In contrast, the correlations between $\mathcal{A}_N$ and the model, cybotactic parameters $E_T(30)$, Z, and Ω are good.

Conclusions

Since the nonmodel, cybotactic solvent polarity parameter $\mathcal{A}_N$ correlates closely (ca. 90%) with the model, cybotactic solvent polarity parameters and only poorly with the nonmodel, noncybotactic solvent polarity parameters, it seems reasonable to infer that the cybotactic probe nature of a solvent polarity parameter is considerably more important than whether it involves a model chemical transformation.

Since there is a good correlation between $\mathcal{A}_N$ and $E_T(30)$, Z, and Ω, $\mathcal{A}_N$ would make a useful solvent polarity parameter, especially in cases where values for the other parameters cannot be obtained because of solubility limitations, spectral interference, etc.

Acknowledgments. This work was supported by the State University of New York Research Foundation and the SUNY/Oneonta Research Committee. We are grateful to Mr. Ralph Mollison and the SUCO Physics Department for providing access to the ESR spectrometer.

References and Notes

(1) For a review, see K. Dimroth, *Angew. Chem., Int. Ed. Engl.*, **4**, 29 (1965).
(2) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948); S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **73**, 2700 (1951); A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).
(3) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958); cf. ref 6, p 301.
(4) K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Justus Liebigs Ann. Chem.*, **661**, 1 (1963).
(5) (a) The cybotactic region is the volume around a solute molecule in which the order of the solvent molecules has been affected by the solute. J. R. Partington, "An Advanced Treatise on Physical Chemistry", Vol. 2, Longmans, Green and Co., London, 1951, p 2. (b) J. R. Partington, *ibid.*, Vol. 5, p 390 ff.
(6) For a detailed discussion of the factors to be considered in choosing an empirical solvent polarity parameter, see E. M. Kosower, "An Introduction to Physical Organic Chemistry", Wiley, New York, N.Y., 1968, p 293 ff.
(7) T. Kawamura, S. Matsunami, and T. Yonezawa, *Bull. Chem. Soc. Jpn.*, **40**, 1111 (1967).
(8) K. Umemoto, Y. Deguchi, and H. Takaki, *Bull. Chem. Soc. Jpn.*, **36**, 560 (1963).
(9) K. Mukai, H. Nishiguchi, K. Ishizu, Y. Deguchi, and H. Takaki, *Bull. Chem. Soc. Jpn.*, **40**, 2731 (1967).
(10) O. Kikuchi and K. Someno, *Bull. Chem. Soc. Jpn.*, **40**, 2549 (1967).
(11) H. Lemaire and A. Rassat, *J. Chim. Phys. Phys.-Chim. Biol.*, **61**, 1580 (1964).
(12) R. Briere, H. Lemaire, and A. Rassat, *Tetrahedron Lett.*, 1775 (1964).
(13) R. Briere, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, **11**, 3273 (1965).
(14) A. L. Buchachenko and O. P. Sukhanova, *Zh. Strukt. Khim.*, **6**, 32 (1965).
(15) Th. A. J. W. Wajer, A. Mackor, and Th. J. deBoer, *Tetrahedron*, **25**, 175 (1969).
(16) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).
(17) P. B. Ayscough and F. P. Sargent, *J. Chem. Soc. B*, 907 (1966).
(18) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).
(19) T. Kubota, K. Nishikida, H. Miyazaki, K. Iwatani, and Y. Oishi, *J. Am. Chem. Soc.*, **90**, 5080 (1968).
(20) A. H. Cohen and B. M. Hoffman, *J. Phys. Chem.*, **78**, 1313 (1974); cf. *Inorg. Chem.*, **13**, 1484 (1974); see also *J. Am. Chem. Soc.*, **95**, 2061 (1973).
(21) $\mathcal{A}_N/\mathcal{A}_{NH}$ for phenyl nitroxide does not vary with solvent polarity; see ref 10.
(22) A. K. Hoffmann et al., *J. Am. Chem. Soc.*, **86**, 639 (1964).
(23) K. B. Wiberg, "Laboratory Technique in Organic Chemistry", McGraw-Hill, New York, N.Y., 1960.
(24) J. A. Riddick and W. B. Bunger, "Organic Solvents", 3rd ed, Wiley-Interscience, New York, N.Y., 1970.
(25) These splittings probably result from coupling with the γ and δ hydrogens. See A. Rassat, "Molecular Spectroscopy", P. Hepple, Ed., Elsevier, New York, N.Y., 1968, pp 145–155.
(26) A. Berson, Z. Hamlet, and W. A. Mueller, *J. Am. Chem. Soc.*, **84**, 297 (1962).
(27) E. W. Averill, "Elements of Statistics", Wiley, New York, N.Y., 1972, pp 159 and 160.

Origin of Alkyl Substituent Effect in the Proton Affinity of Amines, Alcohols, and Ethers

Hideaki Umeyama and Keiji Morokuma*

Contribution from the Department of Chemistry, University of Rochester, Rochester, New York 14627.
Received November 19, 1975

Abstract: An energy decomposition analysis within ab initio SCF–MO theory has been carried out for the proton affinity of a series of amines NH_3, CH_3NH_2, $CH_3CH_2NH_2$, $(CH_3)_2NH$, and $(CH_3)_3N$, and of H_2O, CH_3OH, and CH_3OCH_3. The electrostatic energy and the charge transfer energy are found to provide the dominant stabilizing contribution to protonation. The polarization energy contributes less. On the other hand, the alkyl substituent effect, i.e., the order of proton affinity $NH_3 < CH_3NH_2 < CH_3CH_2NH_2 < (CH_3)_2NH < (CH_3)_3N$ and $H_2O < CH_3OH < CH_3OCH_3$, is found to be controlled predominantly by the polarization energy. Methyl groups make amines more polarizable by an approaching proton.

The alkyl substituent effects on the basicity of amines have been studied extensively both experimentally[1-7] and quantum chemically.[8-12] In aqueous solution the order of basicity of simple aliphatic amines is NH_3 < primary < secondary < tertiary. Recent gas-phase measurements of both proton affinities and basicities of amines by Aue et al.[1] have established the following order: $NH_3 < CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N$. Henderson et al.[2] analyzed the gas phase basicity data of alkylamines and attributed the trend to inductive and polarization stabilization effects of the CH_3 group on protonated amines.

An ab initio SCF calculation by Hehre and Pople[8] with a minimal (STO-3G) basis set showed for methylamines that the calculated order of proton affinity is in agreement with experiment, even though the nitrogen atomic charge *decreases* as the number of the CH_3 groups is increased. The same trend was also found for H_2O, CH_3OH, and CH_3OCH_3. Johansson et al.,[9] employing ab initio calculations, showed that methyl and amino groups bonded to the proton acceptor increase its proton affinity, while hydroxyl and fluoro groups decrease the proton affinity relative to the simple hydrides NH_3, H_2O, and HF. The polarization effect was suggested to be responsible for the CH_3 substituent effect.[8,9] No theoretical evidence, however, has yet been presented on the origin of such an effect.

The energy and charge distribution decomposition analysis of Morokuma and co-workers[13-15] decomposes the intermolecular interaction energy ΔE into the electrostatic E_{ES}, exchange repulsion E_{EX}, polarization (or induction) E_{PL}, and charge transfer (or delocalization) E_{CT} energies and their coupling term E_{MIX}. The method has been a powerful tool for the elucidation of the origin of molecular interactions, as exemplified by recent calculations involving hydrogen-bonded complexes and electron donor-acceptor (EDA) complexes.[13-18] Conceptually the individual components have the following meaning. ES is the classical interaction between the undistorted charge distributions on the monomers A and B, including charge-dipole, dipole-dipole, and higher order terms. PL is the energy change resulting from the distortion of the electron clouds of a monomer A by the presence of the other B and vice versa. EX is a direct consequence of the Pauli principle which dictates that electrons on the two molecules not occupy the same portion in space. CT is the interaction of occupied MO's of A with vacant MO's of B and vice versa, and causes electron delocalization and charge transfer. MIX is the sum of various coupling terms between above-mentioned components, and is derived as a difference between the total interaction energy ΔE and the sum of the above four terms. Different components are important in different systems. For instance, in hydrogen bonding, each of two major attractions, E_{ES} and E_{CT}, is often found to be of comparable magnitude with the exchange repulsion E_{EX} at the equilibrium geometry. In weak EDA complexes, the electrostatic interaction E_{ES} has been found to be the dominant term.

In the present paper, we report the results of an energy decomposition analysis for the proton affinity of amines, alcohols, and ethers. Our purpose is to provide insight into the origin of stabilization upon protonation along with a possible elucidation of the nature of substituent effects on proton affinities. After a brief discussion of methods, we present energy decomposition results for $NH_3 + H^+$ as a function of distance and also compare the energy components of the proton affinity among NH_3 and alkyl substituted amines. Similar analyses are then carried out for the proton affinity of H_2O, CH_3OH, and CH_3OCH_3 to demonstrate that conclusions drawn for amines are also applicable for this series. A discussion of the results and their interpretation, followed by a brief comparison of the alkyl substituent effect on electron donor-acceptor complex formation, concludes the paper.

Methods

We use ab initio LCAO-SCF-MO theory with the split-valence 4-31G basis set with the suggested standard scale factors.[19,20] In the energy decomposition analysis the interaction energy ΔE, which is the energy difference between the complex and the isolated molecules, is decomposed into five components in the following manner:[14]

$$\Delta E = E_{ES} + E_{EX} + E_{PL} + E_{CT} + E_{MIX}$$

For the sake of brevity the interested reader should consult ref 13-18 which provide the logic and procedures developed for the analysis. In the case of proton affinity where one of the interacting molecules is a proton, the following special features are obtained. The exchange repulsion term E_{EX} is zero, because the proton has no electron to exchange. The electrostatic energy E_{ES} consists of the interaction of the proton with the electron distribution and nuclei of the base, and is equal to the electrostatic scalar potential of Bonacconsi et al.[21] The proton-nuclei interaction, which is a part of E_{ES}, is responsible for the short-range repulsion in protonation, whereas in other interactions the exchange term E_{EX} is usually the origin of the short-range repulsion. The polarization term E_{PL} in protonation comes only from the polarization of the base by proton, and charge transfer CT can take place only from the base to the proton.

In the charge distribution decomposition analysis,[17] the total change $\Delta\rho(\mathbf{r})$ in the one-electron density function at a position $\mathbf{r}$ in space is decomposed into four components (electrostatic interaction does not change the charge distribution, so $\rho_{ES} = 0$):

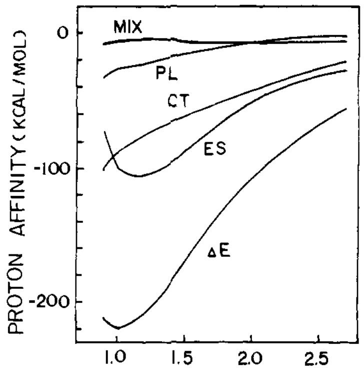

Figure 1. Proton affinity ΔE and its components of NH_3 as functions of $N\cdots H^+$ distance $R_{N\cdots H^+}$.

$$\Delta\rho(\mathbf{r}) = \rho_{EX}(\mathbf{r}) + \rho_{PL}(\mathbf{r}) + \rho_{CT}(\mathbf{r}) + \rho_{MIX}(\mathbf{r})$$

In the case of protonation, this decomposition also has special features, i.e., $\rho_{EX} = 0$, ρ_{PL} is the polarization of electron distribution of the base, and ρ_{CT} is the charge transfer from the base to the proton.

Unless otherwise stated, throughout this paper we assume that the geometry of each base remains unchanged upon protonation. The equilibrium geometry of trimethylamine has C_{3v} symmetry and is taken from experiment:[22] $r(CN) = 1.451$ Å, $r(CH_s) = 1.109$ Å, $r(CH_a) = 1.088$ Å, $\angle CNC = 110.9°$, $\angle NCH_s = 111.7°$, $\angle NCH_a = 110.1°$, $\angle H_aCH_s = 108.1°$, and $\angle H_aCH_a = 108.6°$, where H_s lies on a symmetry plane and two H_a's do not. The conformation of each CH_3 is assumed to be such that upon protonation CH_3 and NR_2H^+ would be in the staggered form about the CN axis. To avoid optimization of geometry for all the compounds studied, the above data are used for dimethylamine, methylamine, and ammonia except for the NH distance, $r(NH) = 1.0124$ Å, which is the experimental value for NH_3.[23] For ethylamine the trimethylamine data were used except for $r(NH) = 1.0124$ Å,[23] $r(CC) = 1.54$ Å,[24] $r(CH)$ in $CH_3 = 1.09$ Å,[25] and CH_3 and CH_2N groups are assumed to be staggered.[25] For dimethyl ether $r(CC) = 1.410$ Å, $r(CH) = 1.096$ Å, $\angle COC = 111.7°$, and $\angle HCH = 109.5°$ are taken from experiment with each CH_3 group in the staggered conformation with respect to a CO axis.[23] For methanol and water, the same parameters are used except for the OH distance, $r(OH) = 0.967$ and 0.956 Å for methanol[24] and water,[23] respectively. This geometry of H_2O is very close to what ($r(OH) = 0.950$ Å and $\angle HOH = 111.3°$) is optimized with this basis set, with an energy difference of less than 0.01 kcal/mol.

In the amines the approach of the proton is assumed to be toward the N atom along the reference C_3 axis of trimethylamine. The approach of the proton to an oxygen atom is assumed to be in the plane defined by the oxygen and the two atoms bonded to it, along the reference C_2 axis of dimethyl ether.

Results

(A) Decomposition Analysis for $NH_3 + H^+ \rightarrow NH_4^+$. Figure 1 shows the calculated proton affinity ΔE and its components for NH_3 as functions of the $N\cdots H^+$ distance $R_{N\cdots H^+}$. As expected, the electrostatic energy which is strongly attractive at longer distances becomes less attractive for $R_{N\cdots H^+} < 1.2$ Å due to the proton-nitrogen nuclear repulsion. In the neighborhood of the calculated minimum, $R_{N\cdots H^+} = 1.02$ Å, it is found that the contribution of the various components, within this basis set, decreases with the following order:

$$\text{ES } (45\%) \sim \text{CT } (40\%) > \text{PL } (13\%)$$

Table I. Proton Affinity, Its Components (kcal/mol), and Other Related Properties of Alkyl Amines

	$N(CH_3)_3$	$NH(CH_3)_2$	$NH_2CH_2CH_3$	NH_2CH_3	NH_3
		Experimental			
	−229.1[a]	−224.9	−221.1	−218.4	−207
	−226.6[b]	−222.4		−216.3	−207
		Calculated			
ΔE	−239.7	−236.1	−232.9	−230.4	−221.9
ES	−84.9	−91.2	−94.6	−96.5	−99.8
PL	−65.4	−53.1	−45.4	−40.2	−27.4
CT	−98.6	−95.1	−93.0	−91.7	−88.3
MIX	9.2	3.4	0.1	−2.1	−6.5
Q_N(calcd)[c]	7.65	7.72	7.80	7.81	7.93
μ_z(calcd)[d] D	1.05	1.38	1.64	1.70	1.99
IP(calcd),[e] kcal/mol	216.0	222.4	230.8	233.0	252.5

[a] Reference 1. [b] Reference 5. [c] The Mulliken gross population on the N atom. [d] Dipole moment component along the z axis, the direction of approach of the proton, and the C_3 axis in NR_3. [e] Ionization potential from the Koopmans theorem.

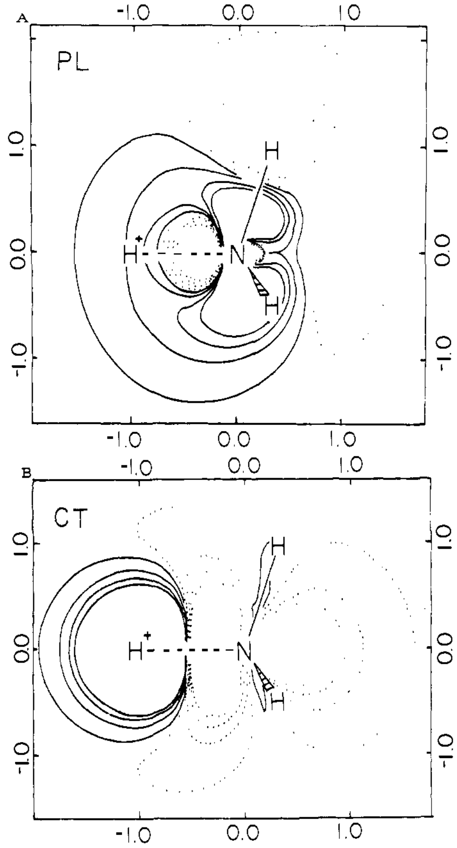

Figure 2. The charge transfer CT and polarization PL components of the electron density change upon protonation of NH_3. Full lines indicate density increases and dotted lines indicate decreases. Values of these lines are successively ±1, ±5, ±9, and ±13 × 10^{-3} bohr^{-3}. The coordinates are in Å relative to the nitrogen atom. The plots are made for the plane including H^+, N, and one of the H's.

The electrostatic and charge transfer energies are the two major contributors to the proton affinity of NH_3. The electrostatic interaction curve qualitatively simulates the shape of the total interaction curve, but accounts for less than half of the affinity. The difference charge density map plotted in Figure 2 reveals the typical behavior of the various components:[17] the charge transfer takes place along the $N \cdots H^+$ axis from NH to H^+, and the polarization exhibits an alternation pattern $H^{+\delta}$–$^{-\delta}N^{+\delta}$ . . .$^{+1-\delta}$H.

(B) Alkyl Substituent Effect on Proton Affinity of Amines. For a series of methyl and ethyl substituted amines the calculated proton affinity and its components are shown in Table I at $R_{N \cdots H^+}$ = 1.02 Å, the calculated minimum mentioned above. Included in the table are the experimental gas-phase proton affinities and other related properties. Though the absolute values are off by 13–15 kcal/mol (a fact which will be discussed later), calculated proton affinities for these compounds satisfy a good linear relationship with gas-phase experimental data. Concerning all the compounds in the table in general, one can summarize *the order of importance of components in the proton affinity as:*

$$\mathrm{ES} \sim \mathrm{CT} > \mathrm{PL}$$

as was found for NH_3.

The order of $|E_{ES}|$:

$$NMe_3 < NMe_2H < NEtH_2 < NMeH_2 < NH_3$$

is found to be completely opposite to the trend of the total proton affinity, $|\Delta E|$:

$$NMe_3 > NMe_2H > NEtH_2 > NMeH_2 > NH_3$$

The nitrogen atom in trimethylamine has less electron density than in ammonia, as is indicated by Q_N in Table I, and, to be consistent with this, the former has a smaller $|E_{ES}|$ than the latter. Table I clearly shows that the observed trend of ΔE is controlled by the polarization E_{PL} and charge transfer E_{CT} energies. Between the two, the polarization is by far the more important, as is indicated by the difference between NMe_3 and NH_3: $\Delta\Delta E = -18$, $\Delta E_{ES} = 15$, $\Delta E_{PL} = -38$, $\Delta E_{CT} = -10$, and ΔE_{MIX} = 16 kcal/mol. Alkyl substitution makes the amines more polarizable by the approach in a proton. We therefore conclude that *the order of importance of components in the alkyl substituent effect of the proton affinity is*

$$\mathrm{PL} > \mathrm{CT} \gg \mathrm{ES}$$

It is the difference in the polarization energy which differentiates the amines in their proton affinity, despite the fact that the polarization is the smallest contributor to the total proton affinity.

Aue et al.[1] found that, if the proton affinity is plotted against ionization potentials for the compounds in Table I, ethylamine deviates from a line formed by the methyl substituted amines and ammonia. We have plotted not only the total stabilization energy, ΔE, but also each of the components. The plots show the following deviations for ethylamine: ΔE = −1.3, ES = +1.1, CT = −0.7, PL = −3.1, and MIX = +1.3 kcal/mol. The data thus allow us to isolate the polarization term as the primary source of the deviation.

(C) Proton Affinities of H_2O, CH_3OH, and CH_3OCH_3. We

Table II. Proton Affinity, Its Components (kcal/mol), and Other Related Properties of Alcohols and Ether

	CH_3OCH_3	CH_3OH	H_2O	H_2O[a]
		Experimental[b]		
	−186	−180	−164	−164
		Calculated		
ΔE	−201.2	−193.6	−181.6	−184.9
ES	−72.9	−76.4	−79.1	−82.1
PL	−54.4	−43.5	−28.6	−25.9
CT	−76.9	−74.5	−70.7	−71.7
MIX	3.1	0.8	−3.2	−5.2
Q_N(calcd)[c]	8.69	8.75	8.80	
μ_z(calcd),[d] D	2.04	2.29	2.49	
IP(calcd),[e] kcal/mol	262.1	276.8	311.4	

[a] Geometry of H_3O^+ is fully optimized with this basis set (ref 26). $R_{O\text{-}H}$ and ∠HOH for H_2O are same as in H_3O^+. [b] Reference 5. [c] The Mulliken gross population on the O atom. [d] Dipole moment component along the z axis, the direction of approach of the proton, and the C_2 axis in OR_2. [e] Ionization potential from the Koopmans theorem.

have found for alkyl amines that the electrostatic and charge transfer energies are the most important contributors to their proton affinity and that the alkyl substituent effect is caused by the difference in the polarization energy. In order to demonstrate that these conclusions apply more generally, we have carried out similar analyses for protonation of H_2O, CH_3OH, and CH_3OCH_3. Figure 3 shows the calculated proton affinity ΔE and its components for H_2O as functions of the $O \cdots H^+$ distance, $R_{O\cdots H^+}$. E_{ES} and E_{CT} are the most important contributors near the calculated equilibrium $R_{O\cdots H^+} = 0.965$ Å. A comparison of Figures 1 and 3 reveals that the ammonia proton affinity is larger than that of water because of larger electrostatic and charge transfer interactions.

Table II shows for the above three compounds the proton affinity, its components, and other related quantities at $R_{O\cdots H^+} = 0.965$ Å. For all the compounds, E_{ES} and E_{CT} are more important contributors to the stabilization than E_{PL} is. The increase of the proton affinity upon methyl substitution, going from H_2O through CH_3OH to CH_3OCH_3, is clearly in accord with the increase of the polarization stabilization $|E_{PL}|$ and the charge transfer stabilization $|E_{CT}|$. This trend is in contrast with the observed decrease in E_{ES}. Notably the increase in $|E_{PL}|$ upon successive methyl substitutions predominantly controls the increase in $|\Delta E|$, as can be seen in the difference of protonation energy terms between $(CH_3)_2O$ and H_2O: $\Delta\Delta E = -20$, $\Delta E_{ES} = +6$, $\Delta E_{PL} = -26$, $\Delta E_{CT} = -6$, $\Delta E_{MIX} = 6$ kcal/mol. Thus our conclusions obtained for alkyl amines are found to be valid for the H_2O-CH_3OH-CH_3OCH_3 as well.

In order to make certain that the conclusions of energy decomposition do not depend upon geometry optimization, an additional calculation was carried out by using the geometry of H_3O^+ ($R_{O\text{-}H} = 0.964$ Å and ∠HOH = 120° with D_{3h} symmetry) which is fully optimized with this basis set[26] and the same $R_{O\text{-}H}$ and ∠HOH for H_2O. The results are in the last column of Table II. The energy decompositions along the two different paths give essentially identical results. Therefore, we may conclude that the lack of use of experimental or theoretically optimized geometry for each isolated molecule, the lack of geometry optimization upon protonation, or the assumption of the direction of proton approach does not seem to affect the conclusions of the present paper, because errors due to these assumptions are of the order of a few kilocalories per mole at most,[9] whereas we will be discussing larger energy differences.

Discussion

We have shown clearly via the energy decomposition analyses (1) the importance of both the electrostatic and charge transfer energies in the total proton affinity and (2) the predominance of the polarization energy in the alkyl substituent effect of proton affinity. The failure of the electrostatic energy to account for the methyl substituent effect warns against the use of the electrostatic potential approximation for predicting a preferred approach of interacting molecules whenever a possibility exists where other terms might make a difference. This is even more important when interactions between neutral molecules are discussed because there the electrostatic potential base on a point charge is a substantial overestimate of the actual electrostatic energy.

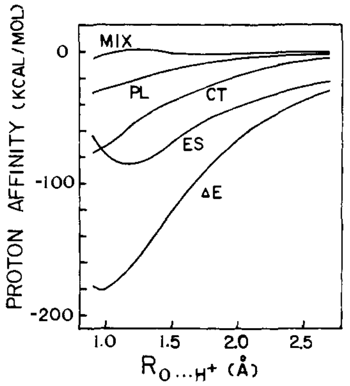

Figure 3. Proton affinity ΔE and its components of H_2O as functions of $O \cdots H^+$ distance $R_{O\cdots H^+}$.

The fact that successive methyl substitutions decrease the electrostatic interaction is consistent with the decrease of the electron density (Mulliken gross atomic population) on the proton-accepting atom (N or O) and with the decrease of the calculated dipole moment along the symmetry axis of NH_3 or H_2O (Tables I and II). However, the polarization is the stronger effect of alkyl substitution. Alkyl substitution makes a base more polarizable by proton, because alkyl groups can supply more electrons to the proton-accepting atom than hydrogen atoms can. In other words, alkyl groups stabilize the cation more than the neutral molecule by a redistribution of the positive charge. In the old organic electronic theory, this result is interpreted as a small $+I$ and a large $-I_d$ effect, though no distinction between the polarization and charge transfer contributions to the I_d effect is made in such a theory.

The alkyl substituent effect in other types of interaction could be quite different from that in protonation. For instance, the stabilization energy for EDA complex formation of BH_3 with methylamines has been calculated to be very insensitive to methyl substitution.[27,28] In this case it has been shown that an increase in the polarization stabilization upon successive methyl substitution is essentially canceled out by an increase in the exchange repulsion between CH_3 groups and BH bonds.[28]

We note that calculated proton affinities are larger than experimental values by 13-18 kcal/mol or 7-11%. This is partly due to the corrections that must be made for changes in the zero point energy upon protonation (estimated to be about 10 kcal/mol for H_2O)[26] and for changes in the correlation energy,[26] and partly due to the tendency of the 4-31 basis set to overestimate the polarity of a molecule, causing both electrostatic and charge transfer energies to be overestimated. Since the energy components involved are larger in magnitude (30-100 kcal/mol) than the error, our conclusions with reference to a series of molecules are expected to be insensitive to the choice of basis set.

While this paper was being refereed, a paper by Pullman and Brochen came to our attention.[29] They found by using the STO-3G basis set that the charge transfer contribution is the predominant term in determining the methyl substituent effect in the proton affinity of amines. This is in contrast to the polarization contribution which is found to be the most important in the present paper with a more flexible 4-31G basis set. Though the minimal set such as STO-3G often gives a correct overall trend in the total interaction energy and its components, it is known to give rise to a large spurious charge transfer energy due to the lack of flexibility.[30] A minimal set can be used successfully for comparison among different states and geometries of a complex.[15,16] The obvious discrepancy between the two calculations suggests that minimal basis sets cannot be used for energy decomposition analysis of the methyl substituent effect. A detailed study of the basis set dependency will be published elsewhere.

Acknowledgment. Authors are grateful to Dr. A. Komornicki for comments on the manuscript. Acknowledgment is made to the National Science Foundation and the Center for Naval Analyses at the University of Rochester for partial support of this research. H. U. is on leave from Kitasato University, Tokyo, Japan.

References and Notes

(1) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **94**, 4726 (1972); M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, *Ibid.*, **93**, 4313 (1971).
(2) W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Am. Chem. Soc.*, **94**, 4724 (1972).
(3) W. G. Henderson, M. Taagepera, D. Holtz, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **94**, 4728 (1972).
(4) J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).
(5) E. M. Arnett, *Acc. Chem. Res.*, **6**, 404 (1973).
(6) J. S. B. Munson, *J. Am. Chem. Soc.*, **87**, 2332 (1965).
(7) J. I. Brauman and L. K. Blair, *J. Am. Chem. Soc.*, **91**, 2126 (1969).
(8) W. J. Hehre and J. A. Pople, *Tetrahedron Lett.*, **34**, 2959 (1970).
(9) A. Johansson, P. A. Kollman, J. F. Liebman, and S. Rothenberg, *J. Am. Chem. Soc.*, **96**, 3750 (1974).
(10) W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 6377 (1971).
(11) L. M. Tel, S. Wolfe, and I. G. Csizmadia, *J. Chem. Phys.*, **59**, 4047 (1973); J. E. Del Bene, *J. Am. Chem. Soc.*, **95**, 5460 (1973).
(12) L. Radom, *Aust. J. Chem.*, **28**, 1 (1975).
(13) K. Morokuma, *J. Chem. Phys.*, **55**, 1236 (1971).
(14) K. Kitaura and K. Morokuma, *Int. J. Quantum Chem.*, **10**, 325 (1976).
(15) K. Morokuma, S. Iwata, and W. A. Lathan, "World of Quantum Chemistry", R. Daudel and B. Pullman, Ed., D. Reidel Publishing Co., Dordrecht, Holland, 1974, p 277.
(16) S. Iwata and K. Morokuma, *J. Am. Chem. Soc.*, **95**, 7563 (1973); **97**, 966 (1975).
(17) S. Yamabe and K. Morokuma, *J. Am. Chem. Soc.*, **97**, 4458 (1975).
(18) W. A. Lathan and K. Morokuma, *J. Am. Chem. Soc.*, **97**, 3615 (1975); W. A. Lathan, G. R. Pack, and K. Morokuma, *ibid.*, **97**, 6624 (1975).
(19) A version of the GAUSSIAN 70 program (W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236, Quantum Chemistry Program Exchange, Indiana University, 1973) was used.
(20) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).
(21) R. Bonacconsi, C. Petrongolo, E. Scrocco, and J. Tomasi, *Theor. Chim. Acta*, **20**, 331 (1971).
(22) J. E. Wollrab and V. W. Laurie, *J. Chem. Phys.*, **51**, 1580 (1969).
(23) G. Herzberg, "Electronic Spectra of Polyatomic Molecules", Van Nostrand, New York, N.Y., 1966.
(24) L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions", The Chemical Society, London, 1958.
(25) L. Radom, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **94**, 2371 (1972).
(26) (a) M. D. Newton and S. Ehrenson, *J. Am. Chem. Soc.*, **93**, 4971 (1971). (b) The D_{3h} symmetry of this optimized geometry disagrees with the C_{3v} symmetry obtained with the STO-3G basis set and with larger basis sets including polarization functions. See P. A. Kollman and C. F. Bender, *Chem. Phys. Lett.*, **21**, 271 (1973).
(27) R. R. Lucchese and H. F. Schaefer, *J. Am. Chem. Soc.*, **97**, 7205 (1975).
(28) H. Umeyama and K. Morokuma, *J. Am. Chem. Soc.*, in press.
(29) A. Pullman and P. Brochen, *Chem. Phys. Lett.*, **34**, 7 (1975).
(30) A. Johansson, P. A. Kollman, and S. Rothenberg, *Theor. Chim. Acta*, **26**, 167 (1973).