

Molecular orbital approach to substituent effects in amine-CO₂ interactions

A. K. Chakraborty, K. B. Bischoff, G. Astarita, and J. R. Damewood

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tivation due to accumulation of P on the catalyst. For example, P from decomposed PH_3 diffuses in and out of Pt(111) above 300 K and is very difficult to remove by oxidation, especially at high coverages.⁷ The key to these oxidative processes is the removal of P by PO_x formation and desorption *before* atomic P forms.

In a recent study by Smentkowski et al.¹⁰ catalytic decomposition of DMMP was observed on Mo(110) above 898 K in a 2:1 O_2 -DMMP molecular beam without accumulation of P or C on the surface. The Mo(110) surface formed a stable oxide layer that catalyzed DMMP decomposition but prevented accumulation and bulk diffusion of P. Our results for DMMP decomposition on $\alpha\text{-Fe}_2\text{O}_3$ ⁹ show that it is active for DMMP decomposition but deactivates as phosphate forms.

Unlike Mo, Pt does not readily form a stable bulk oxide. Thus, removal of P can occur only when gas-phase oxygen is present to drive the formation of PO_x . In the absence of O_2 , these PO_x species are stable only below 500 K. The dominant PO_x species observed in this study is PO. In the absence of O, it decomposes with an activation barrier of 35.9 kcal/mol, about 23 kcal/mol lower than its desorption barrier from Pt.¹¹ Thus removal of PO in a catalytic process of Pt will require high temperature to overcome the desorption barrier and high pressures of O_2 to maintain P-O bonds. Our results suggest that, in the absence of O_2 , DMMP decomposition on Pt(111) above 600 K will lead to phosphorus

accumulation and catalytic deactivation.

5. Summary

(1) At 100 K on Pt(111), DMMP adsorbs molecularly through the oxygen lone pairs of the -P=O group. This structure is stable to 300 K.

(2) TPD after a multilayer exposure of DMMP at 100 K gives multilayer desorption (220 K) and 0.09 ML of DMMP decomposition. The products are 0.27 ML of CO (437, 505, 586 K), 0.79 ML of H_2 (340, 448, 504 K), surface P, and a small amount of surface C.

(3) TPSSIMS results indicate that, between 300 and 500 K, DMMP decomposes in steps to PO_x . Near 300 K PO-C bonds cleave, with some P-OC bond cleavage at high-DMMP coverages. At higher temperatures, P-C bonds cleave, leaving at least two PO_x species on the surface.

(4) The dominant PO_x species is PO, which is characterized by a 1255-cm^{-1} $\nu(\text{P=O})$ loss in HREELS and an intense PO^+ SSIMS signal. It is stable to at least 500 K.

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Molecular Orbital Approach to Substituent Effects in Amine-CO₂ Interactions

A. K. Chakraborty, K. B. Bischoff,* G. Astarita, and J. R. Damewood, Jr.

Contribution from the Departments of Chemical Engineering and Chemistry and The Center for Catalytic Science and Technology, University of Delaware, Newark, Delaware 19716.

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Abstract: The effects of substituents at the α -carbon atom on the donor properties of primary amines and amino alcohols have been studied. Such substituted amino species have important applications in industrially relevant gas-separation processes. Qualitative molecular orbital arguments, along with detailed calculations at the MNDO level of theory, show that upon methyl substitution at the α -carbon atom the interactions of the methyl group orbitals with the nitrogen lone-pair orbital lead to subtle but significant changes in the donor properties of the amino species. Infrared spectroscopic data supporting the calculations are also described. The implications of changes in the donor properties of the amino species on its reactions with acidic gases, such as CO_2 , have been considered. These studies serve to elucidate previous phenomenological results regarding the macroscopic kinetic and equilibrium behavior of substituted amino species in CO_2 absorption applications.

1. Introduction

The removal of acidic gases such as CO_2 , H_2S , and SO_2 from gas streams is widespread in the chemical processing industries.¹ This separation is commonly accomplished by absorbing the acidic gas into a chemically reactive liquid. Carrying out such processes efficiently is of crucial importance from several viewpoints, and a detailed understanding of these reacting, two-phase systems is therefore necessary.

The absorption of an acidic gas into a chemically reacting liquid is a mass-transfer process accompanied by a Lewis acid-base reaction. There are therefore two aspects of the problem that need consideration. On one hand, the facilitated-transport problem of mass transfer with chemical reaction needs to be understood within the framework of macroscopic phenomenological models. On the other hand, a comprehensive understanding of the system is possible only if the fundamental molecular chemistry and its macroscopic manifestations are clearly elucidated. Such an un-

derstanding is crucial if one is to attain the goal of being able to "tailor-make" molecules that could carry out chemical absorption based separations in a very specific manner.

While the literature (particularly in engineering science) is rich with work on the facilitated-transport problem,²⁻⁵ relatively little emphasis has been placed on a fundamental understanding of the molecular chemistry of these systems. In this paper, the reactions of a model acidic gas (CO_2) with various amines and amino alcohols are investigated. In particular, the effects of substituents on the Lewis acid-base interaction is investigated within the theoretical framework of perturbation molecular orbital theory⁶

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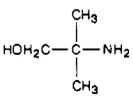
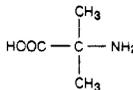
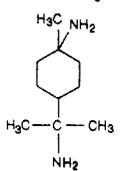
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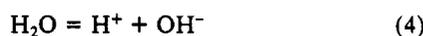
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Table I. Examples of the Primary Amines Introduced by Sartori and Savage¹² for Acid Gas-Separation Applications

structure	name
	2-amino-2-methyl-1-propanol (AMP)
	2-amino-2-methylpropionic acid
	1,8- <i>p</i> -methanediimine

and detailed molecular orbital calculations using the MNDO method.⁷ Experiments that support the results obtained by molecular orbital theory are also described. The understanding of the effects of substituents on the donor properties of amino species resulting from these studies is then related to previous macroscopic kinetic and equilibrium observations.⁸⁻¹²

The reaction of a Lewis acid such as CO₂ with a Lewis base such as an amine or an amino alcohol (wherein the donor atom is nitrogen) represents a classical donor-acceptor interaction. The donor orbital in this case is nonbonding, while the acceptor orbital is antibonding. On the basis of their own macroscopic kinetic and equilibrium data, data in the literature, and the work of Astarita and co-workers¹³ and Danckwerts,¹⁴ Chakraborty et al.¹¹ have postulated the reaction pathway (eq 1-4) for the reactions of CO₂



with primary amines in aqueous solutions. In the reaction pathway shown above, R represents the substituent attached to the amino nitrogen. This reaction pathway involves an amine-CO₂ interaction to form a 1:1 acid-base adduct, which may then undergo two different transformations. If the N-C bond in the adduct is strong, there will be a concomitant depopulation of the N-H bonding (Π_{NH_2}) orbitals. If sufficiently strong, the depopulation of these orbitals may lead to the loss of a proton and the formation of the carbamate species. In aqueous solution, the acid-base adduct may also react with OH⁻ (or water) and a base displacement reaction may take place resulting in the formation of the bicarbonate species. In addition, amine protonation and water dissociation occur in solution as represented by steps 3 and 4. If the step leading to the formation of the carbamate species is neglected, the proposed pathway corresponds to a classical homogeneous catalysis mechanism for the formation of the bicarbonate species.

In 1983 Sartori and Savage¹² presented a significant advance in acid gas-separation technology by introducing the use of a new class of amines, which proved to have higher rates and equilibrium

capacities of absorption than the amino species used previously. Primary amines wherein the amino nitrogen is attached to a tertiary carbon atom are members of this class. Some examples are listed in Table I. Many of the primary amines introduced by Sartori and Savage¹² for acid gas-separation applications (and certainly those listed in Table I) have methyl substituents attached to the α -carbon atom. Sartori and Savage attributed the favorable behavior of these amines to the relative instability of the carbamate species. Chakraborty et al.¹⁰ have reported ¹³C NMR data that show that the carbamate of 2-amino-2-methyl-1-propanol is formed to a much lesser extent than the carbamate of the corresponding unsubstituted amine (ethanolamine). Sartori and Savage¹² ascribed the instability of the carbamate species to steric constraints imposed by the alkyl groups attached to the amino group. However, both Sartori and Savage¹² and Chakraborty and co-workers^{10,11} provide only intuitive explanations for the cause of this lower carbamate stability and their other kinetic and equilibrium observations.

In this work, a further examination of the effects of substituents on the carbon atom adjacent to the amino group is described. In particular, the manifestations of changes in the electronic and structural characteristics of these amines upon such substitutions in the acid-base reactions under consideration are investigated in detail.

2. Effect of Substituents

It has been recognized for a long time that acids and bases cannot be completely characterized by a single parameter such as the pK_a. One successful attempt at rationalizing the vast body of experimental data available in the literature is the hard and soft acid-base (HSAB) principle developed by Pearson and co-workers.¹⁵⁻¹⁸ The HSAB principle characterizes acids and bases as being either hard or soft by using properties such as charge, size, extent of electron delocalization and distortability, etc. Pearson and co-workers rationalized the available data by formulating the hypothesis that like species prefer to interact with each other. This generalization applies to both the equilibrium and the rates of the reactions under consideration.

These empirical generalizations were put on a more quantitative basis by Klopman¹⁹ within the framework of perturbation molecular orbital theory.²⁰ Klopman²¹ developed the following expression for the energy of interaction of two species R and S, interacting at the sites r and s (eq 5) where q_i is the charge at

$$\Delta E = -\frac{q_r q_s \Gamma}{\epsilon} + \sum \sum 2 \frac{(c_r^m)^2 (c_s^n)^2 \beta^2}{E_m - E_n} + \Delta_{\text{solvn}} \quad (5)$$

the i th interacting site; c_j^i is the coefficient of the atomic orbital, i , in the molecular orbital, j ; β is the resonance integral; E_i corresponds to the energy of the molecular orbital, i ; ϵ is the dielectric constant of the medium; Γ is the coulomb repulsion term; Δ_{solvn} is the energy associated with desolvation; and ΔE represents the energy associated with the partial formation of a bond (in a given medium) between R and S.

Since eq 5 was developed within the framework of PMO theory, it is rigorously applicable to the early part of the reaction coordinate. The first term (the "charge-control" term) represents the coulombic interaction between the donor and the acceptor sites. The second term (the "orbital-control" term) represents the interactions of the molecular orbitals of the interacting species. If one considers only the interactions of the frontier orbitals then E_m and E_n correspond to the energies of the highest occupied molecular orbital (HOMO) of the donor species and the lowest unoccupied molecular orbital (LUMO) of the acceptor species, respectively. Hence, for the interaction of a given acid (i.e. with

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a fixed value of E_n , as long as $E_m < E_n$, the higher the energy of the HOMO, the greater the importance of the orbital-control term. Similarly, the lower the charge at the donor site, the less important the charge-control term. These and other arguments^{18,22} show that a donor species with a high-lying, more delocalized (or diffuse) HOMO with a low charge at the donor site corresponds to a soft base in the Pearson sense. Although molecular orbital arguments will be used frequently in this paper, for ease of reference, a donor with a higher and more delocalized HOMO and a lower charge at the donor site will therefore be referred to as a "softer" base.

A series of papers authored by Parr and co-workers²³⁻²⁵ pioneered the use of density functional theory²⁶ in chemistry. Within the framework of density functional theory, Pearson and Parr²⁷⁻²⁹ have shown that a species may be characterized by its electronegativity (or potential), χ (or μ), and its hardness, η . Within the framework of density functional theory these quantities are defined in finite difference form as shown in eq 6 and 7

$$\chi = -\mu = (I + A)/2 \quad (6)$$

$$\eta = (I - A)/2 \quad (7)$$

wherein I is the ionization potential and A is the electron affinity. Pearson and Parr have shown that the lower the value of η , the softer the species. Since the value of η reflects the HOMO-LUMO energy separation in a given species, this implies that the smaller this energy separation, the softer the species. Pearson and Parr's work within the framework of density functional theory also serves to place the HSAB concept on a more fundamental and quantitative basis.

As mentioned earlier, many of the amino species that have recently been found to be useful in acid gas-separation applications have methyl substituents attached to the carbon atom adjacent to the amino group. One of the goals of this paper is to examine at a molecular level the effects of substituents on the behavior of amino species in industrially relevant gas-absorption applications. Therefore, it is appropriate to first examine the effects of methyl substitution at the α -carbon atom on the electronic environment at the donor site, nitrogen. Changes in the electronic environment at the donor site will determine the donor properties of the amino species and hence its interactions with Lewis acids. Some noteworthy experimental studies on the effects of substituents on the basicities of amines (particularly with regard to proton affinities) have been carried out by Munson,³⁰ Brauman et al.,³¹ Aue and co-workers,^{32,33} Wooden and Beauchamp,³⁴ and Arnett and co-workers.³⁵

In order to examine the effects of methyl substitution at the α carbon atom attention should be focussed on the possible interactions of the nonbonding nitrogen lone-pair orbital with the orbitals of methyl group. Methyl groups possess two pairs of degenerate orbitals of Π -type symmetry,³⁶ that are symmetry compatible with the lone-pair orbital. One pair is occupied (Π_{Me}),

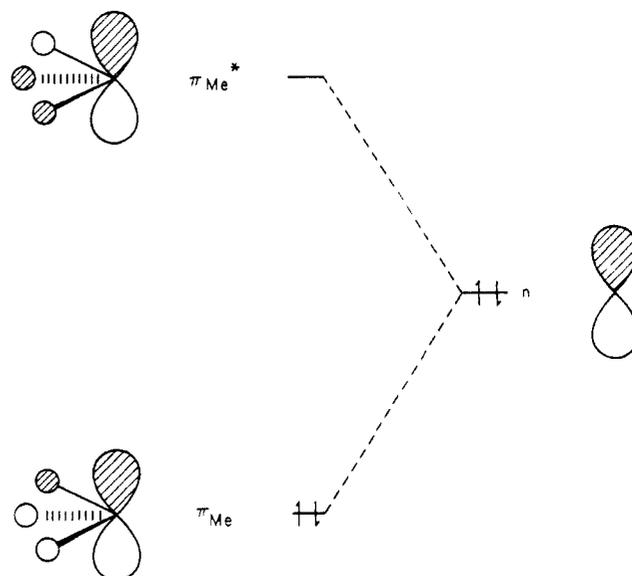


Figure 1. Energy diagram depicting the interactions of the nonbonding nitrogen lone-pair orbital with the Π_{Me} and Π_{Me}^* orbitals of the methyl substituents. For simplicity the interaction with only one of each pair of methyl group orbitals exhibiting Π -type symmetry is shown.

and the other is unoccupied (Π_{Me}^*). One possible interaction is that of the lone-pair orbital with the symmetry compatible Π_{Me} -filled orbitals of the methyl groups. Pellerute and Brauman³⁷ have considered the possibility of such interactions while investigating the effects of methyl substitution on the chemistry of carbon acids. Pross and Radom³⁸ and DeFrees et al.³⁹ have also considered the possibility of such interactions while examining the effects of methyl substitution at anionic centers. This interaction leads to an overall destabilization and thus would result in a higher energy, more delocalized HOMO. There would, however, be no significant redistribution of electron density as a result of this interaction. The result of this interaction is consistent with the traditional view that the methyl group acts as an electron donor.^{18,38} It is worth noting, however, that, being a four-electron interaction, it is inherently weak; furthermore, since in the case under consideration here the methyl substituents are one carbon atom removed, the effects of this interaction should be further attenuated.

Another potentially important interaction is that between the nitrogen lone-pair orbital and the antibonding Π_{Me}^* orbitals of the methyl substituents. Such a Π back-bonding is a two-electron interaction and hence should be an inherently stronger interaction than the four-electron interaction considered above. However, the lone-pair orbital lies closer in energy to the Π_{Me} orbitals than to the Π_{Me}^* orbitals, and this factor favors the interaction with the filled Π_{Me} orbitals. The relative strength of the interactions of the lone-pair orbital with the Π_{Me} and Π_{Me}^* orbitals is determined by both these factors. Hehre and Pople⁴⁰ have carried out ab initio calculations for amines with methyl substituents at the heteroatom, nitrogen, and have observed a back-donation from the nitrogen to the methyl groups. Fujimoto et al.⁴¹ have also carried out calculations for amines with methyl substituents at the heteroatom. DeFrees et al.³⁹ and Pross and Radom³⁸ have considered the interactions of the Π -type methyl orbitals with those of the parent molecule while discussing the effects of methyl substitution at anionic centers and on the chemistry of carbon acids, respectively. The interaction of the nitrogen lone-pair orbital

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with the Π_{Me}^* antibonding orbitals of the methyl substituents has several important implications. This interaction has a net stabilizing effect, but more importantly, it leads to the redistribution of electron density. Hehre and Pople⁴⁰ have observed that upon methyl substitution at the heteroatom this interaction leads to a lower charge at the donor site. This Π back-donation leads to a higher electron density on the two methyl hydrogens that are trans to the lone-pair orbital. In fact, for methyl substitution at the nitrogen donor site, Hehre and Pople⁴⁰ have found that the two methyl hydrogens out of plane with the lone pair become more negatively charged. We predict a similar, although attenuated effect upon methyl substitution at the α carbon atom. Due to the strength of this interaction the three methyl hydrogens are expected to be observably nonequivalent.

Interactions of the lone-pair orbital with the Π -type filled and unfilled orbitals of the methyl substituents at the α carbon atom are hence predicted to change the electronic environment around the nitrogen donor site relative to the unsubstituted case. An energy diagram representing these interactions is shown in Figure 1. In summary, the interaction of the lone-pair orbital with the Π_{Me}^* unfilled methyl group orbitals (Π back-donation) should lead to a lower charge at the donor site. As a result of this Π back-donation the methyl hydrogens trans to the lone-pair orbital should have a higher electron density. The interaction of the lone-pair orbital with the Π -type filled methyl orbitals should result in a slightly higher and more delocalized HOMO for the amino species. However, this interaction will not lead to any significant redistribution of electron density.

Translated into hard and soft acid-base theory, the effects of methyl substitution at the α carbon atom outlined above imply that the amino species becomes a softer base upon such substitution. In terms of PMO theory, methyl substitution at the α carbon atom is predicted to enhance the relative importance of the orbital-control term and reduce the importance of the charge-control term for the interactions of the donor with a given Lewis acid.

The arguments made so far predict that the interactions of the nitrogen lone-pair orbital with the methyl group orbitals exhibiting Π -type symmetry alter the electronic environment at the donor site. The electronic properties of the molecule are altered such that the donor has a higher and more delocalized HOMO with a lower charge at the donor site. The macroscopic implications of the donor (RNH_2) being a softer base in the reaction pathway represented by steps 1-4 are now discussed.

3. Implications for the Reaction Pathway

CO_2 is a relatively hard acid; i.e., the Π_u^* orbital that forms its LUMO lies relatively high in energy. Therefore, the softer the base RNH_2 , the weaker the N-C bond in the adduct formed in the first step of the proposed reaction pathway. Consequently, the depopulation of the Π_{NH_2} bonding orbitals should also be less. If this depopulation is small enough, the step leading to the formation of the carbamate species will be suppressed. On the other hand, since OH^- is hard base, the softer the base, RNH_2 , the more step 2 is driven to the right. This enhances the formation of the bicarbonate species. Thus, the predicted interactions of the nitrogen lone-pair orbital with the methyl group orbitals that lead to the base becoming softer upon methyl substitution at the α carbon atom, in turn result in suppressing the formation of the carbamate species and enhancing the formation of the bicarbonate species. This prediction is based only on the changes in the electronic environment at the donor site upon methyl substitution at the α carbon atom; the possible changes in solvation energies upon such substitution, however, are not incorporated. The macroscopic kinetic and equilibrium observations of Chakraborty et al.^{10,11} and Sartori and Savage¹² show that upon methyl substitution at the α -carbon atom the formation of the carbamate species is suppressed, and for all practical purposes the bicarbonate species is the only product of the reaction (i.e. a "chemical sink" for CO_2). The effects of methyl substitution on the intrinsic donor properties of the amine and its consequent implications on the various steps of the reaction pathway are therefore consistent with,

Table II. Some MNDO Results for Three Pairs of Amines

molecules compared	charge on nitrogen	HOMO energy
AMP compared to MEA	3.4% lower	1.6 kcal/mol higher
TBA compared to ETA	4% lower	1.2 kcal/mol higher
TAM compared to PAM	4% lower	0.4 kcal/mol higher

Table III. Comparison of Energies of Π_{NH_2} Orbitals in Methyl-Substituted and Unsubstituted Amino Species

molecules compared	energy of Π_{NH_2} orbital
AMP compared to MEA	11.46 kcal/mol higher
TBA compared to ETA	9.96 kcal/mol higher
TAM compared to PAM	10.81 kcal/mol higher

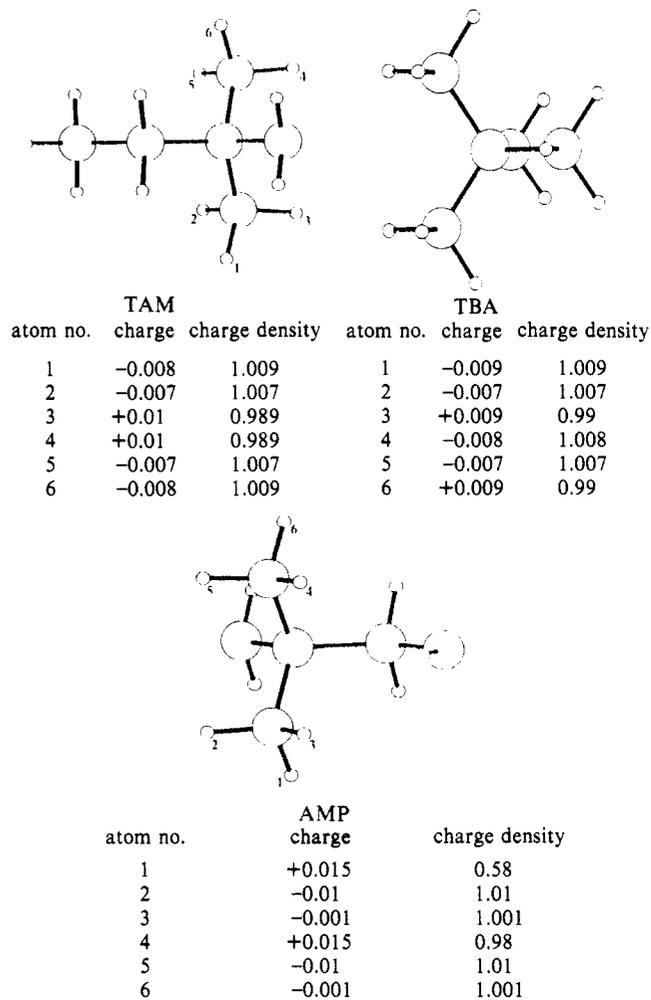


Figure 2. Calculated partial charges on the various atoms of amines and amino alcohols. Hydrogens on methyl substituents at the α -carbon atom are not equivalent.

and serve to explain, the macroscopic kinetic and equilibrium observations.

In order to substantiate the qualitative arguments made so far and to place the discussion on a more quantitative basis, detailed molecular orbital calculations have been performed. The results of these molecular orbital calculations using the MNDO method^{7,42,43} and infrared spectroscopic experiments will now be discussed.

4. Results and Discussion of MNDO Calculations

The MNDO computational procedure is a semiempirical method first proposed by Dewar and co-workers.⁷ The approxima-

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Table IV. Comparison of Measured³² and Calculated (This Work) Ionization Potentials

amine molecule	ionization potential, kcal/mol		deviation	
	measd	calcd	kcal/mol	%
ethylamine	218.4	242.5	24.1	~11
<i>n</i> -propylamine	216.8	241.3	24.5	~11
<i>tert</i> -butylamine	213.4	241.3	27.9	~13
<i>tert</i> -amylamine	212.2	240.9	28.7	~13

Table V. MNDO Results Comparing HOCH₂(OCH₃)₂NH₂ and CF₃CH₂NH₂ to Ethanolamine and Ethylamine, Respectively

molecules compared	HOMO energy	charge on nitrogen
CF ₃ CH ₂ NH ₂ compared to ETA	20 kcal/mol lower	5% higher
HOH ₂ C(OCH ₃) ₂ CNH ₂ compared to MEA	3 kcal/mol lower	25% higher

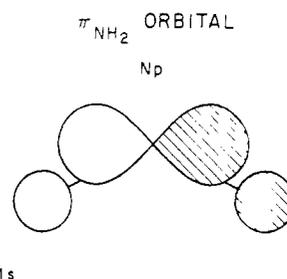
tions embodied in the MNDO method are those inherent to the NDDO formalism.^{42,43} The reported computational results are for completely optimized structures.

Tables II and III and Figure 2 show some of the relevant results of the MNDO calculations performed for three pairs of amines and aminoalcohols. The common structural feature relating these three pairs is that *tert*-butylamine (TBA), *tert*-amylamine (TAM), and 2-amino-2-methyl-1-propanol (AMP) are methyl substituted at the α -carbon atom relative to ethylamine (ETA), *n*-propylamine (PAM), and ethanolamine (MEA), respectively.

The results shown in Table II clearly indicate that upon methyl substitution at the α -carbon atom the charge at the nitrogen donor site is lower. The HOMO of the amino species is less localized and resides higher in energy for the methyl-substituted molecules. It is worth noting that, in an attempt to correlate the proton affinities of nitrogen and oxygen bases to their 1s binding energies and ionization potentials, Catalan et al.⁴⁴ have reported the energies of the HOMOs of *tert*-butylamine and ethylamine. Catalan and co-workers' STO-3G minimal basis set calculations also show that the HOMO of *tert*-butylamine resides higher in energy than that of ethylamine. Figure 2 depicts the calculated charges on the atoms in 2-amino-2-methyl-1-propanol, *tert*-amylamine, and *tert*-butylamine. These results show that the methyl hydrogens that are trans to the lone-pair orbital have negative partial charges. This provides evidence of Π back-bonding; i.e., the interaction of the lone-pair orbital with the antibonding Π_{Me}^* orbitals of the methyl substituents. Thus, the Π back-donation observed by Hehre and Pople⁴⁰ upon methyl substitution at the nitrogen donor site is also important upon methyl substitution one carbon atom removed. The partial charges on the α -carbon atom for methyl-substituted molecules are calculated to be negative as compared to the positive charges in the unsubstituted molecules. This is perhaps due to the fact that in addition to the lone-pair orbital, the α -carbon orbitals also interact with the filled Π orbitals of the methyl substituents. The possibility of such interactions in methyl-substituted carbon acids has been considered by Pross and Radom.³⁸

Aue and co-workers³² have reported the gas-phase ionization potentials for four of the amino species investigated in this work (ETA, TBA, PAM, and TAM). In Table IV the ionization potentials measured by Aue and co-workers³² using photoelectron spectroscopy are compared with the ionization potentials calculated in this work using the MNDO method and Koopmans' theorem.⁴² Table IV shows that the trend in the variation of the ionization potential with structure is reproduced well. The absolute values of the ionization potentials, however, are not reproduced exactly by the calculations (average deviation ~12%). Furthermore, the results shown in Table IV show that the lowering of the ionization potential (or raising of the HOMO) upon methyl substitution at the α -carbon atom is underestimated by the MNDO calculations.

(44) Catalan, J.; Mo, O.; Perez, P.; Yanez, M. *J. Chem. Soc., Perkin Trans. 2* 1982, 1415.

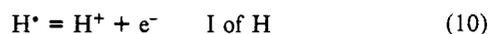
**Figure 3.** Simplest possible representation of the Π_{NH_2} bonding orbital. For methyl-substituted systems this orbital is destabilized by about 10 kcal/mol.

This is perhaps to be expected since the MNDO method is known to underestimate hyperconjugative effects.⁴³ The MNDO predictions of the effects of orbital interactions considered in this paper are thus lower limits. Aue and co-workers have performed CNDO/2 calculations on unoptimized structures in order to calculate the proton affinities of amino species. Their calculations do not reproduce the experimental proton affinities well (50% too high). Aue et al.³² have rationalized their experimental data via polarizability stabilization arguments.

The hardness parameter, η , introduced by Parr and Pearson²⁷⁻²⁹ can be calculated from the MNDO results by using Koopmans' theorem; i.e. by approximating the ionization potential as $-E_{HOMO}$ and the electron affinity as $-E_{LUMO}$. The parameter, η , reflects the HOMO-LUMO energy separation. The MNDO calculations carried out in this work show that, on an average, the HOMO-LUMO energy gap is reduced by about 4.5 kcal/mol upon methyl substitution at the α -carbon atom. This lowering of the HOMO-LUMO energy gap provides further evidence that the base becomes softer upon methyl substitution at the α -carbon atom.

A measure of the strength of the N-H bonds in a primary amino species is the energy of the Π_{NH_2} bonding orbitals. In its simplest representation the Π_{NH_2} bonding orbital is obtained by a constructive combination of the hydrogen 1s orbitals with a nitrogen p orbital. This simple representation of the Π_{NH_2} bonding orbital is depicted in Figure 3. Of course, in any given molecular environment there are contributions from other atomic orbitals to this simple representation. The results of the MNDO calculations reported in Table III show that the Π_{NH_2} bonding orbital is destabilized by about 10 kcal/mol upon methyl substitution at the α -carbon atom. This relative destabilization may be explained as follows. For the unsubstituted molecules, there is a σ contribution to the Π_{NH_2} bonding orbital from the hydrogens on the α -carbon atom. However, for the methyl-substituted molecules there is a σ contribution from the p orbitals of the carbons of the methyl substituents. The overlap with the p orbitals in this σ interaction is smaller, and hence the Π_{NH_2} orbital is destabilized upon methyl substitution.

On the basis of ion cyclotron resonance experiments Brauman and Blair⁴⁵ have reported that amines with large alkyl groups are more acidic. They⁴⁵ propose the steps in eq 8-10 for the loss of



a proton where DH_0 is the dissociation energy of the species, AH . Brauman and Blair⁴⁵ have ascribed the relative ease of proton abstraction from amines that have large alkyl substituents to polarizability stabilization of the charge on the anion by large alkyl groups. It is to be noted that charge stabilization changes the electron affinity (corresponding to step 9). The results reported in Table III show that the dissociation energy (corresponding to step 8) is also lowered upon methyl substitution at the α -carbon atom. This change in the dissociation energy has been observed

(45) Brauman, J. I.; Blair, L. K. *J. Am. Chem. Soc.* 1971, 93, 3911.

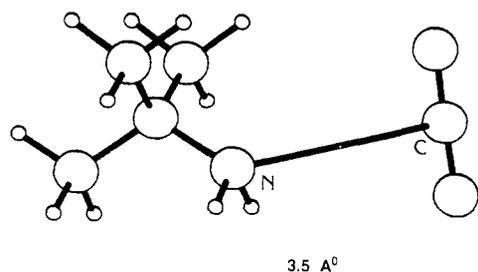


Figure 4. Calculations along the reaction coordinate for the CO_2 -*tert*-butylamine interaction. The C-N distance (reaction coordinate) is 3.5 Å.

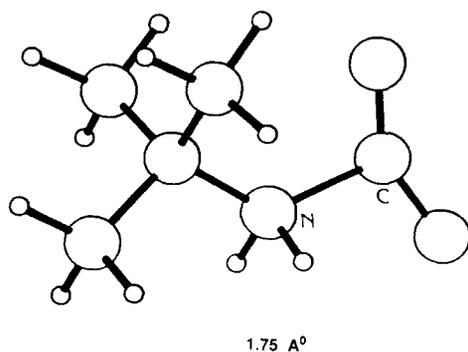


Figure 5. Calculations along the reaction coordinate for the CO_2 -*tert*-butylamine interaction. The C-N distance (reaction coordinate) is 1.75 Å.

experimentally⁴⁵ for the series NH_3 , CH_3NH_2 , and $(\text{CH}_3)_2\text{NH}$. The results reported here show that methyl substituents at the α -carbon atom also weaken the N-H bond within a series of primary amino compounds.

In an effort to explore the reaction coordinate for CO_2 -amine interactions, MNDO calculations were performed at various amine- CO_2 separations for ethylamine and *tert*-butylamine. The distance between the carbon atom in CO_2 and the nitrogen donor site of the amino species was chosen as the reaction coordinate. Figures 4 and 5 show the results of these calculations driving along the reaction coordinate for the *tert*-butylamine- CO_2 interaction. Figure 4 shows the optimized configuration when the C-N reaction coordinate distance is 3.5 Å. At this point the CO_2 molecule is still linear, and no significant interaction appears to have occurred. Figure 5 shows the optimized configuration at another point along the reaction coordinate. This figure clearly shows how the CO_2 molecule folds toward a bent structure. The important features to notice in Figure 5 are the folding of the CO_2 molecule as it approaches the amino species and that there seem to be no obvious steric constraints imposed by the methyl groups on the α -carbon atom. In an effort to quantify possible steric effects, the energy barrier to the rotation of the CO_2 molecule about the C-N axis in an approximate transition state was calculated for both ethylamine and *tert*-butylamine. This rotation was found to be almost equally facile for both amines. This allows one to conclude that, with respect to this rotational mode, there appears to be little change in steric constraints due to the methyl substituents at the α carbon atom.

The observed instability of the carbamate species has been explained by the fact that since the base becomes softer upon methyl substitution at the α -carbon atom, the N-C bond in the adduct is not strong enough to lead to the loss of a proton. MNDO calculations show this change in the electronic environment at the donor site upon methyl substitution at the α -carbon atom. The relative instability of the carbamate species could be further investigated computationally by calculating the overall stabilization of step 1 in the reaction pathway. To calculate this overall heat of reaction, step 1 may be represented as eq 11. The calculated



differences in the heats of reaction ($-\Delta H$) for the overall reaction

Table VI. Overall Stabilization Energies and C-N Orbital Energies in Ethylcarbamic Acid and *tert*-Butylcarbamic Acid

amine interacting with CO_2	$-\Delta H$, kcal/mol	C-N orbital energy, eV
ETA	8.6	-20.36
TBA	5.1	-19.46 (20.7 kcal/mol higher)

(eq 11) for different substituents, R, serve as a rough indicator of the relative stabilities of the carbamate species. Furthermore, the energy of the C-N bonding orbital in the carbamic acid would be indicative of the strength of the interaction. Calculations performed for ethylamine and *tert*-butylamine show that eq 11 leading to the formation of ethylcarbamic acid is more favorable than that leading to the formation of *tert*-butylcarbamic acid (Table VI). This provides further evidence for the intrinsic instability of the carbamate species upon methyl substitution at the α carbon atom. The predominantly σ -type C-N bonding orbital is also found to reside about 20 kcal/mol higher in energy for *tert*-butylcarbamic acid compared to ethylcarbamic acid, thus offering additional evidence that the higher and more delocalized HOMO and the lower charge at the donor site leads to weaker amine- CO_2 interactions.

In an effort to further quantify any steric effects upon methyl substitution at the α carbon atom, the energy barriers for the rotation of the carboxylic group about the C-N bond in ethylcarbamic acid and *tert*-butylcarbamic acid have been calculated. These calculations were performed by allowing the rest of the molecule to fully relax in the various fixed rotational configurations. At the MNDO level of theory, the difference in the energy barrier for rotation of the $-\text{COOH}$ group between ethylcarbamic acid and *tert*-butylcarbamic acid is found to be 0.7 kcal/mol. This small difference suggests again that, with respect to this rotational mode, steric effects are not significantly altered upon methyl substitution at the α -carbon atom. Further detailed studies need to be conducted to preclude the presence or absence of steric effects with respect to other modes. Furthermore, methyl substituents at the donor site, or bulkier substituents at the α -carbon atom may lead to steric limitations.

It is interesting to investigate the effects of methoxy or trifluoromethyl substitution at the α -carbon atom on the chemistry of primary amino donors. In these cases qualitative arguments suggest that inductive effects should result in the base becoming harder with a higher charge at the donor site. However, the possibility of interactions with the methyl moieties of the methoxy substituents cannot be ruled out a priori. Table V shows the results of MNDO calculations performed for the doubly methoxy-substituted amino alcohol and 2,2,2-trifluoroethylamine. (The methoxy-substituted amino alcohol has not been reported in the literature. However, the purpose of this calculation is to examine the effects of polar substituents of this type on the donor properties and its concomitant implications for acid gas-separation processes.) These results show that the base does become harder upon such substitutions. This observation suggests that perhaps this is the kind of amine or amino alcohol that should be used to separate an acidic gas such as SO_2 that has a soft acid site. For the methoxy-substituted molecule, no evidence of Π back-bonding can be seen at the MNDO level of theory. Thus, the results reported in this work, along with those of Hehre and Pople,⁴⁰ show that while the interaction of the lone-pair orbital with the Π_{Me}^* antibonding methyl group orbitals is important for methyl substitution at the heteroatom as well as the α -carbon atom, it is unimportant when the methyl moieties are two atoms removed. This is due to the negligible overlap in this case.

The MNDO calculations show that, upon methyl substitution at the α -carbon atom, the nitrogen lone-pair orbital interacts with the Π -type filled and unfilled methyl group orbitals. This changes the donor properties of the amino species. In particular, it leads to a lower charge at the donor site and a less localized and higher energy HOMO. The calculated results also show the relative importance of lone-pair interactions with the Π_{Me}^* antibonding methyl orbitals with changes in the substitution site. The Π_{NH_2} bonding orbitals of the amine are also shown to be destabilized

Table VII. Frequencies of the N-H Asymmetric Stretching Vibration for *n*-Propylamine and *tert*-Amylamine in CCl₄ solution

amine	N-H asymmetric stretching mode, cm ⁻¹
PAM	3391
TAM	3378

Table VIII. Band Assignments of C-H Stretching Vibrations of *n*-Propylamine and *tert*-Amylamine in CCl₄ Solution

amine	ν , cm ⁻¹	assgnt
PAM	(1) 2960	asym -CH ₃
	(2) 2875	sym -CH ₃
	(3) 2932	asym -CH ₂
	(4) 2856	sym -CH ₂
TAM	(1) 2963	-CH ₃
	(2) 2937	
	(3) 2879	
	(4) 2923	asym -CH ₂
	(5) 2854	sym -CH ₂

upon methyl substitution at the α -carbon atom.

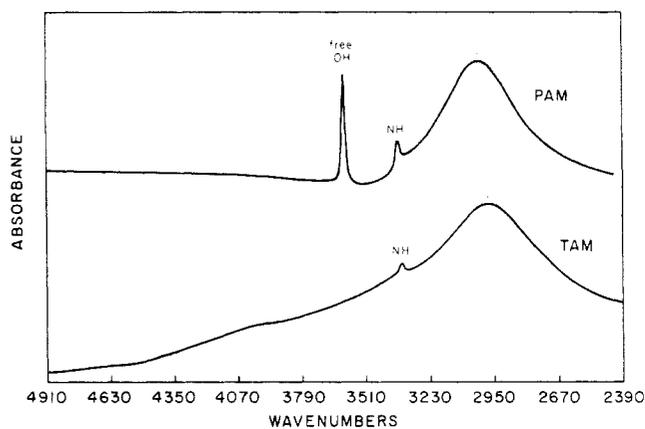
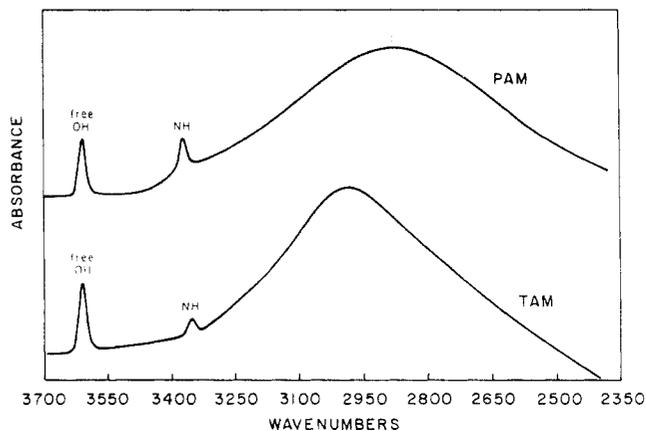
It is appropriate at this point to discuss the results of some infrared spectroscopic experiments that further substantiate the MNDO results regarding the changes in the donor properties of aliphatic amino species upon methyl substitution at the α carbon atom.

5. Infrared Experiments

The infrared experiments reported in this work were performed with spectral-grade reagents without further purification. All samples were prepared in a dry glovebox with thoroughly dried glassware. The spectra were obtained on a Nicolet 7000 series Fourier transform infrared spectrometer at a resolution of 0.24 cm⁻¹.

The infrared spectra of the amines in carbon tetrachloride were obtained at room temperature (21 °C). Experiments were performed over a wide range of concentration levels in order to ascertain that association effects were eliminated. Table VII shows the asymmetric stretching frequencies of the N-H bonds of *tert*-amylamine (TAM) and *n*-propylamine (PAM) in CCl₄ at very high dilution. These values are consistent with Kreuger and Smith's⁴⁶ investigations of the N-H stretching frequencies of primary amino species. Structurally, the two amines are different in that *tert*-amylamine is methyl substituted at the α -carbon atom compared to *n*-propylamine. The frequencies reported in Table VII indicate that the N-H bond is weakened upon methyl substitution at the α -carbon atom. This result is consistent with MNDO calculations reported earlier that show that the Π_{NH_2} orbital is destabilized upon methyl substitution at the α -carbon atom. As discussed earlier, this change in the N-H bond strength can be related to the changes in the acidity of the amino species observed in somewhat similar systems by Brauman and Blair.⁴⁵

Table VIII reports the frequencies of the observed C-H stretching modes in the 2850-3000-cm⁻¹ region for *tert*-amylamine and *n*-propylamine. Table VIII indicates that the band pattern in this region is different for the two amines. In particular, the spectrum of *tert*-amylamine shows the existence of a band at 2937 cm⁻¹ in addition to the four bands corresponding to the standard asymmetric and symmetric stretching modes of methyl and methylene groups. Several workers in the past⁴⁷⁻⁵⁰ have observed the appearance of an extra band in the C-H stretching region when methyl groups are in the vicinity of a lone pair. The existence of this extra band was initially ascribed to Fermi resonance with one of the C-H deformation modes.⁴⁸ However, later work⁵⁰ has shown that an interaction with the lone pair is the probable cause. The MNDO calculations reported earlier in this paper show that upon methyl substitution at the α -carbon atom, the Π -type lone-pair orbital interacts with the Π_{Me}^* antibonding methyl orbitals. This leads to a higher electron density on the two methyl hydrogens that are trans to the lone pair. Consequently, the three hydrogens are not equivalent, and more than two bands for the C-H stretching modes of the methyl groups in *tert*-amylamine should be observed. On the basis of this argument the

**Figure 6.** Resolved infrared spectra showing the bonded -OH bands for the interactions of *tert*-amylamine (TAM) and *n*-propylamine (PAM) with phenol.**Figure 7.** Resolved infrared spectra showing the bonded -OH bands for the interactions of *tert*-amylamine (TAM) and *n*-propylamine (PAM) with *p*-chlorophenol.

extra band may be tentatively assigned to the methyl groups attached to the α -carbon atom. Currently, partial deuteration studies are under way in this laboratory to ascertain this assignment.

The infrared spectra of *tert*-amylamine and *n*-propylamine thus indicate that upon methyl substitution at the α -carbon atom the N-H bond is weakened and that the interaction of the lone-pair orbital with the Π_{Me}^* methyl orbitals leads to the three methyl hydrogens being inequivalent.

A major research effort by the Drago group⁵¹⁻⁵⁴ has established that the frequency shifts of the -OH band ($\Delta\nu_{\text{OH}}$) of phenolic acids upon complexation with nitrogen and oxygen donors can be linearly related to the bond strength in the adduct. With nitrogen or oxygen donors phenolic acids form a rather strong hydrogen bond. This leads to a weakening of the adjacent -OH bond in the phenolic acid. This consequently results in a broadening and downfield shift of the band corresponding to the -OH stretching mode. The Drago group's work establishes that this downfield shift is directly related to the strength of the hydrogen bond. Hence, by carrying out complexation reactions of a series of well-characterized phenolic acids with a series of bases, one could ascertain the relative hardness or softness of the donor species. In particular, the changes in the donor properties of amino species upon methyl substitution at the α -carbon atom could be characterized by performing such complexation studies using infrared spectroscopy. The results of complexing a pair of amines, *tert*-amylamine, and *n*-propylamine with phenol and *p*-chlorophenol are reported here. It has been established by Drago and co-workers⁵³ that *p*-chlorophenol has the harder acid site compared to phenol. Thus, on the basis of the results of complexing *n*-propylamine and its methyl-substituted analogue, *tert*-amylamine with these two phenolic acids, one should be able to conclude about the relative hardness or softness of the two donors.

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The phenolic acid-amine complexes were prepared by adding amine directly to the phenolic acid and then diluting with the solvent, carbon tetrachloride. Enough amine was added to complex about 90% of the phenolic acid. As in the case of the amine spectra, experiments were done over a wide range of concentration levels to eliminate association effects. The reactions were carried out at room temperature (21 °C), and the spectra were also recorded at room temperature.

Figure 6 depicts the resolved spectra obtained on complexing the two amines (represented as TAM and PAM) with phenol. The free-OH band is shown for reference. All other bands corresponding to the amine and phenol have been subtracted out. The bands labeled N-H are the downfield shifted N-H asymmetric stretching bands corresponding to the complexed amines. The broad band is the downfield shifted-OH band for the complexed phenol. Figure 7 shows similar spectra for the interactions of the two amines with *p*-chlorophenol.

The differences in $\Delta\nu_{\text{OH}}$ and peak width of the complexed -OH bands for the four interactions depicted in Figures 6 and 7 are indeed interesting. Figure 6 shows that for the interactions with phenol, the bonded -OH band is more downfield shifted and has a greater peak width in the phenol-*tert*-amylamine complex. This implies that with the softer acid, phenol, the methyl-substituted *tert*-amylamine forms the stronger bond. In contrast, Figure 7 shows that with *p*-chlorophenol the bonded -OH band is more downfield shifted and has a greater bandwidth in the *p*-chlorophenol-*n*-propylamine complex. This implies that, with *p*-chlorophenol, which has the harder acid site, *n*-propylamine forms the stronger bond. Hence, these data allow us to conclude that the donor amine does become softer upon methyl substitution at the α -carbon atom. The complexation studies are thus consistent with the MO arguments presented in this work.

Drago and co-workers^{52,55} and Klopman¹⁹ have suggested the use of the E & C equation along with the $\Delta\nu_{\text{OH}}$ values to further quantify the relative hardness or softness. However, since the peak width of the bonded -OH bands are large, it has not been deemed fit to quantify the relative softness of the systems studied in this work in this manner.

The differences in donor properties upon methyl substitution, as evidenced by the molecular orbital calculations and the infrared studies, rationalize some of the macroscopic observations of amine-CO₂ reactions in solution.⁹⁻¹² Of course, it is recognized that differences in solvation effects could be important. However, changes in the intrinsic chemistry alone (without accounting for solvation effects) predict the trends in the macroscopic behavior upon methyl substitution at the α -carbon atom. While it is true that for the ionic species such as the protonated amine and the carbamate anion differences in solvation energies upon methyl substitution could be important, in the cases under investigation the interaction of the free amine with CO₂ is of primary consideration. Hence, one needs to focus on the possible differences in solvation energies of the free amine itself upon methyl substitution at the α -carbon atom. It is therefore appropriate to briefly examine some of the possibly reasons for differences in solvation energies of the free amines upon such substitutions.

The amino species considered in this work are a series of primary amines or amino alcohols. Hence, the number of hydrogen bonds that can be formed is the same for substituted and unsubstituted molecules. Thus, differences in amine solvation energies due to different degrees of hydrogen bonding should not be significant. The difference in the partial charge at the nitrogen donor site upon methyl substitution at the α -

carbon atom could contribute to different solvation energies. Calculations using the Born equation,^{56,57} however, predict that for the charge differences reported in this paper this effect should be small. Steric inhibition to solvation due to relatively small methyl groups at the α -carbon atom should also not be significant.³³ These qualitative arguments suggest that the change in the solvation energy of the free amine upon methyl substitution at the α -carbon atom should not be significant. This is consistent with the Trotman-Dickenson proposal.⁵⁸ Arnett and co-workers³⁵ have reported that the difference in the free energy of solvation between ethylamine and *tert*-butylamine is only 0.24 kcal/mol. This experimental result supports the qualitative arguments suggesting that the difference in solvation energies is not significant for the free amine and hence its interactions with CO₂. Furthermore, as noted recently by Pearson,²⁹ if the net charge on a molecule or pair of interacting molecules does not change significantly, then the hardness parameter as determined from the gas-phase ionization potential and electron affinity is a fairly good approximation even in solution. The extension of the molecular orbital arguments, the MNDO results, and the infrared studies toward rationalizing the macroscopic behavior in a qualitative sense is thus justified. Development of quantitative structure-activity relationships will, however, require a detailed accounting of solvation effects.

6. Concluding Remarks

Qualitative molecular orbital arguments, MNDO calculations, and infrared data reported in this paper demonstrate that methyl substitution at the α -carbon atom in primary amines and amino alcohols leads to subtle but significant changes in the electronic environment of the donor site, nitrogen. These changes are due to the interactions of the nitrogen lone-pair orbital with the Π_{Me} and Π_{Me}^* methyl group orbitals. These interactions result in the donor species having a lower charge at the donor site and a higher and more delocalized HOMO (i.e., making it a softer base). Furthermore, the N-H bond of the amine is weakened upon methyl substitution at the α -carbon atom.

The results reported in this paper show that the differences in the donor properties of amino species upon methyl substitution at the α -carbon atom should lead to the experimentally observed differences in reactivity and selectivity in amine-CO₂ reactions. Since the effects of the orbital interactions considered in this paper are probably underestimated by MNDO calculations,⁴³ *ab initio* calculations have recently been carried out in this research group to further study the orbital interactions discussed in this work. These results will be reported in an ensuing publication⁵⁹ and show that *ab initio* calculations using extended basis sets predict the effects reported in this paper to be further accentuated.

Registry No. AmP, 124-68-5; MEA, 141-43-5; TBA, 75-64-9; ETA, 75-04-7; TAM, 594-39-8; PAM, 107-10-8; CO₂, 124-38-9; CF₃CH₂NH₂, 753-90-2; HOH₂C(OCH₃)₂CNH₂, 115515-23-6; ethylcarbamic acid, 7409-13-4; *tert*-butylcarbamic acid, 69777-55-5; phenol, 108-95-2; *p*-chlorophenol, 106-48-9.

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