

Beyer and Jacobs²¹ observed a three-step reduction of Ag^+ in chabazite corresponding to 50%, 66%, and 100% reduction. This corresponds to the formation of respectively Ag_2^+ , Ag_3^+ , and a completely reduced Ag -chabazite. For the charged clusters the Ag^+ ion was supposed to be located in the hexagonal prism of chabazite (analogous to site I in faujasite-type zeolites). This charge distribution follows the common coordination chemistry knowledge that the most highly charged cations tend to have the highest coordination number (in the present case 6 for Ag^+ and 3 for Ag^0). Thus both the dinuclear and trinuclear clusters can formally be represented $\text{Ag}^0\text{-Ag}^+$ and $\text{Ag}^0\text{-Ag}^+\text{-Ag}^0$ with Ag^+ on site I, coordinated to six oxygens, and Ag^0 and site I', coordinated to three oxygens.

Ozin et al.¹¹ proposed an alternative interpretation of the 3.10-eV band of trinuclear clusters. They ascribed it to a transition from filled d-type valence levels to the half-filled s-type level of Ag_3^{2+} . This proposal was made on the basis of $X\alpha$ calculations on naked clusters. It seems that more extensive calculations with inclusion of the zeolitic environment are necessary to distinguish between our interpretation and Ozin's.

The description of the Ag_3 cluster in zeolite A (model 4) follows the same lines as exposed for the dinuclear and trinuclear clusters in zeolite X and Y. Thus, a neutral cluster is unlikely to occur because of the negatively charged framework of the zeolite. The two external Ag's are coordinated to lattice oxygens. They are expected to carry the positive charge, and a cluster, formally represented as $\text{Ag}^+\text{-Ag}^0\text{-Ag}^+$, seems to be the most reasonable formulation. This has been proposed already in the literature.³ As for the yellow zeolites X and Y, the visible absorption band of yellow zeolite A is due to a charge transfer, but now from a MO mainly localized on the central Ag to a MO localized on the external Ag atoms. This cluster carries an unpaired electron. We have been able to measure a small amount of paramagnetism on

the yellow and brick red AgA zeolites, which have the characteristic absorptions at 2.85 and 2.48 eV, respectively.³ If the magnetic moment of Ag^0 is taken as the spin-only value of $1.75 \mu_B$, the experimental magnetic moment corresponds to 0.7 Ag^0 and 1.2 Ag^0 per unit cell for yellow and brick red AgA, respectively. These numbers are two times smaller than those obtained from X-ray diffraction studies.³ In any case these experiments show that a small amount of paramagnetic Ag species are likely to be present in yellow and brick red AgA.

An interesting problem arises about the geometry of these positively charged, trinuclear clusters. For the free clusters, Ag_3^+ or Ag_3^{2+} , the most stable configuration is the equilateral triangle.¹³ In zeolites, the clusters are linear or nearly so. It must be that the zeolite lattice imposes strong constraints on the construction of metallic clusters. It is worth mentioning that they are destroyed by treatment with H_2 and H_2O but not by an O_2 treatment.^{4,7} This may be a consequence of the fact that H_2 and H_2O can penetrate the cubooctahedra but O_2 cannot or at least can only with great difficulty.

Conclusions

The spectroscopic properties of Ag clusters in zeolites are explained with the cluster models proposed in the literature on the basis of X-ray diffraction data. The absorption band of Ag^0 in site I is a 5s-5p transition. The yellow color of zeolites X and Y is due to a charge transfer from a MO on Ag in I' to a MO on Ag in I. The cluster can be Ag_2 or Ag_3 , and the most likely charge is 1+. The positive charge is carried by Ag in I. The yellow color of zeolite A is due to a charge transfer from the central Ag to the external Ag atoms of the Ag_3 clusters. The most likely formulation of this cluster is $\text{Ag}^+\text{-Ag}^0\text{-Ag}^+$. The linear geometry of all these clusters is imposed by the zeolitic framework.

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MNDO Studies of Proton Affinity as a Probe of Electronic Structure. 1. General

Overview

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MNDO calculations have been performed on 43 molecules and ions and their protonated counterparts. The calculated proton affinities give a mean error of 8%, in comparison to available experimental results. The calculated structures of the protonated molecules agree well with experiment and/or ab initio LCAO-SCF-MO theory. Extensive charge redistribution is brought about by protonation of a substrate molecule. Generally the proton receives electron density from regions of the molecule far removed from the site of attack. Both the frontier orbital theory and calculated atomic charges serve as useful guidelines to predict the site of proton attack in molecules such as CO, NH_3 , HNC, N_2O , ketene, and furan. The most stable site of attack also gives the proton the most electron density in these protonated molecules. A crude correlation exists between calculated ionization energy and proton affinity. A correlation also is found between the final atomic charge on the attacking proton and the proton affinity. The MNDO method underestimates the alkyl substituent effect but overestimates the fluoro substituent effect on proton affinity. This has adverse effects in the use of MNDO to calculate the site of proton attack in perfluoro compounds such as NF_3 .

Introduction

Experimental studies of proton affinity have advanced rapidly over the last 15 years, particularly with the advent of ion cyclotron resonance spectroscopy.^{1,2} At the same time

theoretical studies³ have provided insight into the energetics of protonation and into the geometrical changes and charge

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Table I. Experimental and Calculated Proton Affinities (kcal/mol)

molecule	exptl	MNDO	% error	ref	molecule	exptl	MNDO	% error	ref
H ₂	101	107	6	a	CH ₃ OH	184.9	173	6	a
O ₂	101.1	96	5	a	C ₆ H ₆	185.8	178	4	a
HF	112	156	39	a	PH ₃	191.1	160	16	a
N ₂	113.7	129	13	a	CH ₃ CO ₂ H	190.7	191	0	a
CH ₄	128.2	108	16	a	C ₄ H ₄ O (furan)	195.5	187	4	j
CF ₄	121	129	7	b	CH ₃ CN	190.9	177	7	b
N ₂ O	135.6	157	16	a	(CH ₃) ₂ C=O	193.9	189	3	g
HCl	141	122	13	c	CH ₂ =C=O	195.9	196	0	k
CO	141.4	175	24	d	NH ₃	205.0	195	5	a
NF ₃	151	139	8	e	C ₆ H ₅ NH ₂	211.5	202	5	a
CH ₃ F	151	156	3	b	CH ₃ CH ₂ NH ₂	217.1	199	8	a
C ₂ H ₂	154	158	3	c	C ₅ H ₅ N	220.4	207	6	a
SiH ₄	155	160	3	f	NH ₂ (CH ₃)	214.1	196	8	a
(CF ₃) ₂ CO	159.3	137	14	g	NH(CH ₃) ₂	220.5	193	13	a
C ₂ H ₄	163.0	161	1	h	N(CH ₃) ₃	224.3	189	16	a
H ₂ O	165.3	171	4	h	N ₃ ⁻	344	345	0.3	l
H ₂ S	176.6	155	12	a	NCO ⁻	353	341	3	i
HCN	178.9	174	3	a	F ⁻	370.5	408	10	m
H ₂ CO	177.2	177	0	a	OH ⁻	395	421	7	n
C ₅ H ₈ (cyclopentene)	178	197	11	c	H ⁻	400.4	439	10	o
CH ₂ =CH=CH ₂	184.9	169	9	a	NH ₂ ⁻	404	419	4	p
HN=C=O	181	179	3	i					

^a Reference 2. ^b Blint, R. J.; McMahon, T. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *96*, 1269. ^c Walder, R.; Franklin, J. L. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *36*, 85. ^d Bohme, D. K.; Mackay, G. I.; Schiff, H. I. *J. Chem. Phys.* **1980**, *73*, 4976. ^e Holtz, D.; Beauchamp, J. L.; Henderson, W. G.; Taft, R. W. *Inorg. Chem.* **1971**, *10*, 201. ^f Cheng, T. M. H.; Lampe, F. W. *Chem. Phys. Lett.* **1973**, *19*, 532. ^g Drummond, D. F.; McMahon, T. B. *J. Phys. Chem.* **1981**, *85*, 3746. ^h Bohme, D. K.; MacKay, G. I. *J. Am. Chem. Soc.* **1981**, *103*, 2173. ⁱ Reference 20. ^j Houriet, R.; Schwarz, H.; Zummack, W. *Angew. Chem., int. Ed. Engl.* **1980**, *19*, 905. ^k Vogt, J.; Williamson, A. D.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 3478. ^l Pellerite, M. J.; Jackson, R. L.; Brauman, J. I. *J. Phys. Chem.* **1981**, *85*, 1624. ^m See footnote 11 of ref 5b. ⁿ Kari, R. E.; Csizmadia, I. G. *J. Am. Chem. Soc.* **1977**, *99*, 4539. ^o DeFrees, D. J.; Hehre, W. J.; McIver, R. T., Jr.; McDaniel, D. H. *J. Phys. Chem.* **1979**, *83*, 232. ^p Pellerite, M. J.; Jackson, R. L.; Brauman, J. I. *Ibid.* **1981**, *85*, 1624.

redistribution caused by protonating a substrate molecule.

The proton affinity of a molecule is one of its fundamental properties, just as is its heat of formation, ionization energy, or dipole moment. A correlation of proton affinity with core⁴ and valence⁵ ionization energies has provided insight into the

electronic structure of atoms and molecules.

The reaction of a proton with a molecular substrate is the simplest possible chemical reaction that the substrate can undergo. As such it should be amenable to a variety of theoretical treatments. For example, some studies⁶ relate proton affinity to the electrostatic and polarization potential energies of substrate molecules, and recently Klopman et al.⁷ have extended this approach to the "reaction potential method". It is well-known that the electrostatic potential alone is insufficient to predict the site of proton attack on a substrate molecule.⁸ One of our goals was to determine whether there is a simple method by which the site of proton attack could be predicted.

We have begun our studies of proton affinity using the MNDO molecular orbital method.⁹ In numerous publications this method has been shown to be efficient in terms of computation time and to provide accurate heats of formation and structures of molecules.¹⁰ Only a few reports¹¹ have appeared in which the MNDO method has been applied to proton affinity studies and then to only selected molecules. The defi-

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- (3) A partial list of references is given here: (a) Hopkinson, A. C.; Csizmadia, I. G. *Theor. Chim. Acta* **1974**, *34*, 93. (b) Del Bene, J. E. *J. Am. Chem. Soc.* **1979**, *100*, 1673. (c) Jorgensen, W. L.; Cournoyer, M. E. *Ibid.* **1979**, *100*, 5278. (d) Doiron, C. E.; Grein, F.; McMahon, T. B.; Vasudevan, K. *Can. J. Chem.* **1979**, *57*, 1751. (e) Rouse, R. A. *Theor. Chim. Acta* **1976**, *41*, 149. (f) Köhler, H.-J.; Lischka, H. *J. Am. Chem. Soc.* **1979**, *101*, 3479. (g) Fluck, E.; Pavlidou, C. M. E.; Janoschek, R. *Phosphorus Sulfur* **1979**, *6*, 469. (h) Curtiss, L. A.; Hehre, W. J.; Lisle, J. B.; Pople, J. A. *Prog. Phys. Org. Chem.* **1974**, *11*, 175. (i) Green, S.; Schor, H.; Siegbahn, P.; Thaddeus, P. *Chem. Phys.* **1976**, *17*, 479. (j) Kollman, P.; Rothenberg, S. *J. Am. Chem. Soc.* **1977**, *99*, 1333. (k) Umeyama, H.; Morokuma, K. *Ibid.* **1976**, *98*, 4400. (l) Pollack, S. K.; Devlin, J. L.; Summerhays, K. D.; Taft, R. W.; Hehre, W. J. *Ibid.* **1977**, *99*, 4583. (m) Catalán, J.; Yáñez, M. *Ibid.* **1979**, *101*, 3490. (n) Modro, T. A.; Liauw, W. G.; Peterson, M. R.; Csizmadia, I. G. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1432. (o) Riley, J. P.; Heatley, F.; Hillier, I. H.; Murray-Rust, P.; Murray-Rust, J. *Ibid.* **1979**, 1327. (p) Rauscher, H.-J.; Heidrich, D.; Köhler, H.-J.; Dieter, M. *Theor. Chim. Acta* **1980**, *57*, 255. (q) Desmeules, P. J.; Allen, L. C. *J. Chem. Phys.* **1980**, *72*, 4731. (r) Fossey, J.; Loupy, A.; Strzelecka, H. *Tetrahedron* **1981**, *37*, 1935. (s) Eades, R. A.; Weil, D. A.; Ellenberger, M. R.; Farneth, W. E.; Dixon, D. A.; Douglass, C. H., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 5372. (t) Eades, R. A.; Scalton, K.; Ellenberger, M. R.; Dixon, D. A.; Marynick, D. S. *J. Phys. Chem.* **1980**, *84*, 2840. (u) Green, S. *Ibid.* **1981**, *85*, 1676. (v) Kozmutza, C.; Kapuy, E.; Robb, M. A.; Daudel, R.; Csizmadia, I. G. *J. Comput. Chem.* **1982**, *3*, 14. (w) Greenberg, A.; Liebman, J. F. *J. Org. Chem.* **1982**, *47*, 2084. (x) Del Bene, J. E.; Frisch, M. J.; Raghavachari, K.; Pople, J. A. *J. Phys. Chem.* **1982**, *86*, 1529. (y) Smith, S. F.; Chandrasekhar, J.; Jorgensen, W. L. *J. Phys. Chem.* **1982**, *86*, 3308.
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Table II. H-C and H-N Bond Lengths (Å) in $H^+(CO)_n$ and $H^+(N_2)_n$ ($n = 1-6$)

n	H-C	H-N	no. of bonds
1	1.08	1.03	1
2	1.32	1.27	2
3	1.32	1.27	2
	3.34	3.38	1
4	1.32	1.27	2
	3.37	3.39	2
5	1.32	1.27	2
	3.42	3.40	3
6	1.32	1.27	2
	3.48	3.47	4

iciencies of the MNDO method are well-known for neutral molecules and will be delineated as we take up specific protonated molecules. Ab initio calculations have been used extensively to study proton affinity with a flexible basis set,^{3y} and such calculations have even been done with corrections for zero-point vibrational energy and correlation effects.^{3x} Typically the error compared to experiment is less than 5%, but even for the proton affinity of HF the error is 12%,^{3x} indicating that proton affinity is not an easy property to calculate accurately.

In summary, we have chosen the MNDO method because it has definite fiscal virtues¹⁰ and because our ultimate interest was to report proton affinity calculations on the cluster molecules consisting of boranes and carboranes. In the latter areas, ab initio calculations have encountered difficulty in reproducing ground-state experimental geometries for relatively "simple" molecules such as B_4H_{10} .¹²

Results and Discussion

In Table I we present the calculated proton affinities for 37 molecules and 6 ions and compare these results to the experimental proton affinities. The geometries of the molecular substrates and of the protonated species have been optimized completely, with attention paid to searching for a global rather than a local minimum on the energy surface. The proton affinities were calculated from the computed heats of formation and by utilization of the experimental heat of formation of the proton, 365.7 kcal/mol.^{13,14}

Large differences between calculated and experimental proton affinities occur for the diatomic HF and CO molecules; other than these two molecules the error is never more than 16% and the mean percent error is only 8%. Nevertheless, it must be admitted that the MNDO method is not accurate enough to allow good quality prediction of unknown PA values. The experimental studies mostly utilize a bracketing technique to obtain the proton affinity, and the error involved in different experimental approaches to a given proton affinity is generally only 1-3%.

Structural Results. Besides an examination of reaction energetics we wish to put the MNDO method to a more severe test by comparing the calculated structures to those obtained experimentally or calculated with high-quality ab initio calculations. The molecules chosen for highlighting here are either of special chemical interest or else of interest in checking MNDO's structure-finding abilities. The potential application is tremendous, for it is experimentally common to determine proton affinities without determining protonated structures.

Table III. Relative Energies (kcal/mol)

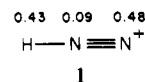
structure	MNDO ^a	ab initio ^b	structure	MNDO ^a	ab initio ^b
HNCO	0.0	0.0	HCNO	62.0	74.4
HOCN	3.0	18.9	HONC	73.0	73.4

^a This work. ^b Reference 19.

$H^+(CO)_n$ and $H^+(N_2)_n$, $n = 1-6$. MNDO calculated structures for $H^+(CO)_n$ ($n = 1-4, 6$) and $H^+(N_2)_n$ ($n = 1-4, 6$) are in agreement with ab initio 4-31G results.¹⁵ Bond length information is summarized in Table II. The agreement includes the $n = 3$ case, where MNDO favors a T-shaped structure over an equilateral triangle structure by 20 kcal/mol for both CO and N_2 . Calculated structures for $H^+(CO)_3$ are given in the supplementary material.

The MNDO structures support the theory that $H^+(CO)_2$ and $H^+(N_2)_2$ compose linear cores that are essentially undeformed by the approach of further groups, which form weak van der Waals bonds perpendicular to the linear cores. In the $n = 5$ case, MNDO favors a trigonal-bipyramidal structure over the reported square-pyramidal structure.¹⁵ We believe that MNDO is correct on this point and have so verified by repeating the ab initio 4-31G calculations on both structures.¹⁶ The trigonal-bipyramidal structure also is more consistent with the aforementioned theory. The van der Waals bonds are predicted to be too long by the MNDO method, but this is a well-known problem.¹⁷

Another interesting aspect of these results is the calculated charge redistribution that occurs as a result of protonation. The charge donation to the proton comes primarily from the terminal atom rather than the atom bonded to the proton. Both MNDO and ab initio results show this effect throughout ($n = 1-6$). For N_2 , electronic charge donation comes almost exclusively from the terminal nitrogen atom (1).



Although these results contradict formal charge ideas, they are in agreement with chemical intuition. Protonation of a given nitrogen atom results in σ and π bond polarization of the triple bond so that the central nitrogen atom loses only 0.09 electron in the population analysis.

HNCO, HCNO, HONC, and HOCN. We take up the calculation of isocyanic acid and three of its isomers because this essentially allows us to calculate the proton affinity of OCN^- and ONC^- . The most stable isomer of the former is calculated to be HNCO and of the latter HCNO; these results are in agreement with experiment as are the calculated proton affinities of the anions (Table I). Furthermore, MNDO structural properties are in good agreement with both experiment¹⁸ and ab initio calculations.¹⁹ Bond lengths are consistently accurate to within 0.04 Å, and bond angles are accurate to within 4° for these isomers. For example, MNDO's prediction that HCNO is linear whereas the others are trans matches the ab initio findings. For HNCO, MNDO calculates an NCO bond angle of 168°, which compares with an experimental value of 172° and ab initio value of 175°. The

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 (13) Lias, S. In "Kinetics of Ion-Molecule Reactions"; Ausloos, P., Ed.; Plenum Press: New York, 1978; p 233.
 (14) Some authors who previously have used MNDO to calculate proton affinities¹¹ have employed $\Delta H_f(H^+) = 326.7$ kcal/mol (as calculated by MNDO). Most authors have not stated which value of $\Delta H_f(H^+)$ they have employed, but it is important to do so because of the 39 kcal/mol difference in values.

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Table IV. Relative Energies (kcal/mol) of Protonated Ketene Isomers

structure	MNDO	ab initio ^a	exptl ^b
CH ₃ CO ⁺	0	0	0
CH ₂ COH ⁺	27	35	18 ± 8
CH ₂ CHO ⁺	54		

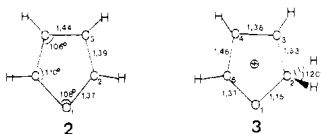
^a Yarkony, D. R.; Schaefer, H. F., III *J. Chem. Phys.* 1975, 63, 4317. ^b Vogt, J.; Williamson, A. D.; Beauchamp, J. L. *J. Am. Chem. Soc.* 1978, 100, 3478.

relative energies of the isomers, however, are in somewhat poorer agreement with those calculated by ab initio methods (see Table III).

Protonated HNCO and CH₂CO. MNDO favors nitrogen protonation over oxygen protonation of HNCO by about 12 kcal/mol. This is in agreement both with the suggestion made by Wight and Beauchamp²⁰ based on ion cyclotron resonance results and with the results of ab initio calculations;²¹ the latter predicts the difference in energy between the two isomeric forms to be about 18 kcal/mol.

Isoelectronic with HNCO is ketene, CH₂CO, which is calculated to protonate at the methylene carbon atom, analogous to the protonation site of HNCO. MNDO relative isomeric energies for protonated ketene are compared with experimental and ab initio results in Table IV.

Protonated Furan. Recent ICR studies have shown furan to protonate at the α -carbon in the gas phase.²² MNDO calculations agree; the energy of the β -protonated furan is 5.5 kcal/mol and of the oxygen-protonated furan is 23.0 kcal/mol, relative to the α -protonated isomer. The calculated structural changes that occur as a result of protonation are exhibited in 2 and 3. The calculated atomic charges show that C₅ is more positive than C₂ by 0.28 charge unit.

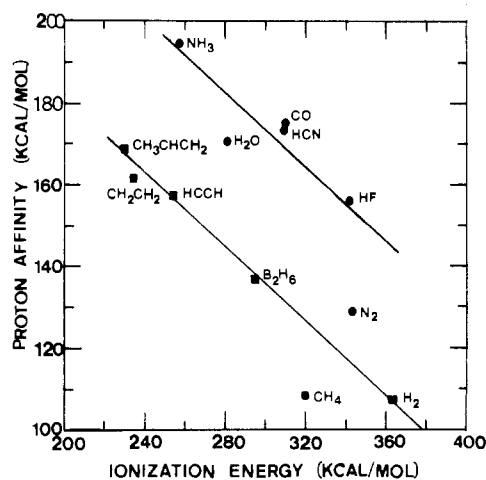


Protonated Ethene and Ethyne. The relative stabilities of the "open" and "bridged" structures for the protonated cations of ethene and ethyne have long been of interest and have been extensively studied by theorists in recent years. Although a great many calculations have favored the open structures, the most recent results, which are extended-basis SCF calculations and include correlation energy, prefer the bridge structure for protonated ethene^{3x,23} and ethyne.^{3x,24} Our MNDO calculations favor the open structures, by 15.1 kcal/mol for ethene and 24.4 kcal/mol for ethyne. MNDO has a known propensity, however, to underestimate the strengths of multicenter bonds.²⁵

Methyl and Fluoro Substituent Effects. We also have completed MNDO calculations on N(CH₃)_nH_{3-n} (n = 0-3) in order to test the ability of MNDO to mimic the subtle differences in proton affinity for these molecules (Table I). The results are not in good agreement with experiment, in that NH₂(CH₃) is calculated to have a larger PA than NH₃ but further methyl substitution results in a calculated decrease in PA. Ab initio calculations²⁶ including double- ζ plus polari-

Table V. Site of Proton Attack

mole- cule	site	charge on site atom	% HOMO on site atom	rel resultant charge on proton	rel energy, kcal/ mol
CO	C	0.12+	73	0.33+	0
	O	0.12-	27	0.43+	31
N ₂ O	N	0.07-	35	0.34+	26
	O	0.27-	63	0.31+	0
H ₂ CCO	C (CH ₂)	0.28-	60	0.12+	0
	O	0.17-	25	0.30+	27
HNCO	N	0.35-	61	0.30+	0
	O	0.21-	35	0.31+	12
HN ₃	N (HN)	0.29-	64	0.22+	0
	N _{terminal}	0.05-	36	0.25+	24
furan	O	0.13-	0	0.33+	23
	α -C	0.01-	36	0.13+	0
	β -C	0.13-	14	0.14+	5.5
pyridine	N	0.23-	0	0.25+	0
	β -C	0.12-	26	0.13+	34
aniline	N	0.23-	1	0.21+	0
	para C	0.06-	29	0.09+	0.05

**Figure 1.** Plot of calculated proton affinity vs. calculated ionization energy.

zation basis functions were able to reproduce the experimentally observed trend. Comparison of MNDO and experimental results on acetone/formaldehyde and C₂H₅NH₂/NH₃ also shows that MNDO consistently underestimates the alkyl substituent effect (Table I).

Calculations on a series of fluorinated acetones²⁷ show that MNDO tends to enhance the fluorine substituent effect. For example, the calculated PA of acetone is in good agreement with experiment (Table I) whereas that for hexafluoroacetone is too low by about 20 kcal/mol. The situation is even worse for NF₃, where the calculated proton affinity reported in Table I refers to F protonation and the resulting structure is essentially calculated to be NF₂⁺...FH. Experimentally there seems little doubt that the correct ion is HNF₃⁺, but MNDO incorrectly predicts N protonation to be less stable by 51 kcal/mol.

Site of Protonation. Wherever appropriate, we have carried out calculations for more than one site of protonation. We here attempt to relate the protonation site to calculated atomic charges in the neutral ground-state molecule, to the extent of localization of the highest occupied molecular orbital at the site of attack, and to the resulting charge on the attacking

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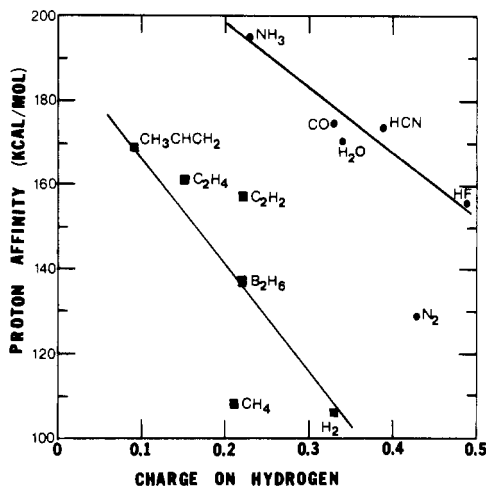


Figure 2. Plot of calculated proton affinity vs. resultant charge on the hydrogen atom.

proton. Such results are presented in Table V for eight molecules. It is clear that the frontier orbital theory and the charge on the attacked atom can serve as useful guidelines to predict the site of proton attack. In four of the eight cases both guidelines predict the same site of attack, in two cases

the atomic charge alone predicts the correct site, and in two cases the frontier orbital theory alone predicts the correct site. In all cases except pyridine and aniline, the most stable site of attack results in the least positive charge on the proton.

Proton Affinity Correlations. In Figures 1 and 2 we present plots of calculated proton affinity vs. ionization energy (Koopmans' theorem) and vs. resultant charge on the proton. These plots are presented for a select few simple molecules of the sort for which we previously have examined the experimental data.^{5b} There does appear to be a hint of the type of correlation we observed before. That is, substrate molecules can be classified as to whether they are lone-pair electron donors or bond-pair electron donors.

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Supplementary Material Available: A listing of calculated MNDO heats of formation and ionization energies from Koopmans' theorem and a figure showing calculated structures for $H^+(CO)_3$ (6 pages). Ordering information is given on any current masthead page.

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MNDO Studies of Proton Affinity as a Probe of Electronic Structure. 2. Boranes and Carboranes

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The protonation of the boranes and carboranes B_nH_{n+4} , B_nH_{n+4} ($n = 2, 5, 6$), $C_2B_nH_{n+2}$ ($n = 3, 4, 5, 10$), CB_3H_9 , and $B_nH_n^{2-}$ ($n = 4, 6, 7$) has been studied by the MNDO method. Calculated proton affinities and protonated structures are reported. The calculations predict B-B edge protonation for B_6H_{10} and 1,6- $C_2B_4H_6$, B-B-B face protonation for $B_6H_6^{2-}$, $B_7H_7^{2-}$, 2,4- $C_2B_3H_7$, and 1,12- $C_2B_{10}H_{12}$, proton attack resulting in a three-center B-H₂ bond for B_2H_6 , B_4H_{10} , and B_5H_9 , carbon protonation for 1,5- $C_2B_3H_5$ and 2- CB_3H_9 , and formation of a two-center B-H bond upon protonation of $B_4H_4^{2-}$. The site of protonation is correlated with the electronic structure of the substrates. Selected ab initio calculations employing the 3-21G basis set have been performed.

Introduction

The boranes¹ and carboranes² from a class of molecules of exceeding interest from a structure and bonding viewpoint. Studies in the past decade have shown that it is useful to relate the structure and bonding of transition-metal organometallic cluster molecules to those of the main-group boranes and carboranes through the isolobal principle.³

In this work we set out to use the proton as a probe of the electronic structure of the boranes and carboranes. Our approach is to use the MNDO molecular orbital method,⁴ building on our earlier work of MNDO proton affinity studies.⁵ We shall pay particular attention to the site of proton attack on the substrate molecule and the resulting geometry changes and charge redistribution caused by protonation.

The experimental proton affinities are known for a few boranes⁶ and carboranes⁷ from gas-phase studies, but the protonated structures are unknown. Protonation of B_6H_{10} has been carried out in solution, and NMR studies show that the B-B edge has been protonated to form $B_6H_{11}^+$.⁸ We were also intrigued by the fact that ion cyclotron resonance experiments⁷ on 1,6- $C_2B_4H_6$ have indicated it to have a basicity (proton affinity) equal to that of ammonia, in spite of the fact that it is an "electron deficient" molecule. Therefore, one of our goals was to determine whether the MNDO method could provide a rationale for the high basicity of 1,6- $C_2B_4H_6$.

A study of the scope that we have undertaken would be next to impossible using ab initio methods with a high-quality basis set. It is well-known that ab initio methods have difficulty obtaining the correct structure for a borane as small as B_4H_{10} , even when configuration interaction is included.⁹ We have

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