavenger was required. The N_2O concentration was not measured but was likely ~ 0.1 M.¹⁰ Most glasses were slightly crazed or cracked.

The experimental procedures and equipment have been described previously.^{8,11,12} Single 40-ns pulses of 35-MeV

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