[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Steric Effects in Displacement Reactions. XII. Linear Strain Energy Relationships Involving Reactants of Large Steric Requirements. Steric Strains in the Transition State[1]

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The order of base strengths, observed in aqueous solution and with methanesulfonic acid, pyridine < 2-picoline < 2,6-lutidine, varies systematically to the opposite order, pyridine > 2-picoline > 2,6-lutidine, with increasing steric requirements of the reference acid, $H^+ < BH_3 < BF_3 < BMe_3$. In the same way the base strengths of the 2-alkylpyridine bases vary systematically from pyridine ≪ 2-methyl- > 2-ethyl- > 2-isopropyl- > 2-*t*-butyl- to pyridine ≫ 2-methyl- > 2-ethyl- > 2-isopropyl- ≫ 2-*t*-butyl. It is concluded that the base strength must be considered a function of the steric requirements of the reference acid. The available data permit an estimate of the strains present in addition compounds and their homomorphic derivatives. A procedure is proposed for estimating the strain in highly strained homomorphs which have not yet been synthesized. The activation energy data for the reaction of methyl iodide with the pyridine bases exhibit the same effects of structure as the corresponding molecular addition compounds. It is concluded that the steric requirements of the transition state must be closely related to the steric requirements of molecular addition compounds of related structure. The existence of linear energy relationships is examined in the data for the reaction of various acids with the pyridine bases and for the reaction of methyl iodide with these bases. When the steric requirements of the two reactions being compared are similar, satisfactory linear relationships are observed. Where the steric requirements are not similar, then the *ortho* substituted bases exhibit deviations, and these deviations increase with the increasing steric requirements of the substituent and the increasing disparity in the steric requirements of the two reactions undergoing comparison. Strains in the methyl iodide transition states are two-thirds of the strains in the homomorphic borane addition compounds. It is concluded that molecular addition compounds provide promising models for the study of the structure of related transition states.

The ionization of simple acids and bases has played a major role in the development of modern theories of organic chemistry. Indeed, many of the currently accepted theoretical concepts receive their most direct and best confirmation from acid–base phenomena.[4–6] It is probable that the major role which this reaction has played in the development of organic theory is due not to any inherent importance of the ionization reaction, but rather to the lack of other simple reversible reactions of wide applicability.

It was pointed out by G. N. Lewis that the essential process in the ionization of acids and bases is the coördination of the proton with the free electron pair of the base. He suggested, therefore, that molecules such as boron trichloride and stannic chloride, which also possess the ability to accept the electron pair of a base, should also be considered acids.[7] Irrespective of whether this definition is accepted, it is apparent that the coördination of such Lewis acids with bases represents a simple reversible process of far greater versatility than the original reaction involving the transfer of a proton.

$$H^+ + :\text{Base} \rightleftharpoons H:\text{Base}^+$$

$$^1/_2(BH_3)_2 + :\text{Base} \rightleftharpoons H_3B:\text{Base}$$

$$BF_3 + :\text{Base} \rightleftharpoons F_3B:\text{Base}$$

$$BMe_3 + :\text{Base} \rightleftharpoons Me_3B:\text{Base}$$

$$AlMe_3 + :\text{Base} \rightleftharpoons Me_3Al:\text{Base}$$

$$GaMe_3 + :\text{Base} \rightleftharpoons Me_3Ga:\text{Base, etc.}$$

The proton is a charged particle of negligible steric requirements. As long as organic theory concerned itself primarily with the factors controlling the addition or removal of a proton from an organic moiety, it was natural that the theory should emphasize the role of the electrical factor in organic phenomena to the detriment of the steric factor. Extension of the study of acid–base phenomena to Lewis acids with varying steric requirements has led to a clearer appreciation of the role of the steric factor in organic theory.[8,9]

In view of the lack of quantitative data in this field, many of the original investigations and conclusions were necessarily based upon qualitative observations.[8] The present availability of quantitative data on the heats of reaction of methanesulfonic acid,[10a] diborane,[10b] boron trifluoride[10c] and trimethylboron[10d] renders feasible a systematic examination of the importance of the steric requirements of the reference acid on the relative strengths of two groups of closely related pyridine bases.

For convenience in following the discussion, the available data are summarized in Table I.

The Strength of Pyridine Bases as a Function of the Steric Requirements of the Reference Acid.—The introduction of a methyl group in the 4-position of pyridine (pK_a pyridine, 5.17) results in an increase in base strength (ΔpK_a 0.85). A methyl group in the 2-position has a similar effect (ΔpK_a 0.80). From the pK_a value of 2,6-lutidine, 6.75, it appears that a second methyl group has essentially the same effect as the first (ΔpK_a 0.78).[11] This change produced by the methyl group is attributed

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[1] Based upon theses submitted by Daniel Gintis and Lionel Domash in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Research assistant at Purdue University, 1951–1952, on a contract supported by the Atomic Energy Commission.

[3] Atomic Energy Commission Predoctoral Fellow, 1950–1952.

[4] H. B. Watson, "Modern Theories of Organic Chemistry," 2nd. ed., Oxford University Press, Oxford, England, 1941.

[5] G. W. Wheland, "The Theory of Resonance," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1955.

[6] H. C. Brown, D. H. McDaniel and O. Häfliger, "Dissociation Constants," Chapter 14 in "Determination of Organic Structures by Physical Methods," ed. by E. A. Braude and F. C. Nachod, Academic Press, Inc., New York, N. Y., 1955.

[7] G. N. Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

[8] H. C. Brown, H. I. Schlesinger and S. Z. Cardon, THIS JOURNAL, **64**, 325 (1942).

[9] H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

[10] (a) H. C. Brown and R. R. Holmes, THIS JOURNAL, **77**, 1727 (1955); (b) H. C. Brown and L. Domash, *ibid.*, **78**, 5384 (1956); (c) H. C. Brown and R. H. Horowitz, *ibid.*, **77**, 1733 (1955); (d) H. C. Brown and D. Gintis, *ibid.*, **77**, 5378 (1956).

[11] H. C. Brown and X. R. Mihm, *ibid.*, **77**, 1723 (1955).

TABLE I

SUMMARY OF RATE AND EQUILIBRIUM DATA FOR REACTIONS INVOLVING THE PYRIDINE BASES

Substituent in pyridine base	pKa, 25°	Heat of reacn., $-\Delta H$, kcal./mole				Rate data for CH_3I[a,g]	
		CH_3SO_3H[a,b]	$^1/_2(BH_3)_2$[a,c]	BF_3[a,d]	BMe_3[a,e]	$10^5k_2^{25}$[f]	E_{act}
Hydrogen	5.17	17.1	17.9	32.9	21.4	34.3	13.9
4-Methyl	6.02	18.4	18.5	33.4	22.0	76.0	13.6
4-Ethyl	6.02	18.3		33.2		77.7	
4-Isopropyl	6.02	18.4		33.3		76.7	
4-*t*-Butyl	5.99	18.3		33.2		75.7	13.7
3-Methyl	5.68	17.8	18.2	33.2	21.7	71.2	13.6
3-Ethyl	5.70	18.1		33.1		76.1	
3-Isopropyl	5.72	18.0		33.2		81.0	
3-*t*-Butyl	5.82	18.2		33.5		95.0	
2-Methyl	5.97	18.3	17.2	31.2	16.1	16.2	14.0
2-Ethyl	5.92	18.2	16.9	30.6	15.1	7.64	14.2
2-Isopropyl	5.83	18.1	16.7	29.6	13.7	2.45	14.8
2-*t*-Butyl	5.76	18.0	12.1	22.7	0	0.0080	17.5
2,6-Dimethyl	6.75	19.5	16.3	25.4	0	1.45	15.1
2,4,6-Trimethyl	7.59	20.7		26.4		3.75	14.8

[a] Nitrobenzene solution. [b] Reaction: $CH_3SO_3H(soln.) + Py(soln.) = PyH^{+-}O_3SCH_3(soln.)$, ref. 10a. [c] Reaction: $^1/_2B_2H_6(g) + Py(soln.) = Py{:}BH_3(soln.)$, ref. 10b. [d] Reaction: $BF_3(g) + Py(soln.) = Py{:}BF_3(soln.)$, ref. 10c, 19. [e] Reaction: $BMe_3(g) + Py(soln.) = Py{:}BMe_3(soln.)$, ref. 10d. [f] L. mole^{-1} sec.$^{-1}$. [g] Ref. 20, 19.

to its electrical effect, increasing the electron density on the nitrogen atom of the base and making it better able, thereby, to unite with a proton. From the observation that the two methyl groups in 2,6-lutidine have essentially twice the effect of the single methyl group in 2-picoline, it is concluded that steric effects involving the addition of a proton to 2,6-lutidine or the solvation of the resulting pyridinium ion cannot be important in this base.[12]

The increase in the heat of neutralization of 4-picoline by methanesulfonic acid in nitrobenzene solution ($\Delta\Delta H$ 1.3 kcal./mole) and by diborane, boron trifluoride and trimethylboron ($\Delta\Delta H$ 0.6, 0.5, and 0.6, respectively) likewise points to the importance of the electrical effect of the methyl group in increasing the strength of the base. The larger effect observed in the transfer of a proton to the nitrogen atom ($\Delta\Delta H$ 1.3 kcal./mole) as compared to the Lewis acids ($\Delta\Delta H$ 0.5–0.6 kcal./mole) presumably reflects the greater demand made by a formal positive charge at the nitrogen atom as compared to the dipoles in the addition compounds.

A methyl group in the 2-position increases the heat of reaction with methanesulfonic acid by 1.2 kcal./mole. The second methyl group in 2,6-lutidine has an identical effect ($\Delta\Delta H$ 1.2 kcal./mole). Here also it may be concluded that there is no significant steric effect in the transfer of a proton to 2,6-lutidine.

The situation changes when we examine the reactions of diborane with these two bases. Instead of the increase of 0.5–0.6 kcal./mole predicted for 2-picoline, there is observed a *decrease* of 0.7 kcal./mole. The two methyl groups in 2,6-lutidine result in a decrease of 1.6 kcal./mole. These decreases are attributed to steric interactions between the borane group and the methyl substituents. In other words, the change from the minor steric requirements of the proton to the much larger steric requirements of borane has resulted in a reversal from the original order of base strength, pyridine < 2-picoline < 2,6-lutidine, to the opposite order, pyridine > 2-picoline > 2,6-lutidine.

On the basis of the estimated increases in the heat of reaction per methyl group, the magnitude of the steric interaction is estimated to be 1.3 kcal./mole in 2-picoline–borane and 2.7 kcal./mole in 2,6-lutidine–borane.

Consideration of the molecular dimensions of boron trifluoride and trimethylboron leads to the conclusion that the steric requirements of these acids should be much greater than those of borane. Indeed, the heats of reaction of boron trifluoride with 2-picoline and 2,6-lutidine are 2.2 and 8.5 kcal./mole less than the calculated values.

The heat of reaction of trimethylboron with 2-picoline is 5.9 kcal./mole less than the estimated value and no reaction is observed with 2,6-lutidine. It is apparent that the strains increase markedly with the predicted increase in the steric requirements of the reference acid, $H^+ < BH_3 < BF_3 < BMe_3$.

The changing orders of base strengths of these three bases with the increasing steric requirements of the reference acids are represented graphically in Fig. 1.

The changes in the structure of the alkyl group in the 4-alkylpyridines (alkyl = methyl, ethyl, isopropyl, *t*-butyl) have little effect upon the base strength.[11] In the 2-position there is observed a small decrease in base strength with increasing steric requirements of the proton. This slight decrease may indicate a small steric effect accompanying the addition of a proton to the nitrogen atom and the solvation of the pyridinium ion.

The results with methanesulfonic acid in nitrobenzene closely parallel the results in aqueous solution. Moreover, with increasing steric requirements of the reference acid, $BH_3 < BF_3 < BMe_3$, there are observed increasing deviations between the predicted and observed base strengths. The effects of the conflicting steric requirements of the reference acid and the 2-alkyl group are illustrated in Fig. 2.

The present results are in complete agreement

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[12] Steric hindrance to addition of a proton and, possibly, to solvation of the resulting anilinium ion appears to be of major importance in the weakness of 2,4,6-tri-*t*-butylaniline as a base; P. D. Bartlett, M. Roha and R. M. Stiles, *ibid.*, **76**, 2349 (1954).

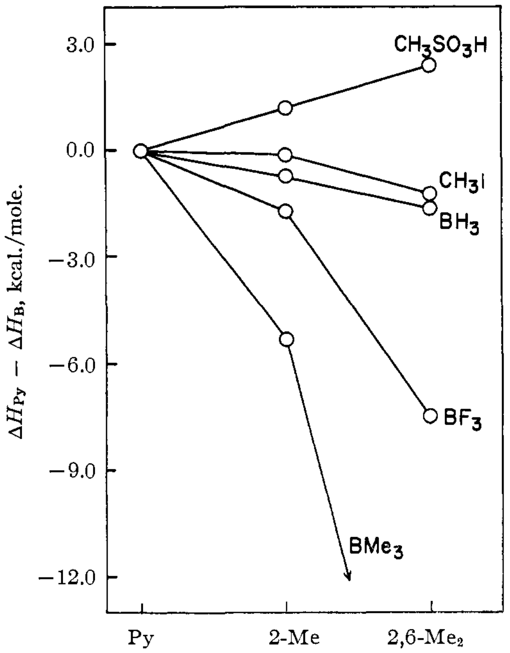

Fig. 1.—Comparison of methyl iodide and the Lewis acids in their effect upon the relative strengths of pyridine, 2-picoline and 2,6-lutidine.

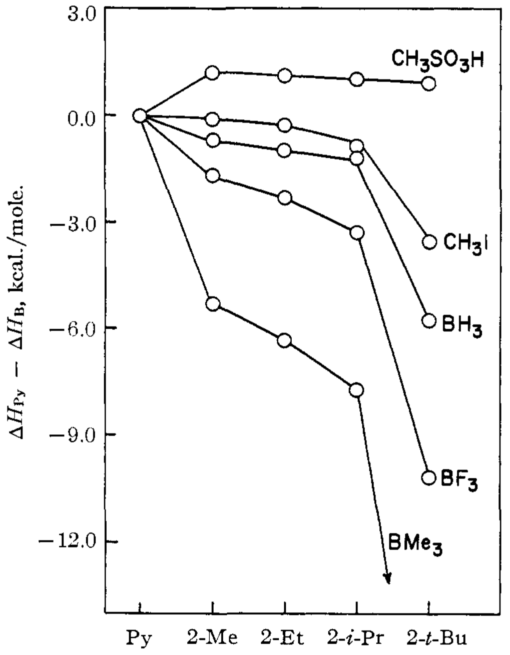

Fig. 2.—Comparison of methyl iodide and the Lewis acids in their effect upon the relative strengths of pyridine and the 2-alkylpyridines.

with the original thesis that the relative strengths of a group of related bases will be a function of the steric requirements of the reference acid.[8]

Strains in Homomorphic Structures.—The synthesis of addition compounds which are related to di-*t*-butylmethane,[13] *o*-*t*-butyltoluene,[10b,d] and hemimellitene[10b] permit an estimate of the strains in such homomorphic structures. Where it has

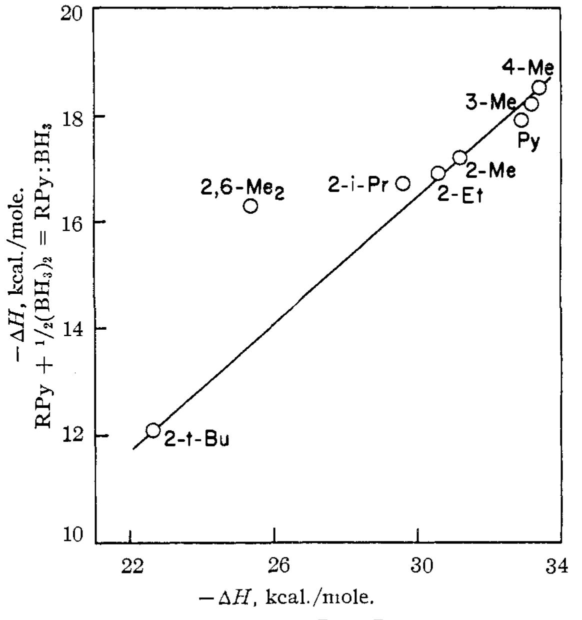

Fig. 3.—Relationship between the heats of reaction of the pyridine bases with diborane and boron trifluoride.

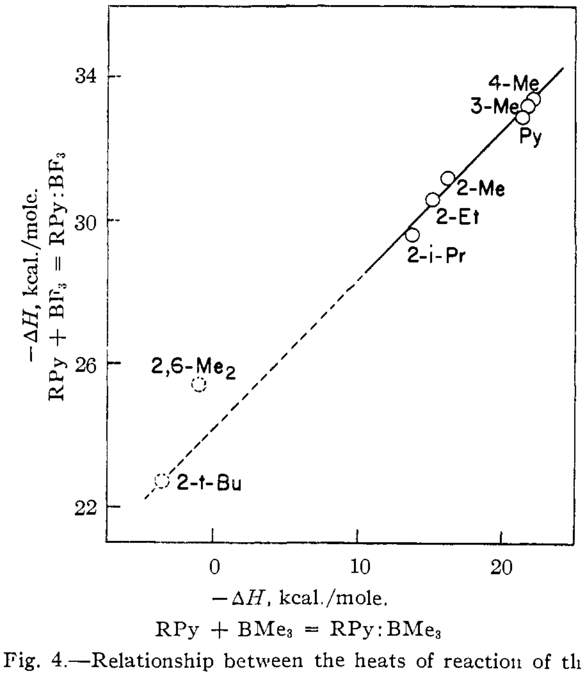

Fig. 4.—Relationship between the heats of reaction of the pyridine bases with boron trifluoride and trimethylboron.

proved possible to estimate the strains in two or three related homomorphs, the results have yielded excellent agreement.

For example, from the difference in the heat of dissociation of *n*-butylamine–trimethylboron (18.4 kcal./mole) and *t*-butylamine–trimethylboron (13.0 kcal./mole), the strain in the latter compound is estimated as 5.4 kcal./mole.[13] From the discrepancy between the calculated and observed heat of combustion of di-*t*-butylmethane,[14] the strain in

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[13] H. C. Brown and G. K. Barbaras, THIS JOURNAL, **75**, 6 (1953).

[14] W. H. Johnston, E. J. Prosen and F. D. Rossini, *J. Research Natl. Bur. Standards*, **38**, 419 (1947).

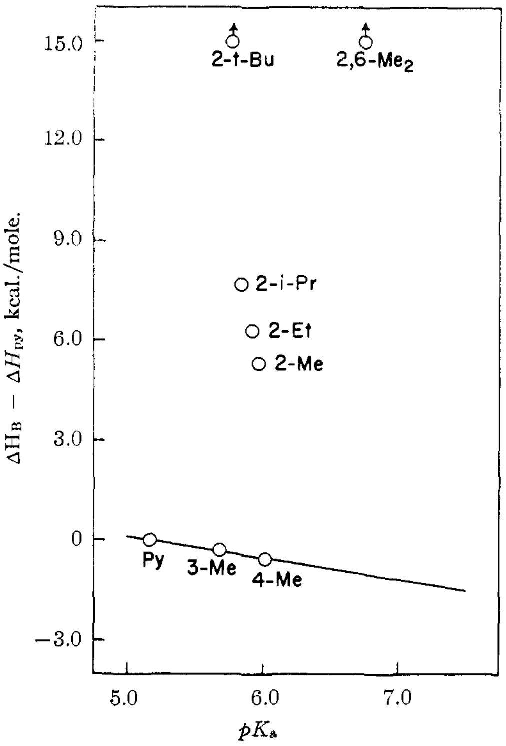

Fig. 5.—Relationship between strengths of alkylpyridine bases and their heats of reaction with trimethylboron.

this hydrocarbon may be estimated as 5.2 kcal./mole.[15]

Similarly, the strain in 2-*t*-butylpyridine–borane has been estimated as 6.3 kcal./mole,[8b] that in 2-picoline–trimethylboron as 5.9 kcal./mole,[8d] while *o*-*t*-butyltoluene is 5.6 kcal./mole less stable than the *m*- and *p*-isomers.[16]

Strains of 2.7 kcal./mole are observed in 2,6-lutidine–borane, while the difference in the heats of combustion of hemimellitene and mesitylene suggests strains of 1.6 kcal./mole. Since the latter value represents a small difference between large heats of combustion, it is believed that the former value is more reliable. Strain of 2.7 kcal./mole is therefore assigned to homomorphs of hemimellitene.[8d]

All attempts to prepare homomorphs with the *o*-di-*t*-butylbenzene[17] or the 2,6-dimethyl-*t*-butylbenzene[18] structure have failed. However, it appears that an estimate can be made of the strains present in *o*-di-*t*-butylbenzene and a minimum value set for the strains in 2,6-dimethyl-*t*-butylbenzene by utilizing the data reported in this group of papers.

Even though the steric requirements of borane are considerably less than those of boron trifluoride, it is possible to show a reasonably good linear relationship (Fig. 3) between the heats of reaction of pyridine and the 2-monoalkylpyridines with diborane and boron trifluoride. (The position of 2,6-lutidine will be considered later.) It is assumed that a similar linear strain energy relationship will exist between the heats of reaction of these bases with boron trifluoride and trimethylboron (Fig. 4). On this basis, Δ*H* for the reaction of trimethylboron with 2-*t*-butylpyridine can be estimated as +3.5 kcal./mole and the strain in homomorphs of *o*-di-*t*-butylbenzene estimated to be 25.5 kcal./mole.

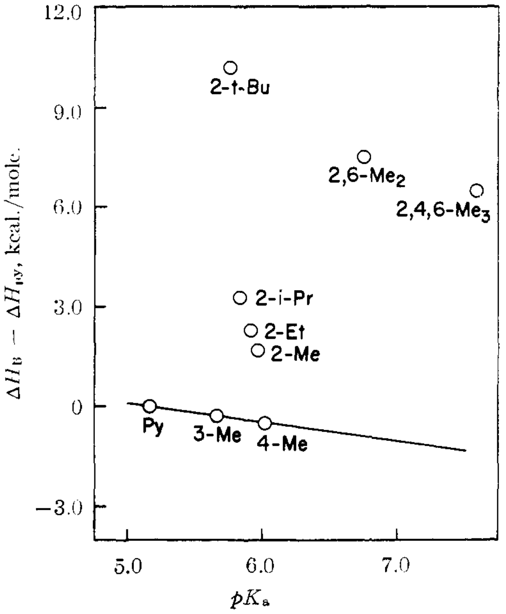

Fig. 6.—Relationship between the strengths of the alkylpyridine bases and their heats of reaction with boron trifluoride.

As was pointed out earlier, the linear strain energy relationship appears to be able to accommodate large steric interaction on one side of the adding group, but steric interaction on both sides appears to cause a breakdown.[19] This is indicated by the position of 2,6-lutidine in Fig. 3.

A factor of 4 is observed between the strain in 2-picoline–boron trifluoride and that in 2,6-lutidine–boron trifluoride. If we assume that a similar factor will hold for the strains in 2-picoline–trimethylboron and 2,6-lutidine–trimethylboron, we arrive at an estimate of 24 kcal./mole for the strain in this addition compound and its homomorphs.

In essence this treatment is equivalent to the assumption that disubstitution will produce a displacement of 2,6-lutidine in Fig. 4 equivalent to that observed for this base in Fig. 3.

These estimated strains are quite large. However, the carbon–carbon bond strength is considerably greater. Consequently, the existence of *o*-di-*t*-butylbenzene and 2,6-dimethyl-*t*-butylbenzene appears quite possible. The synthesis will probably require reactions of unusually high driving forces and the avoidance of conditions conducive to molecular rearrangement and isomerization.

The available results and estimated strains in homomorphic systems are summarized in Table II.

Some fifteen years ago it was suggested that the quantitative study of molecular addition compounds should provide a versatile technique for studying steric strains as well as other types of in-

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(15) H. C. Brown, G. K. Barbaras, H. L. Berneis, W. H. Bonner, R. B. Johannesen, M. Grayson and K. L. Nelson, THIS JOURNAL, **75**, 1 (1953).

(16) Private communication from E. J. Prosen.

(17) H. C. Brown and K. L. Nelson, THIS JOURNAL, **75**, 24 (1953).

(18) H. C. Brown and M. Grayson, *ibid.*, **75**, 20 (1953).

(19) H. C. Brown, D. Gintis and H. Podall, *ibid.*, **78**, 5375 (1956).

teractions related to molecular structures.[8] The intervening years have seen ample verification for this proposal. It is our belief that the full possibilities of this approach have yet to be realized and we wish to encourage other workers to adopt this technique for the study of structural problems.

Steric Requirements of the Transition State.— It has been pointed out that the phenomena observed in typical displacement reactions resemble closely those noted in the behavior of related addition compounds.[20] It was therefore suggested that the steric strains in the transition states (I) of such displacement reactions might be very similar to the strains in addition compounds of related structures (II).

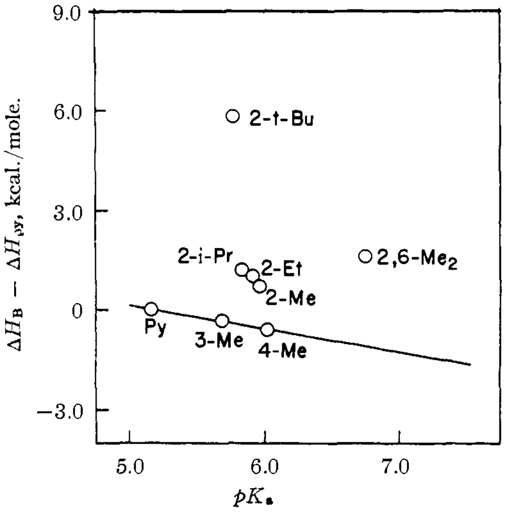
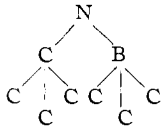
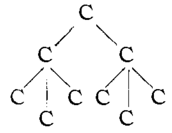
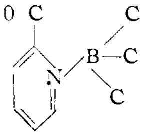
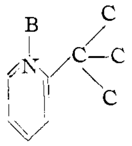
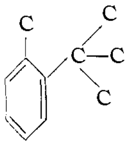
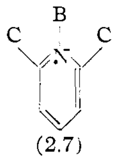
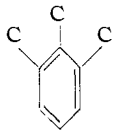
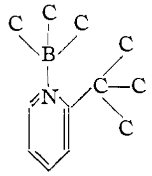
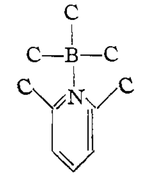


Fig. 7.—Relationship between the strengths of the alkylpyridine bases and their heats of reaction with diborane.

TABLE II

STERIC STRAINS IN RELATED HOMOMORPHS

Parent homomorph	Assigned strain	Structures (strains in kcal./mole)
Di-*t*-butylmethane	5.3	 (5.4)  (5.2)
o-*t*-Butyltoluene	6.0	 (5.9)  (6.3)  (5.6)
Hemimellitene	2.7	 (2.7)  (1.6)
o-Di-*t*-butylbenzene	25.5	 (25.5)[a]
2,6-Dimethyl-*t*-butylbenzene	24	 (24)[a]

[a] Estimated from Fig. 4.

A linear energy relationship was realized between the reactions of monoalkylpyridines with methyl iodide and boron trifluoride.[10c] However, this relationship broke down in attempting to extend it to pyridine bases containing two alkyl substituents in the *ortho* positions.[19] The breakdown was attributed to the large steric requirements of the boron trifluoride group in the addition compounds (II) as compared to those of the methyl group in the transi-

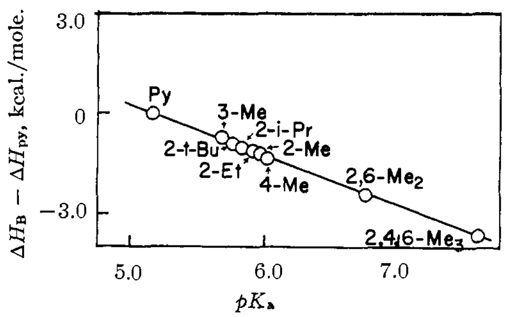


Fig. 8.—Relationship between the strengths of the alkylpyridine bases and their heats of reaction with methanesulfonic acid.

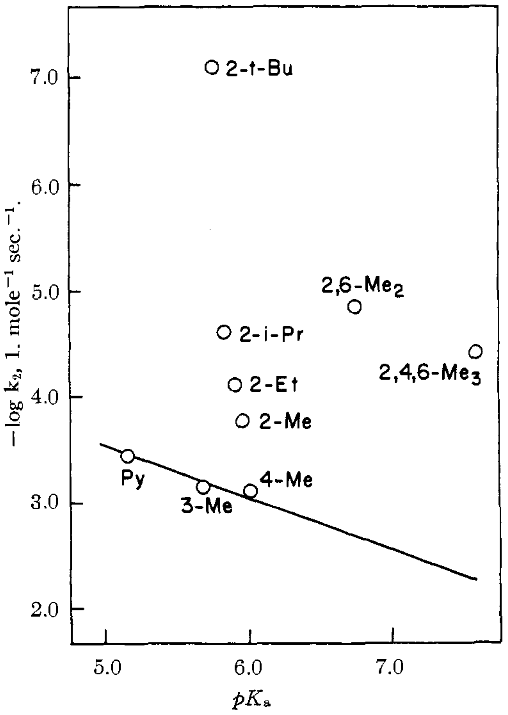


Fig. 9.—Relationship between the strengths of the alkylpyridine bases and their rates of reaction with methyl iodide.

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[20] H. C. Brown and A. Cahn, THIS JOURNAL, **77**, 1715 (1955).

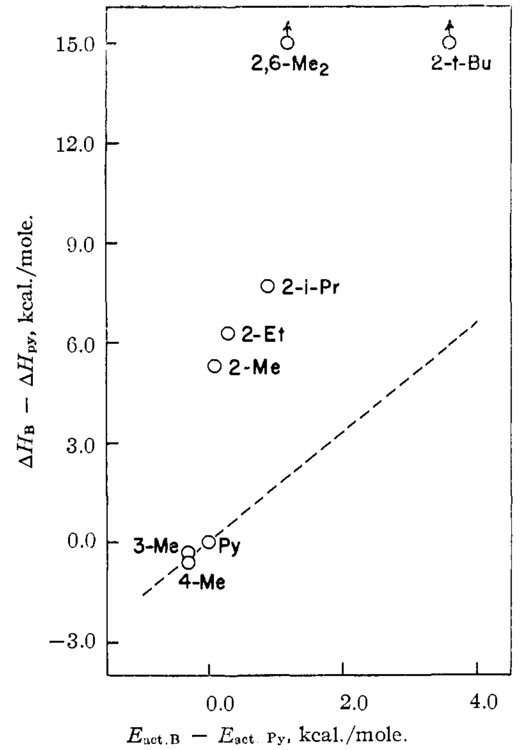
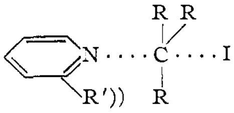


Fig. 10.—Relationship between the energies of activation for the reaction of methyl iodide with the alkylpyridines and the heats of reaction of these bases with trimethylboron.

tion states (I). It appeared that the borane addition compounds should provide much better models for comparison with the transition states. The available data now permit a critical examination of the proposal that selected addition compounds of the pyridine bases may serve as suitable models for the transition states of displacement reactions involving these pyridine bases.



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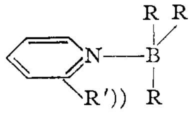

II

It was pointed out that pyridine, 2-picoline and 2,6-lutidine constitute a closely related series of bases of increasing steric requirements. In aqueous solution the order of base strength is pyridine < 2-picoline < 2,6-lutidine. As the steric requirements of the reference acid are increased ($CH_3SO_3H < BH_3 < BF_3 < BMe_3$), there is observed a regular and progressive change in the order to: pyridine >> 2-picoline >> 2,6-lutidine.

An examination of the activation energies for the reactions of methyl iodide with these three bases reveals a similar behavior. Indeed, if the activation energy data are treated in the same fashion as the heat of reaction data for the addition compounds, the three bases define a line which bears a marked similarity to that for borane (Fig. 1). In the same way the activation energy data for the 2-alkylpyridines define a line which is just above that for borane (Fig. 2).

The marked similarity in the activation energy curves in the two cases to those observed for the reaction of the different reference acids supports the thesis that strains in the transition state may be related to strains in molecular addition compounds of similar steric requirements.

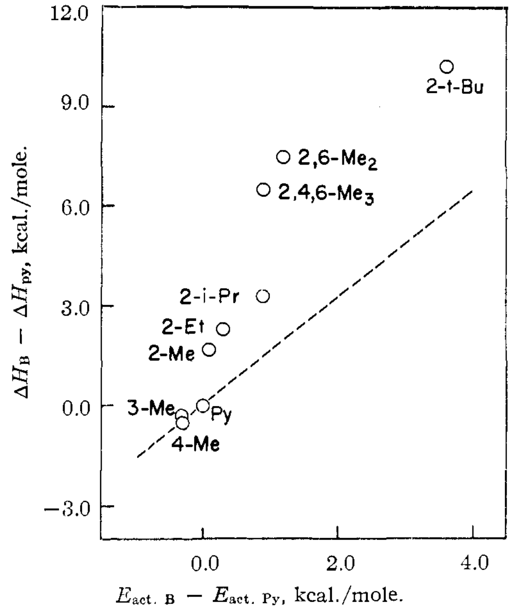

Fig. 11.—Relationship between the energies of activation for the reaction of methyl iodide with the alkylpyridines and the heats of reaction of these bases with boron trifluoride.

Linear Energy Relationships Involving Addition Compounds.—It was pointed out by Hammett that numerous linear free energy relationships exist for rate and equilibrium data involving *meta* and *para* aromatic derivatives.[21,22] *Ortho* substituted compounds do not conform to the relationship. The existence of linear relationships for the *meta* and *para* derivatives is believed to indicate that such substituents influence the reactions largely through their electronic effect on the potential energies of the reacting molecules. The failure of the *ortho* substituted compounds to conform is attributed to the fact that in addition to the electronic influence of the substituent it may alter the reaction rate or equilibrium through its steric requirements, through steric inhibition of resonance, hydrogen bonding, etc.

Ortho substituted pyridine bases appear to be relatively free from many of these complications, including internal hydrogen bonding and steric inhibition of resonance. Consequently, such pyridine bases appear to constitute an excellent reference system for investigating the nature and magnitude of these *ortho* effects.[23]

Accordingly, it appeared desirable to examine the possible existence of linear energy relationships between the heats of reaction of various reference

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[21] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

[22] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[23] Deviations exhibited by *ortho* derivatives from such linear energy relationships have been used to estimate the importance of F-strain, steric inhibition of resonance and hydrogen bonding in the ionization of *ortho* substituted benzoic acids, phenylboric acids, phenols, thiophenols and anilines; D. H. McDaniel and H. C. Brown, THIS JOURNAL, **77**, 3756 (1955).

acids with the alkylpyridines and their pK_a values. The results are shown in Figs. 5–8 in the order of decreasing steric requirements of the reference acid: $Me_3B > BF_3 > BH_3 > HO_3SCH_3$. In order to facilitate comparison the scales used for the ordinate and abscissa have been maintained constant.

In Fig. 5 the points for pyridine, 3- and 4-picoline exhibit a reasonably good linear relationship. However, the 2-alkylpyridines deviate from this line and the extent of the deviation, given by the vertical displacement from the line, increases with increasing steric requirements of the alkyl substituent: 2-Me < 2-Et < 2-*i*-Pr << 2-*t*-Bu, 2,6-Me$_2$. It should be pointed out the points for 2-*t*-butylpyridine and 2,6-lutidine represent minimum values and the actual values would probably lie considerably higher.

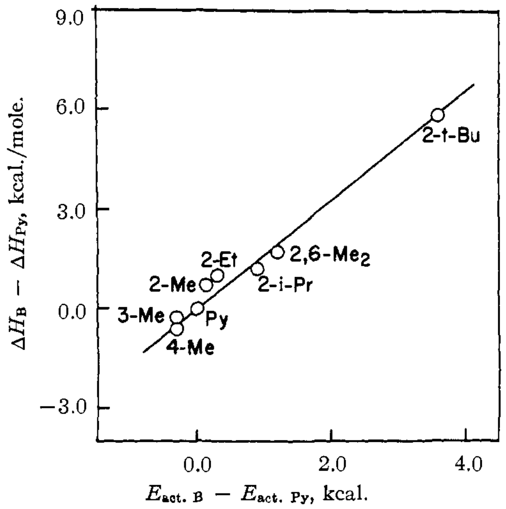

Fig. 12.—Relationship between the energies of activation for the reaction of methyl iodide with the alkylpyridines and the heats of reaction of these bases with diborane.

With boron trifluoride (Fig. 6), a linear relationship is likewise observed for pyridine, 3- and 4-picoline. Here also the 2-alkylpyridines deviate. However, the deviation is considerably less than in the case of the trimethylboron.

The deviations are even less in the case of borane as the reference acid (Fig. 7). Finally, with methanesulfonic acid as the reference acid (Fig. 8), all points give an excellent linear relationship.

It is evident that where the steric requirements of the reaction on the ordinate are greater than that of the abscissa, deviations from a linear energy relationship occur and the extent of the deviation is related to the steric requirements of the reference acid. Where the steric requirements of the two reactions are similar, an excellent linear energy relationship is realized.

In previous papers the strains in molecular addition compounds were based upon differences between the observed and calculated heats of reactions. The vertical displacement of each point from the lines in Figs. 5–8 provides a more elegant procedure for estimating the strains.

Linear Energy Relationships[24] Involving the Displacement Reaction.—Rate as well as equilibrium data may be utilized in the Hammett treatment. Accordingly, we examined the behavior of our data for the reaction of methyl iodide with the pyridine bases in this treatment (Fig. 9).

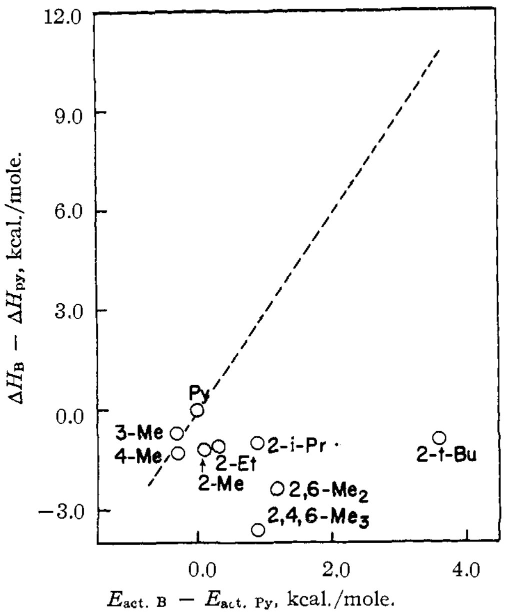

Fig. 13.—Relationship between the energies of activation for the reaction of methyl iodide with the alkylpyridines and the heats of reaction of these bases with methanesulfonic acid.

The spread between the rate data for pyridine, 3- and 4-picoline is smaller than for the addition compounds and the data do not clearly define the line. However, it is clear that the 2-alkylpyridines and 2,6-lutidine values deviate markedly from any probable line and the extent of the deviation increases with the increasing steric requirements.

The results are so similar to those observed in the corresponding plots for the addition compounds (Figs. 5–8), that there can be little doubt that identical phenomena must be responsible for the deviations in the two systems.

The possible existence of linear energy relationships between the heat of reaction data and the rate data was next examined. In Figs. 10–13 are plotted the heat of reaction data (as ordinate), in order of decreasing steric requirements of the reference acid, against the activation energy for the methyl iodide reaction (as abscissa).

With trimethylboron (Fig. 10) large deviations are observed. These decrease with boron trifluoride (Fig. 11). A linear relationship, including even the disubstituted base, 2,6-lutidine, is realized with borane (Fig. 12). Finally, with methanesulfonic acid (Fig. 13), the deviations are in the opposite direction.

In other words, where the steric requirements of the reaction on the ordinate are *greater* than those of the reaction on the abscissa, the *ortho* substituted bases lie *above* the line defined by pyridine and the

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[24] Other linear strain energy relationships have been explored by R. Taft. He has also proposed an interesting new approach to the deviations exhibited by *ortho* substituted benzene derivatives to the Hammett treatment. R. Taft, THIS JOURNAL, **74**, 2729, 3120 (1952); **75**, 4231, 4534, 4538 (1953).

3- and 4-substituted bases. Where the steric requirements of the ordinate reaction are *less* than those of the abscissa reaction, the *ortho* substituted bases lie *below* the line. When the steric requirements of the two reactions are similar (Figs. 8, 12), all of the points lie on a single line.

Strains in the Transition State.—From the available data the steric requirements of a borane group in an addition compound must be quite similar to the steric requirements of a methyl group in a hydrocarbon. However, in the transition state (I) the geometry of the methyl group must be quite different from that of the borane group (II). It is therefore pertinent to inquire into the relative strains observed in an addition compound with the strains in the corresponding transition state.

In the reaction of methyl iodide with 2-*t*-butylpyridine the activation energy is 3.8–3.9 kcal./mole greater than in the corresponding reactions of 4-alkylpyridines. Consequently, it is considered that strain of this magnitude must be present in the transition state. The strain in the homomorphs of *o*-*t*-butyltoluene is considerably larger, 6.0 kcal./mole (Table II).

Similarly, from the activation energy for the reaction of pyridine and 4-picoline with methyl iodide, an activation energy of 13.3 kcal. is estimated for 2,6-lutidine. In view of the observed value, 15.1 kcal./mole, a strain of 1.8 kcal./mole is calculated for the transition state in the reaction of methyl iodide with 2,6-lutidine. An identical value is obtained for 2,4,6-collidine. The strain in homomorphs of hemimellitene is estimated to be 2.7 kcal./mole (Table II).

Thus, both in the transition state involving 2-*t*-butylpyridine and that involving 2,6-lutidine the strain estimated is approximately two-thirds the value of the strains present in the homomorphic addition compounds. If this simple relationship proves to hold in other, more hindered systems, it should provide a valuable insight into the geometry and structure of the transition state.

In conclusion, it appears that the results support the proposal that molecular addition compounds of the pyridine bases may serve as reasonably good models for transition states involving these bases and alkyl halides. Consequently, it may be hoped that the study of selected series of addition compounds may contribute to a better understanding of the precise nature of the transition states in related chemical reactions.

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[CONTRIBUTION FROM THE INSTITUTE OF RUBBER RESEARCH, UNIVERSITY OF AKRON]

The Branching Reaction. I. Chain Transfer of Styrene with Thiol, Alcohol and Nitrile[1]

BY MAURICE MORTON, J. A. CALA AND IRJA PIIRMA

RECEIVED FEBRUARY 21, 1956

The chain transfer activity of 2-methyl-2-propanethiol, 2-methylpropionitrile, 2-propanol and 2-methyl-2-propanol in the polymerization of styrene was measured. This work was intended to measure the relative ease of formation of certain sulfur-, oxygen- or carbon-headed free radicals and thus to establish the relative activity of these radicals in abstracting hydrogen from a given compound, as it may apply to the formation of branches on a polymer chain. The following values were obtained for the rate expressions for the transfer reaction between a styrene radical and each respective compound: 2-methyl-2-propanethiol, $1.0 \times 10^6 \exp(4400/RT)$; 2-methylpropionitrile, $2.0 \times 10^6 \exp(10400/RT)$; 2-propanol, $2.3 \times 10^6 \exp(12500/RT)$; 2-methyl-2-propanol, $4.2 \times 10^6 \exp(13800/RT)$. Furthermore, measurements of the isotope effect with deuterium indicate that it is the hydroxyl hydrogen in the tertiary alcohol and the secondary hydrogen in the secondary alcohol which are involved in the chain transfer. Hence some conclusions can be drawn concerning the reactivity of the corresponding radicals in abstracting hydrogen atom. In general, the oxygen-headed free radical can be expected to be the most reactive in this respect. However, since it would only be ten to one hundred times as reactive as a carbon-headed radical, this suggests that the initiator radical could not be expected to play a major role in the branching reaction.

In the polymerization of olefinic compounds branched chains can be formed whenever a growing chain undergoes a chain transfer reaction with either a monomer or a polymer molecule. Monomer chain transfer, however, leads only to the formation of a terminal double bond in the polymer chain, and it is this double bond which can ostensibly be incorporated into another polymer chain, leading to a branched chain. Hence a monomer transfer step does not by itself lead to a branched chain but only opens the possibility of such a branched chain. Chain transfer constants for several monomers have been determined,[2-4] and these may help in estimating the possible frequency of branched chains.

It is, therefore, safe to assume that the formation of branched chains occurs predominantly through chain transfer between radicals and polymer chains, generally by abstraction of hydrogen (or other atoms) from the polymer. One of the questions which often arises concerning polymeric chain transfer is whether the attacking radical is more likely to be an initiator fragment or the chain radical itself. In view of the great predominance in concentration of the latter over the former, one

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(2) J. L. O'Brien and F. Gornick, THIS JOURNAL, **77**, 4757 (1955).

(3) F. R. Mayo, R. A. Gregg and M. S. Matheson, *ibid.*, **73**, 1691 (1951).

(4) B. Baysal and A. V. Tobolsky, *J. Polymer Sci.*, **8**, 529 (1952).