

more intense. This behavior may readily be understood if one formally derives these compounds from **3** by adding one (**13**) or two (**14**) *s-cis*-1,3-butadiene bridges (Figure 16). For each of these two molecules, different orbitals of texaphyrin and butadiene will interact for symmetry reasons. In the case of **13**, the second HOMO (s) will interact with the lowest π -orbital of butadiene and the HOMO orbital (a) with the second lowest orbital of butadiene. Considering the energy differences and the values of LCAO coefficients (Figure 14), we may expect a similar shift of both HOMO orbitals toward higher energy. Thus, the value of Δ HOMO should remain approximately unchanged. Δ LUMO is not expected to change, either, since the interaction of the LUMO orbitals with the orbitals of butadiene may be neglected due to small values of LCAO coefficients in both LUMO orbitals. Thus, the similarity of the MCD spectra of **3** and **13** is not surprising. One should, however, expect the two lowest excited states of the latter compound to lie at lower energies than the corresponding transitions of the former, since both HOMO orbitals now lie at higher energies. This is indeed observed (cf. Figures 1 and 11).

In compound **14**, the orbital interaction picture is different. Now, the HOMO orbital (s) interacts with the second occupied orbital of butadiene, while the a orbital interacts with the first one. Since the energy difference between the interacting pair of orbitals is much smaller in the former case, one should expect that the s orbital

should be destabilized to a much higher degree than the a orbital. One now predicts Δ HOMO < Δ LUMO, and henceforth a -, + sequence of μ^+ contributions to the *B* terms. Additional amplification of this effect with respect to **13** stems from the fact that the shifts now result from the interaction with two butadiene units.

The prediction of a -, + sequence of relatively large *B* terms for **14** is in perfect agreement with experiment and provides yet another argument for the s, a, -s, -a orbital ordering. The a, s, -s, -a sequence leads to a prediction of benzannelation effects that cannot be reconciled with the observed spectra.

In summary, our results show that the perimeter model accounts in a simple way for the signs of the MCD *B* terms of the low-lying electronic transitions of metallo-texaphyrins. They demonstrate the s, a, -s, -a orbital energy pattern for the hexaalkylated parent metallo-texaphyrins, **3** and **4**, and show that in these, the values of Δ HOMO and Δ LUMO are nearly the same, so that they are soft MCD chromophores. This equality may easily be destroyed by substitution in positions 16 or 17 by electron-donating substituents, but not by electron-withdrawing ones.

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Heats of Reaction of Resonance-Stabilized Carbenium Ions with Nitrogen Bases

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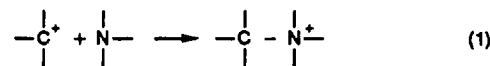
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Heats of reaction (ΔH_{rxn}) are reported for five resonance-stabilized carbenium ions with ten aliphatic amines and seven pyridines in sulfolane at 25 °C to produce substituted ammonium ions. Heats of reaction (ΔH_{rxn}) for these neutral bases fall in the same range as the corresponding heats of reaction of the carbenium ions with a variety of resonance-stabilized anions (carbanions, and oxyanions) whose $\text{p}K_{\text{a}}$ s are comparable to those of the amines and pyridines. Although the ΔH_{rxn} s do not correlate with the aqueous $\text{p}K_{\text{BH}^+}$ s of the amines, good correlations are obtained using the $\text{p}K_{\text{R}^+}$ s of the carbenium ions and with the gas-phase heats of reaction of the amines with trimethylboron. Also, the ΔH_{rxn} s of pyridines with the carbenium ions correlate fairly well with the $\text{p}K_{\text{R}^+}$ s of the carbenium ions and are surprisingly insensitive to steric hindrance.

Introduction

In 1933, Hughes, Ingold, and Patel published their comparison of the attack of hydroxide ion on trimethyl-*n*-decylammonium and trimethylbenzhydrylammonium ions.¹ The dramatic difference in kinetic order established a duality for displacement reactions which is now familiar to every student of introductory organic chemistry. However, with the exception of Ritchie's equilibrium studies² and the recent flash photolysis work of McClelland³

there are no published accounts of the thermodynamics of reaction between amines and carbenium ions in solution (eq 1). In addition, Katritzky's group has studied



displacements on a wide range of ammonium ions⁴ and have also examined the gas-phase fragmentation of a series of alkylpyridinium ions to form carbenium ions and a pyridine molecule.⁵

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Table I. $-\Delta H_{\text{rxn}}$ s (kcal/mol) for Reactions of Alkylamines with Carbenium Ions in Sulfolane at 25 °C

amine	pK_{BH^+}	pK_{GB}	trityl (-6.63) ^a	xanthylium (-0.85) ^a	9-Ph Xa ⁺ (1.10) ^a	TPCP ⁺ (3.10) ^a	tropylium ⁺ (4.70) ^a	BMe ₃ ^b
quinclidine	10.95	223.6	34.55 ± 0.34	27.23 ± 0.40	24.74 ± 0.20	19.50 ± 0.29	20.56 ± 0.15	19.94
tri- <i>n</i> -butylamine	9.93	227.0	35.00 ± 0.58	30.38 ± 0.36	25.01 ± 0.60	20.41 ± 0.40	16.78 ± 0.51	
<i>tert</i> -butylamine	10.68	212.9	35.56 ± 0.17	30.37 ± 0.25	26.93 ± 0.30	25.55 ± 0.18	25.97 ± 0.22	12.99
triethylamine	10.80	223.4	36.52 ± 0.46	23.46 ± 0.66	28.27 ± 0.75	21.82 ± 0.40	14.53 ± 0.23	10.00
morpholine	8.33	211.0	37.83 ± 0.62	32.82 ± 0.50	30.28 ± 0.40	28.00 ± 0.40	27.81 ± 0.30	
cyclohexylamine	10.68	212.9	38.80 ± 0.41	34.46 ± 0.35	30.10 ± 0.40	28.72 ± 0.36	28.02 ± 0.35	
<i>n</i> -hexylamine	10.63	211.7	40.36 ± 0.51	34.44 ± 0.20	32.41 ± 0.28	29.82 ± 0.25	27.78 ± 0.28	18.53
piperidine	11.12	217.2	40.49 ± 0.32	36.70 ± 0.50	32.57 ± 0.18	31.40 ± 0.48	29.98 ± 0.34	19.65
isopropylamine	11.09	211.1	41.28 ± 0.30	35.07 ± 0.44	31.88 ± 0.36	28.92 ± 0.21	27.67 ± 0.34	17.42
<i>n</i> -butylamine	10.66	210.6	42.07 ± 0.56	34.84 ± 0.33	31.08 ± 0.45	29.84 ± 0.57	27.42 ± 0.28	18.41

^a pK_{R^+} values from ref 20. ^b Values from ref 13a.

Table II. $-\Delta H_{\text{rxn}}$ s (kcal/mol) for Reactions of Substituted Pyridines with Carbenium Ions in Sulfolane at 25 °C

pyridine	trityl (-6.63) ^a	xanthylium (-0.85) ^a	9-Ph Xa ⁺ (1.10) ^a	TPCP ⁺ (3.10) ^a	tropylium ⁺ (4.70) ^a	BMe ₃ ^b	BF ₃ ^c
pyridine	19.32 ± 0.21	18.13 ± 0.34	8.93 ± 0.17	12.45 ± 0.25	10.70 ± 0.26	17.0	30.6
2-picoline	21.77 ± 0.60	17.54 ± 0.21	—	9.51 ± 0.19	6.75 ± 0.24	10.0	29.5
4-picoline	20.82 ± 0.24	19.08 ± 0.31	11.51 ± 0.15	12.46 ± 0.27	10.97 ± 0.23	19.4	32.1
2,6-lutidine	23.96 ± 0.21	19.18 ± 0.19	—	9.45 ± 0.30	5.44 ± 0.15	—	23.4
2,6-di- <i>tert</i> -butylpyridine	21.87 ± 0.24	17.34 ± 0.19	—	—	—	—	—
4- <i>tert</i> -butylpyridine	19.89 ± 0.21	19.10 ± 0.13	12.02 ± 0.19	12.34 ± 0.39	10.64 ± 0.08	—	—
2-bromopyridine	16.59 ± 0.10	5.08 ± 0.14	—	—	—	—	—

^a pK_{R^+} values from ref 20. ^b Values from ref 13a. ^c Values from ref 14.

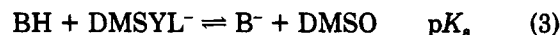
Our previous publications⁶ have described heats of reaction as well as kinetics, equilibria, and electron transfer for the reactions of a wide variety of anions with resonance-stabilized carbenium ions and their conversion into heats of heterolysis and homolysis.⁷ It is now reasonable to ask how the heats of reaction for such cation-anion reactions compare with those for corresponding systems where a neutral base rather than an anion is involved and to compare the results with related properties reported from other laboratories.

Results and Discussion

Tables I and II display the results for the reactions of the carbenium ions with neutral amines and pyridines expressed in terms of ΔH_{rxn} for eq 1. As before $\Delta H_{\text{rxn}} = -\Delta H_{\text{het}}$, the heat of heterolysis, for the bond from the nitrogen to the carbon of the original carbenium ion. Also listed are several other properties which might reasonably be correlated with the observed heats of reaction. We have assumed throughout the present study that the carbon to nitrogen bond is formed at the carbon formally bearing the charge at the center of the carbenium ion. In the case of attack on the trityl and xanthylium ions it would be a reasonable possibility that the substitution takes place on a peripheral carbon. Although this point was not proved for the compounds in this paper, it was examined in a previous case^{7a} by isolation and NMR examination of the products from reactions with carbanions and is assumed to hold here. HPLC analysis of the product showed that the reactions reported here were clear.

It should be noted at once that the ΔH_{rxn} s for the C-N bonds in these ammonium ions are in exactly the same

range as those found previously for the reactions of the same carbenium ions with resonance-stabilized carbanions to produce neutral products.^{6,7} Clearly, the simple effect of charge is not an overpowering one; of much more relevance is the basicity of the nitrogen compound which must be expressed here in terms of pK_{BH^+} for the protonation equilibrium (eq 2) rather than for the deprotonation process (eq 3) used to compare the carbon, nitrogen, oxygen,



and sulfur acids which form the anions previously reported. Thus, the pK_a of (*p*-methoxyphenyl)malononitrile (5.68)^{8b} is in the same working range of acid strength with the pK_{BH^+} values for the amines in Table I. However, an exact comparison cannot be made because the pK_a s of carbon acids were determined in dimethyl sulfoxide⁹ and the pK_{BH^+} s in water are referred to an aqueous standard state.¹⁰ Furthermore, the trends in the order of basicities are totally different in the two solvents.^{9,10} Also, there are very few published pK_{BH^+} values for nitrogen bases in dipolar nonhydroxylic media.¹¹

Correlations of ΔH_{het} with Other Acid-Base Properties. Previous reports⁷ compared the proton affinities of various carbanions, as expressed by their pK_a s, with the corresponding heats of reaction of the bonds formed through coordination with resonance-stabilized carbenium ions and have frequently found fair to good correlations of these two properties which measure electron transfer

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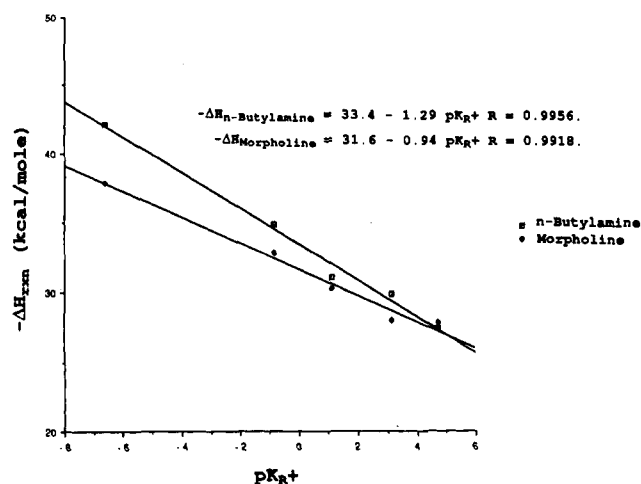


Figure 1. Plots of $-\Delta H_{\text{rxn}}$ s of the reactions of alkylamines with the carbenium ions vs $\text{p}K_{\text{R}^+}$ of the carbenium ions.

to a positively charged acid. An attempted correlation of the ΔH_{het} s in Table I for reaction of the amines with a representative carbenium ion (trityl) vs the aqueous $\text{p}K_{\text{BH}^+}$ s of the amines resulted in a virtual scatter plot ($R = 0.35$). However, a better correlation was found when their gas-phase basicities ($\text{p}K_{\text{GB}}$)¹² were used ($R = 0.8911$).

Excellent correlations were obtained for each amine when the ΔH_{rxn} s were plotted against the $\text{p}K_{\text{R}^+}$ values for the five carbenium ions. Linear equations

$$\Delta H_{\text{rxn}} = a - b\text{p}K_{\text{R}^+} \quad (4)$$

had the following correlation coefficients and slopes: *n*-hexylamine, $R = 0.9983$, $b = 1.10$; *tert*-butylamine, $R = 0.9740$, $b = 0.93$; *n*-butylamine, $R = 0.9956$, $b = 1.29$; morpholine, $R = 0.9918$, $b = 0.94$; cyclohexylamine, $R = 0.9796$, $b = 1.01$; isopropylamine, $R = 0.9962$, $b = 1.24$; piperidine, $R = 0.9807$, $b = 0.96$; triethylamine, $R = 0.9111$, $b = 1.69$; tri-*n*-butylamine, $R = 0.9633$, $b = 1.61$; quinuclidine, $R = 0.9794$, $b = 1.35$. Figure 1 shows a representative plot of the heats of reaction of two amines with carbenium ions vs the $\text{p}K_{\text{R}^+}$ s of the cations.

The slopes of the correlation plots suggest strongly that steric hindrance to formation of the ammonium ion is a significant factor since the slope roughly increases through the series primary < secondary < tertiary and the slope for quinuclidine is less than for triethylamine.

We attribute the good correlations with $\text{p}K_{\text{R}^+}$, as compared to $\text{p}K_{\text{BH}^+}$, to the fact that eq 1 is modeled much better by the heterolysis of oxonium ions, $\text{AR}_3\text{C-O}^+\text{H}_2$ in aqueous sulfuric acid than it is by the simple protonation equilibrium for the amine. Unfortunately, we cannot arrive at any useful conclusions from the slopes of these plots. A similar observation was made in our analysis of the reactions of the carbenium ions with several phenoxides.^{7d}

Another useful comparison can be made with Brown's classic gas-phase coordination reactions of trimethylboron with the amines.¹³ Using this neutral Lewis acid model for the carbenium ions correlations of the type depicted in eq 5

$$\Delta H_{\text{rxn}} = a + b\Delta H_{\text{BMe}_3} \quad (5)$$

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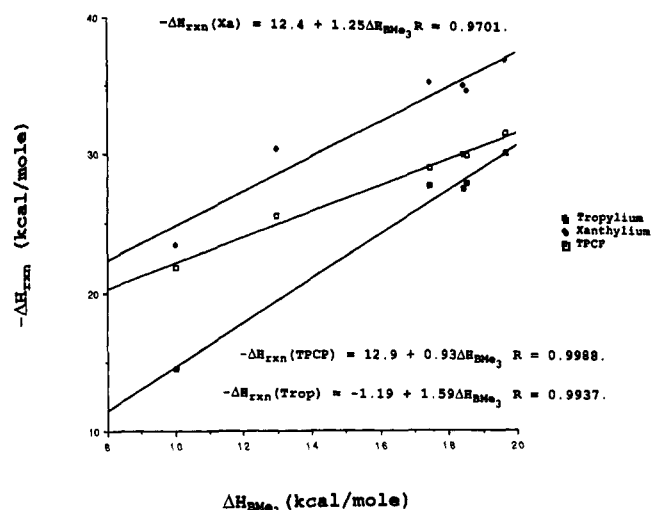


Figure 2. Comparison of ΔH_{rxn} s of amines with carbenium ions and BMe_3 .

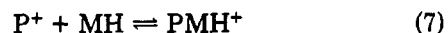
were attempted with results varying from excellent for triphenylcyclopropenylium ($R = 0.9988$) to poor for 9-phenylxanthylium ($R = 0.8711$). Figure 2 shows a representative plot for these correlations (not including the aberrant point for the reaction of tropylium ion with *tert*-butylamine). Following previous successful multiple regression analyses^{5,7} to correlate ΔH_{rxn} for carbenium ions with a variety of anions in terms of basicity data ($\text{p}K_{\text{a}}$ s) and the $\text{p}K_{\text{R}^+}$ s of the carbenium ions, a similar analysis was attempted using ΔH_{BMe_3} and $\text{p}K_{\text{R}^+}$ to fit the equation

$$\Delta H_{\text{rxn}} = a\Delta H_{\text{BMe}_3} + b\text{p}K_{\text{R}^+} + c \quad (6)$$

This did not result in any appreciable improvement of the correlation equation ($R = 0.9580$).

Historically, Brown's extensive study of the gas-phase coordination of amines with alkylated borons has probably provided the most compelling case in the literature for the reality of steric hindrance effects. It is therefore not surprising that we interpret the order of ΔH_{rxn} for carbenium ions with the same amines in terms of steric effects, but it is interesting that the ΔH_{rxn} s for the coordination of the carbenium ions in solution are actually in the same range as those for reactions with BMe_3 in the gas phase. Unfortunately, the extensive Lewis acid-base studies of Gal,¹⁴ Gutmann,¹⁵ and Olofsson¹⁶ do not provide sufficient data overlap for comparison with the present investigation.

To our knowledge, the only other studies for the formation and heterolysis of C-N bonds from carbenium to amine centers are those of Ritchie, Minasz, Kamego, and Sawada^{2d} and Katritzky et al.⁵ Ritchie^{8a} reports equilibrium constants for the process which presumably goes through an alkylmorpholinium ion (eq 7). For morpholine



(MH) reacting with pyronin cation (P^+), the equilibrium constant of $3.0 \times 10^2 \text{ M}^{-1}$ in DMSO corresponds to a standard Gibbs free energy of reaction of -3.37 kcal/mol .

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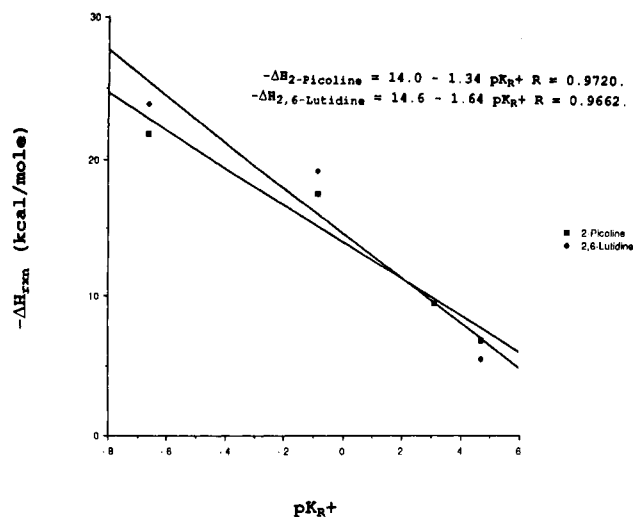


Figure 3. Plots of $-\Delta H_{\text{rxn}}$ s of the reactions of pyridines with the carbenium ions vs pK_{R^+} of the carbenium ions.

Using the correlation equation for morpholine, $\Delta H_{\text{rxn}} = 31.6 - 0.94pK_{\text{R}^+}$, and the pK_{R^+} of 11.51 for pyronin¹⁷ one estimates a $-\Delta H_{\text{rxn}}$ for morpholine reacting with pyronin in sulfolane of -20.78 kcal/mol. Entropy terms, solvation differences, and the heat of ionization of the alkylmorpholinium ion must contribute to this surprisingly large discrepancy between the results.

Katritzky et al.^{4,5} estimated heats of heterolysis for the C-N bonds of a variety of alkylpyridinium ions in the gas phase by collisionally activated dissociation and semi-empirical MO calculations. Their estimate for fragmentation of tritylpyridinium ion is <9 kcal/mol at 0 K. They apply a temperature and internal energy correction factor to their appearance energy parameters (at 0 K) and it leads to an increase of ~ 9 kcal/mol in the energy.⁵ This agrees surprisingly well with our $-\Delta H_{\text{rxn}}$ value of 19.32 ± 0.21 kcal/mol (Table II) under totally different conditions. The excellent agreement is interesting but obviously fortuitous.

ΔH_{rxn} for Pyridines. Table II and Figure 3 present the results for reactions of the pyridines with the carbenium ions. Most surprising is the insensitivity of ΔH_{rxn} to steric effects on the amine moiety. Thus, even 2,6-di-*tert*-butylpyridine (2,6-DTBP), a standard test for such effects,^{13,18,19} lies in the same range of ΔH_{rxn} with trityl and

xanthylium ions as its completely unhindered homologues. The Lewis acid reactivity of the carbenium ions, as represented by their pK_{R^+} s²⁰ plays a much more deciding role than do steric factors since unhindered tropylium ion does not react with 2,6-DTBP, although the relatively more hindered trityl and xanthylium ions do. However, the steric requirements of the carbenium ions do influence these reactions since no heat change was observed for the reactions of either 2,6-DTBP or 2,6-lutidine with 9-phenylxanthylium ion (9-PhXa), but 2,6-lutidine does react with triphenylcyclopropenium ion (TPCP) even though 2,6-DTBP does not. ΔH_{rxn} for the pyridines correlate fairly well with the pK_{R^+} of the carbenium ions (Figure 3). Unfortunately, correlations of ΔH_{rxn} with those of Gal,¹⁴ using heats of reaction with BF_3 or those of Brown^{13a} using BMe_3 are inappropriate because of the lack of overlap in the data sets (Table II).

Experimental Section

A mixture of sulfolane-5% 3-methylsulfolane was used as the solvent for all the calorimetric measurements. The purification of the solvents and the preparations of the cations are described elsewhere.⁷ All the liquid amines and the pyridines (Aldrich) were dried with solid KOH and distilled from CaH_2 . Quinuclidine (Aldrich, 97%) was recrystallized twice from ethyl ether.

Heats of reaction (ΔH_{rxn}) of the carbenium ions with the various neutral amines in the sulfolane solvent mixture were measured using a Tronac 450 titration calorimeter in the isoperibolic mode at 25 °C. In a typical experiment, a solution of the carbenium ion (0.08–0.1 M) was prepared inside an argon-filled drybox. Before each calorimetric run, the calibrated motordriven buret filled with the cation solution and the Dewar calorimeter vessel containing about 30 mL of 0.02–0.04 M amine solution were connected to the calorimeter head assembly. A dry argon atmosphere was maintained at the top of the reaction vessel to protect the solutions from air. The operation of the calorimeter and our standard procedures have been described elsewhere.^{19b}

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