is characterized by broadening of the absorption bands in the 1000-1400-cm^{-1} region. Other optical experiments on (TTF)(TCNQ) in the infrared[42] suggest that a vibrational band at $\sim$1200 cm^{-1} is involved in the electron-optical phonon interference effects observed. It may be possible that these phenomena are associated with one of the two molecular vibrations (i.e., $\omega_1' = 1264$ cm^{-1}) that we have identified as active in the lowest electronic transition of TCNQ$\cdot^-$. This would imply that the deformation of TCNQ$\cdot^-$ due to polarization by charge carriers is similar to that occurring on photon excitation.

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Heats of Alkylation of Substituted Pyridines. A Comparison of Carbon Basicity, Proton Affinity, and Nucleophilicity

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Abstract: Heats of reaction for a series of pyridines with methyl and ethyl fluorosulfonate in nonbasic solvents are reported. These correlate well with the equivalent protonation heats in fluorosulfuric acid and the gas phase. Furthermore, a remarkably good correlation ($r = 0.968$) is found between heats of ethylation for a series of pyridines and the free energies of activation for their reaction with ethyl iodide.[2] Apparently, charge delocalization in the pyridine ring is an important factor in all of these reactions, but some difficulties in specifying the reaction coordinate for this "simple" reaction are considered.

By virtue of their planar ring structure in which a basic *n*-electron pair is coupled to a polarizable π system, the pyridines are an ideal series for the quantitative investigation of electronic factors in nucleophilic substitution. This role was previously overshadowed by the brilliant studies of Brown,[1,2] who used alkylated pyridines to demonstrate the importance of steric effects and, hence, deliberately employed systems in which electronic variations would be minimized.

Recently Taft,[3-5] Beauchamp,[3] Liotta,[6] Aue,[7] Katritsky,[8] and their colleagues, as well as a number of other workers,[9] have developed a considerable body of good thermodynamic data for the protonation of pyridines, covering a broad range of electron-attracting and -releasing groups both in the gas phase[3,5,7] and in solution.[6,8,9] It is now clear that there is a close correlation between the response of ring substituents to the development of positive charge on the pyridine nitrogen atom by gas-phase protonation,[3,4,5,7] by

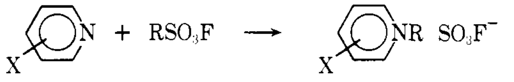
Table I[a]

Substituted pyridine	ΔH_{Rx}, $MeSO_3F$ $\epsilon = 42$ sulfolane	ΔH_{Rx}, $EtSO_3F$ Nitrobenzene	ΔH_{Rx} $MeSO_3F$ $\epsilon = 34.8$, $\delta = 11.1$ Nitrobenzene	ΔH_{Rx} $MeSO_3F$ $\epsilon = 64.4$, $\delta = 13.3$ Propylene carbonate
Quinuclidine	−45.38 ± 0.24			
4-MeO	−38.57 ± 0.55	−35.91 ± 0.36	−38.22	−39.04
4-Me	−37.49 ± 0.26	−34.92 ± 0.51		
3,5-$(Me)_2$		−34.96 ± 0.25		
H	−36.17 ± 0.46	−32.81 ± 0.48	−36.02	−37.07
2,4,6-$(Me)_3$	−35.33 ± 0.26			
3-Cl	−32.22 ± 0.24	−26.1[b]	−32.03	−33.45
4-CF_3	−31.69 ± 0.15			
4-CN	−31.56 ± 0.47	−24.3[b]	−31.07	
3-Br	−31.26 ± 0.26	−27.2[b]	−31.10	−33.95
3,5-$(Cl)_2$	−28.59 ± 0.57	−21.2[b]		
2-Cl	−25.63 ± 0.72			
2-F	−23.96 ± 0.32			

[a] ΔH_{soln} $MeSO_3F$ → sulfolane, +0.56 ± 0.05; ΔH_{soln} $EtSO_3F$ → $PhNO_2$, +0.57 ± 0.05. Values of dielectric constant ϵ and Hildebrand's δ are from ref 22. [b] Estimate due to slow reaction.

lone-pair ionization through photoelectronic excitation,[10] or by protonation in water[6,8,9] or fluorosulfuric acid.[11]

The exploitation of alkyl fluorosulfonates as potent alkylating agents[12,13] in reaction 1 provides us now with a simple


(1)

thermochemical means for comparing substituent effects on alkylation vs. protonation and also the relationship between thermodynamics and kinetics of quaternization, a classic nucleophilic displacement reaction. As will be seen below, the quarternization of pyridines with methyl and ethyl fluorosulfonates is extremely rapid, exothermic, and complete at room temperature in sulfolane and nitrobenzene. Substituent effects on the heats of this nucleophilic substitution reaction (ΔH_{Rx}) are large and provide instructive comparisons with other recently reported means of perturbing charge distribution in these same systems.

Experimental Section

The solution calorimeter and techniques for using it have been described previously elsewhere.[15] Heat of solution measurements were made for solids by injecting a weighed amount of the purified sample contained in an airtight syringe into the calorimeter containing the solvent.[15] Liquid samples were injected from airtight calibrated syringes. Heat of reaction measurements were made by injecting the electrophile (RSO_3F) into a solution of a known excess of the nucleophile in the specified solvent. Several concentrations of nucleophile were run to ensure that enthalpy measurements were not concentration dependent. During measurements the calorimeter was purged constantly with dried argon. Systematic errors were prevented by frequently checking our procedure against well-accepted values for the heat of solution for ethanol into water, and potassium chloride into water.

A variation of Coetzee's method[16] was used in the purification of sulfolane. Sulfolane was stirred with sodium hydroxide pellets (15 g/l. of solvent) while being purged with nitrogen at 170-180 °C for 24 h to remove 3-sulfolene and other acidic impurities. It was then stirred for 6 h with decolorizing carbon (15 g/l.) at 80-90 °C and filtered. Instead of running the remaining solvent through a macroporous mixed bed acid-base resin column as recommended by Coetzee, it was vacuum distilled from a mixture of sulfuric acid and fuming sulfuric acid, 15 g of the mixture per liter of solvent. The ratio of the acid mixture was calculated so that there was just enough excess SO_3 to react with the water in the sulfolane and sulfuric acid. The water content was monitored by Karl Fischer titration, using a Photovolt Aquatest II. The sulfolane was then again vacuum distilled; the distillate, containing less than 20 μ of water per milliliter of solvent, agrees with Coetzee's melting point[16] and formed stable solutions with strong acids.

Nitrobenzene was purified by distillation as described by Brown.[17]

Methyl fluorosulfonate (Magic Methyl) from Aldrich Chemical Co. was distilled under a 1-atm dry argon atmosphere and stored under argon in a freezer. Ethyl fluorosulfonate, also from Aldrich Chemical Co., was distilled under 100-mm pressure and stored under argon in a freezer. Pyridines were all available commercially.

Purity checks on reactants and products employed a Varian A-60 NMR or a Hewlett-Packard 5700 A gas chromatograph with a 9-ft nonpolar column, 10% SF-96 silicone fluid (Chemical Research Services, Inc.) on Chromosorb W-hp 80-100 mesh (Johns-Manville), according to need.

Results

Methyl fluorosulfonate (Cationics), in carefully dried sulfolane solution, reacts instantly (within 5 sec) with the pyridines listed in Table I. Usually, seven replica increments of the alkylating agent were injected into a 1.2 × 10^{-2} M solution of the base at 30 °C in a standard solution calorimeter.[14] Comparable experiments with ethyl fluorosulfonate in nitrobenzene gave closely parallel results, but reactions were slow enough to yield detectable rates in most cases. ΔH_{Rx} is defined as the difference between the heat of solution of RSO_3F in the solution of substituted pyridine and the corresponding heat of solution of RSO_3F in the pure solvent.

Table I also shows virtually no difference between methylations in sulfolane and in nitrobenzene. Slightly more exothermic methylations were observed in propylene carbonate. Methylations with methyl fluorosulfonate were consistently more exothermic than were corresponding ethylations.

Discussion

In keeping with the observations of Taft[3,4] and Ramsey,[10] which show close correlation of gas-phase ionization of pyridines with pK_a's in water, Figure 1 portrays a good correlation ($r = 0.982$, slope = 1.78) between pK_a in water and ΔH_{Rx} (CH_3SO_3F) for comparison with the gas-phase data. Equally good correlations are found for ΔH_{Rx} with heats of ionization (ΔH_i) for the same pyridines in water and HSO_3F[11] provided that the 4-methoxy and 4-cyano derivatives are excluded from the latter plot. These substituents apparently act as strong hydrogen-bond acceptors from HSO_3F. By comparison with correlations of the properties against pK_a, Ramsey's[10] plot of the lone-pair ionization potential has $r = 0.961$, slope = 3.44; Taft's[3,4] $\Delta G_i°$(gas) has $r = 0.906$, slope = 2.17; and $\Delta H_i°$ in water has $r = 0.969$, slope = 1.31.

Pyridinium ions can form fairly strong $pyN^+H\text{-}S$ hydrogen bonds to solvent molecules, but quaternary methylpyridinium ions cannot. One could conclude from Figure 1 either that (a) hydrogen bonding to water is negligible for

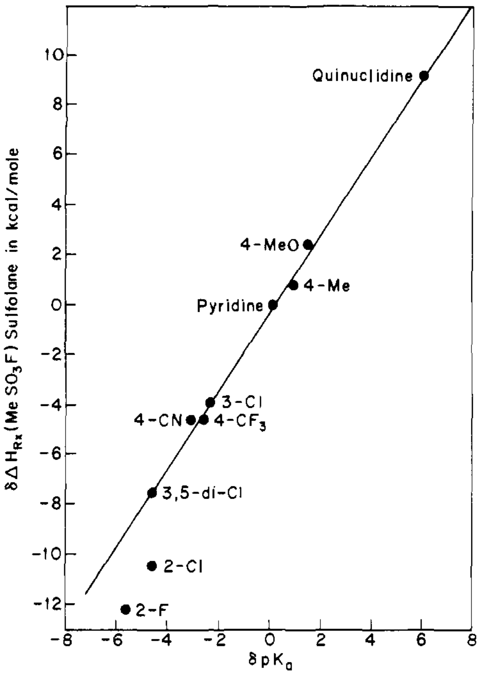


Figure 1. Heats of reaction of substituted pyridine with methyl fluorosulfonate in sulfolane vs. pK_a's of the same compound in water. All values are taken relative to pyridine.

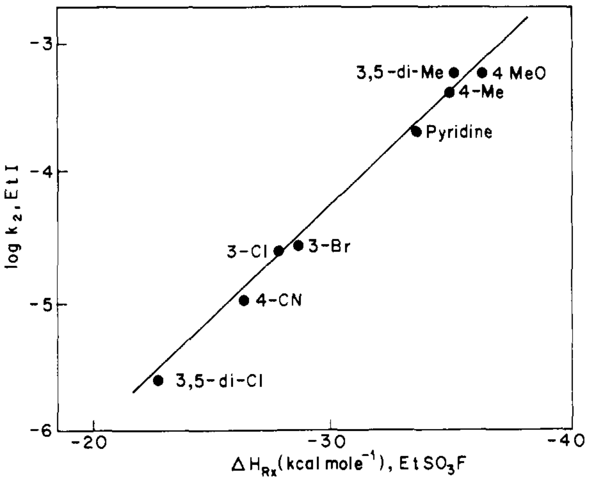


Figure 2. Correlation of rate data for Menschutkin reactions of substituted pyridines with ethyl iodide (ref 20) vs. heats of ethylation with ethyl fluorosulfonate; both reactions in nitrobenzene at 25 °C.

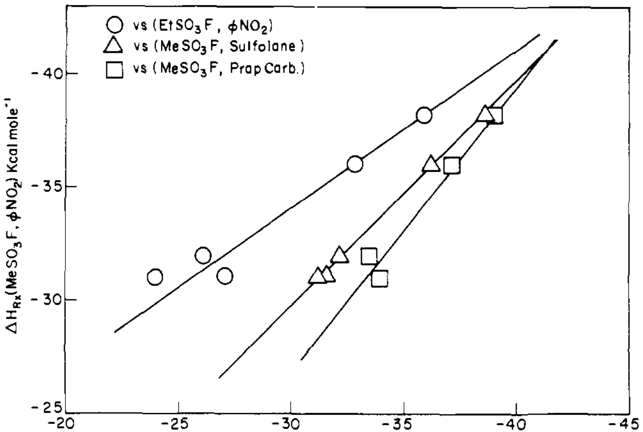


Figure 3. Correlation of heats of reaction for a series of pyridines with methyl fluorosulfonate in nitrobenzene with corresponding data in sulfolane and propylene carbonate and ethylation in nitrobenzene.

substituted pyridinium ions or (b) substituent effects on the strength of such bonds are proportional to the substituent effects on the other properties plotted in Figure 1. Alternative a may be rejected on the basis of measurements of solvation energies of pyridinium ions from the gas phase to water[18] and the NMR study of Delpuech[19] on proton exchange rates in aqueous acid.

Figure 2 compares relative free energies of activation (log k) for ethylation of eight pyridines by ethyl iodide in nitrobenzene[20] with ΔH_{Rx} by $C_2H_5SO_3F$ in the same solvent. Although the properties and processes are entirely different, a close parallel ($r = 0.985$) is found: the pyridines which react most exothermically with ethyl fluorosulfonate give the fastest reactions with ethyl iodide. The Menschutkin reaction has enjoyed a long history of investigation ever since van Halban's[21] pioneering attempt to relate kinetics to thermodynamics for the quarternization of pyridine. The close relationship between the rate data of Fischer, Galloway, and Vaughan[20] for ethylation with our values of ΔH_{Rx} and, hence, to other criteria for charge development in pyridinium ions raises intriguing possibilities for transition state analysis if energies of activation were available for the reaction with alkyl fluorosulfonates. We intend to explore this question.

As things stand, the modest slope of Figure 2 suggests a relatively weak development of charge at the transition state in the iodide substitution compared with fluorosulfonate displacement. Abraham's[22] detailed analysis of solvent effects on the reaction of trimethylamine with methyl iodide implies a clear difference in response between the transition state and the ion-pair product. This contrasts with the earlier proposal of Glasstone, Laidler, and Eyring[23] that the "activated complex undoubtedly resembled the product", a viewpoint strongly supported by the entropy of activation and reaction.[24] The results of Haberfield[25] and Alder, Baker, and Brown[26] show a variable relationship between solvent effects on the reactants, products, and transition states for attack of a series of benzyl chlorides on pyridine. Wigfield and Lem[27] have considered solvent effects on rates of the Menschutkin reaction and concluded that the absence of large solvent effects on rates is not a strong argument against an ionic transition state. Some of the earlier history of solvent effects on this reaction are reviewed by Amis.[29] They do little to simplify interpretations of this reaction.

Consideration of Table I and Figure 3 leads to ranking the effect of dielectric constant or cohesive energy density on ΔH_{Rx} in the same order as would be expected for rate changes: high ϵ increases rates and leads to more exothermic reactions. Again much faster rates are associated with the more exothermic methylation reactions compared with ethylations. In the absence of some remarkable fortuities, the close correspondence between ΔH_{Rx} and log k_{EtI} implies that there is good proportionality all around between heats and free energies of activation and of reaction for ethylation with ethyl iodide and alkylation with the fluorosulfonates.

Consider for a typical Menschutkin reaction that the heat of activation for attack by methyl fluorosulfonate is 10 kcal/mol and that the heat of reaction is 30 kcal/mol. It is remarkable to see how faithfully a small change in lowering the energy of one process (say activation) is reflected in a change in the other (overall reaction) even though the transition state and final product are separated by 40 kcal/mol on a simple S_N2 reaction coordinate plot.

Clearly, on the basis of previous reports and the present case, the transition state for this formally simple displacement reaction is remarkably sensitive to substituent variation in the substrate, the nucleophile, and variation of solvent.

Recent evidence from a variety of sources has begun to elucidate the importance that desolvation of attacking anions can play in nucleophilic displacements. In the present instance, we are at least dealing with nucleophiles which do not require extensive desolvation and which are probably producing completely dissociated ions in the solvents used[28] at our working concentrations.

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Peri- and Regioselectivities of the Nickel(0)-Catalyzed Valence Isomerization of the 1,8-Bishomocubane System. A Molecular Orbital Consideration[1]

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Abstract: Skeletal isomerization of *cis*-9,10-dicarbomethoxypentacyclo[4.4.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]decane (**4**) with nickel(0) complexes has been investigated under various reaction conditions. In ordinary cases, *exo*- and *endo-cis*-9,10-dicarbomethoxytricyclo[4.2.2.$0^{2,5}$]deca-3,7-dienes (**5** and **6**) are produced in high yield. *cis*-9,10-Dicarbomethoxypentacyclo[4.4.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]decane (**7**), if any, is formed only in a small amount. The ease with which the isomerization takes place is profoundly influenced by the catalyst system employed. Bis(1,5-cyclooctadiene)nickel(0) or bis(acrylonitrile)nickel(0) alone does not effect the catalytic transformation. With the aid of appropriate ligands, such as electron-deficient olefins or triphenylphosphine, the isomerization proceeds smoothly, indicating that the formation of soluble, coordinatively unsaturated nickel(0) complexes is crucial for the isomerization of **4**. By the use of the catalyst system derived from bis(1,5-cyclooctadiene)nickel(0) and tetracyanoethylene, the dicyclopropyl isomer **7** is obtained as the major product. The production of Ni^{2+} species would be the cause of the change in the reaction course. The origin of the clean peri- and regioselectivities of the isomerization is explained in terms of the molecular orbital treatment. Judging from the shape of molecular orbitals of 1,8-bishomocubane, only the C(2)–C(5) and the structurally equivalent bonds can have a positive interaction with nickel(0) atom. The catalytic two-bond cleavage of **4** is considered to proceed by a mechanism involving the C(2)–C(5) edge-on coordination complex. The possibility of the concerted process through face-on metal coordination is ruled out.

Numerous examples have been presented of the transition metal-promoted skeletal change of strained polycyclic hydrocarbons.[2] Among a variety of hydrocarbon systems so far investigated, cubane (**1**) is particularly interesting in that the reaction course is dramatically dependent on the transition metal catalysts employed. Two types of symmetry-forbidden (in a formal sense) transformation can be possible with the aid of transition metals. For example, Rh(I) complexes promote the cleavage of a cyclobutane ring in a [$_\sigma 2_s + _\sigma 2_s$] fashion to give the tricyclooctadiene **2**.[3] In the presence of Ag^+ ion, the cyclobutane → diolefin conversion does not take place, but instead there is obtained the