atomic halogen complexes.[10-12] The reaction system which involved three different halogen atoms (Cl + IBr) demonstrated a preference for the geometry having the least electronegative atom in the central position, giving larger cross-section for ClI production (8 kcal/mol exoergicity) than for ClBr (10 kcal/mol exoergicity).

This same preferred geometry is evident in the present experiments. For the F_2 + ICl system prominent peaks in the mass spectrum of ClIF occurred at *m/e* 183 (^{37}ClIF) and *m/e* 181 (^{35}ClIF) as well as *m/e* 146 (IF), but not at *m/e* 56 (^{37}ClF) or *m/e* 54 (^{35}ClF). For F_2 + HI peaks from the ionization of HIF were observed at *m/e* 147 (HIF) and *m/e* 146 (IF), but not *m/e* 20 (HF). These results strongly suggest that the observed products are indeed ClIF and HIF with the F atom attached to I but not to Cl or H as IClF or IHF.

For trihalogen molecules of the type XY_2 or XYZ the most stable geometry is expected to be the one with the least electronegative atom in the central position. For all molecules with more than 12 valence electrons this general conclusion follows from the fact that the charge distribution of the π orbitals is generally more concentrated at the terminal atoms than at the center of the molecule.[13]

Simple theoretical arguments[14,15] predict the bonding in the trihalogen radicals to be similar to that in the trihalide anions. This prediction is borne out by the resemblance of Cl_3 to Cl_3^-.[5,16] These anions are linear or nearly linear and have vibrational force constants roughly one-half the value of those in the free halogens, corresponding to "half-bonds" in these anions.[17]

Additional experiments using hyperthermal molecular beams will undoubtedly be helpful in elucidating the properties and stabilities of triatomic halogen molecules. Studies of systems not involving iodine and fluorine would be especially interesting in the systematic exploration of the effect of changes in the end and central atom identifies on the stability of these molecules.

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A Quantitative Comparison of Gas- and Solution-Phase Basicities of Substituted Pyridines

Sir:

The separation of internal and external factors in the analysis of substituent effects is a longstanding problem in physical organic chemistry.[1,2] For proton transfer equilibria (eq 1) in aqueous solution, for example, the thermodynamic functions $\Delta H°$ and $T\Delta S°$ in water may be formally separated into terms arising from internal or gas-phase effects and external or solvation effects (eq 2 and 3).[3]

$$AH^+ + B \rightleftarrows A + BH^+ \tag{1}$$

$$\Delta H° = \Delta H°_{int} + \Delta H°_{ext} \tag{2}$$

$$T\Delta S° = T\Delta S°_{int} + T\Delta S°_{ext} \tag{3}$$

Analyses of the role of solvent on substituent effects for acid–base equilibria have been limited, however, by a lack of experimental data on which to base the separation of the internal and external substituent effects. Techniques for quantitative measurement of gas-phase basicities[4] provide a direct measure of internal substituent effects, and combination of these gas-phase proton affinity (PA) data with aqueous thermodynamic data allows an evaluation of solvent effects. Linear correlations of PA's and aqueous enthalpies of protonation ($\Delta H°_{prot,s}$) for alkylamines, for example, show that solvation causes a five- to sixfold attenuation of gas-phase basicity changes in solution.[4b,d] This attenuation can be interpreted in terms of electrostatic models relating the solvation energies of the ammonium ions to their charge densities.[4d] The availability of PA and $\Delta H°_{prot,s}$ values for 3- and 4-substituted pyridines now makes a quantitative analysis of the solvation terms $\Delta H°_{ext}$ possible for the important class of pyridine bases.[5-7] In addition, PA's and calorimetric heats of protonation (Table I) of 2-substituted pyridines have been measured for comparison.

The experimental PA and $\Delta H°_{prot,s}$ values for 3- and 4-substituted pyridines are summarized and correlated in Figure 1.[5-7] From the linearity of this plot (correlation coefficient = 0.996, slope = 2.59), it is clear that $\Delta H°$ is proportional to $\Delta H°_{int}$, and $\Delta H°_{int}$ is attenuated 2.6-fold in aqueous solution.[8] The proportionality of $\Delta H°_{int}$ and $\Delta H°$ and the defining equation (eq 2) also require that $\Delta H°_{ext}$ be proportional to $\Delta H°_{int}$ with a proportionality constant h of -0.61 for 3- and 4-substituents.

$$\Delta H°_{ext} = h\Delta H°_{int} \tag{4}$$

The heats of protonation of 2-substituted pyridines do not correlate as well with PA as for the 3- and 4-derivatives, and their slope indicates an attenuation of only 1.82 (correlation coefficient = 0.979). This smaller attenuation could be explained within the framework of Bjerrum and Kirkwood–Westheimer field effect theories[9] as a decrease in the effectiveness of solvent intervention between the charged center and the 2-substituents relative to the 3- and 4-substituents.

The free energy[3] correlations of PA and $\Delta G°_{prot,s}$ in Figure 2 are less precise than the enthalpy correlations in Fig-

Table I. Enthalpies of Protonation of Substituted Pyridines[a]

Substituent	$-\Delta H°_{prot,s}$	Substituent	$-\Delta H°_{prot,s}$
2-CN[b]	−0.91	$2\text{-}CH_2CH_3$	6.58
2-Cl[b]	0.25	$2\text{-}N(CH_3)_2$	7.08
2-Br[b]	0.47	$4\text{-}N(CH_3)_2$	11.73
$2\text{-}OCH_3$	3.88		

[a] Determined calorimetrically in aqueous perchloric acid. All values in kcal/mol. [b] Corrected for incomplete protonation, see ref 7a.

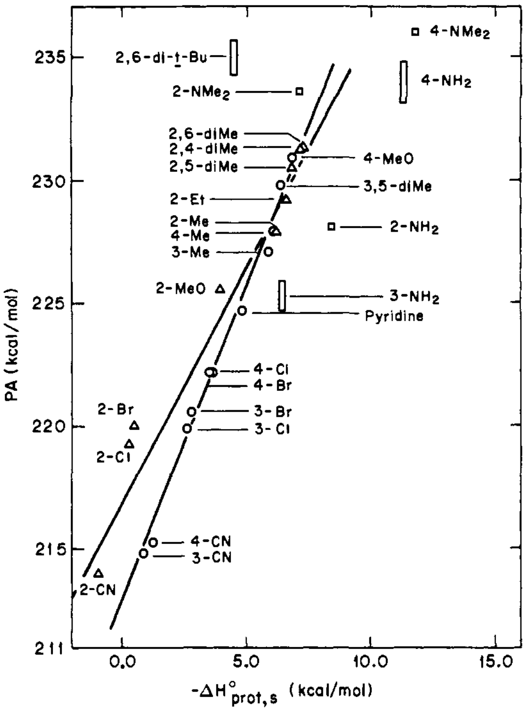

Figure 1. Plot of $\Delta H^\circ_{\mathrm{prot,s}}$ vs. PA for substituted pyridines.

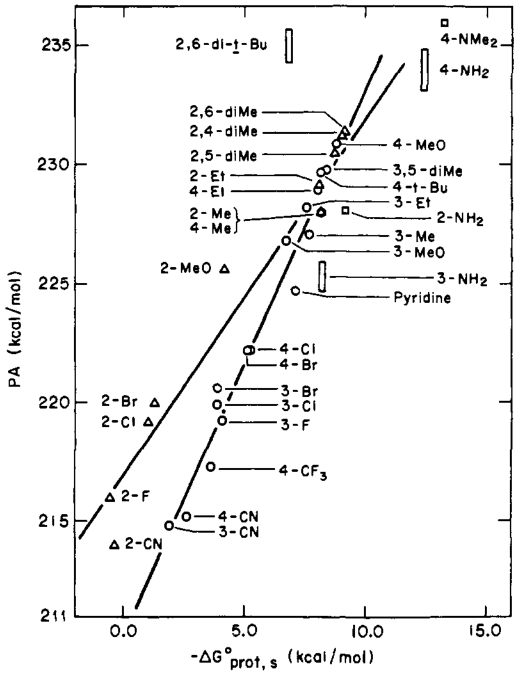

Figure 2. Plot of $\Delta G^\circ_{\mathrm{prot,s}}$ vs. PA for substituted pyridines at 25 °C.

ure 1 and show slightly smaller attentuation effects: for 3- and 4-substituents, slope = 2.31, correlation coefficients = 0.988; for 2-substituents, slope = 1.51, correlation coefficients = 0.968. These free energy correlations show a linear behavior, because the entropy terms, $-T\Delta S^\circ$, are also found to roughly correlate with PA, or $\Delta H^\circ_{\mathrm{int}}$. Since $-T\Delta S^\circ$ is nearly equal to $-T\Delta S^\circ_{\mathrm{ext}}$,[3] it follows that

$$-T\Delta S^\circ_{\mathrm{ext}} \cong Ts\Delta H^\circ_{\mathrm{int}} \qquad (5)$$

The proportionality constant Ts has a value of 0.09 (correlation coefficient = 0.80) for the 3- and 4-substituents and a value of 0.18 (correlation coefficient = 0.69) for the 2-substituents. The irregularities in these small entropy effects then cause the proportionately smaller irregularities observed in the free energy plots. It was originally suggested[2a] that ΔG° should equal $\Delta H^\circ_{\mathrm{int}}$ in acid-base equilibria such as eq 1. Hepler's modified theory, however, predicts that these quantities should simply be proportional.[2b,c] Our results in Figures 1 and 2 now confirm Hepler's suggested free energy correlation, and they also show that an even better correlation exists for ΔH° and $\Delta H^\circ_{\mathrm{int}}$.

The solvation effects, $\Delta G^\circ_{\mathrm{ext}}$, $\Delta H^\circ_{\mathrm{ext}}$, and $-T\Delta S^\circ_{\mathrm{ext}}$, arise from differences in the solvation of the neutral pyridines and their conjugate pyridinium ions.[10] Since they reflect the change induced by introduction of a proton and its attendant positive charge onto the neutral pyridine, these solvation effects may be regarded as electrostatic effects by this definition. Furthermore, since the $\Delta H^\circ_{\mathrm{int}}$ effects can be considered to be largely electrostatic in origin,[1d,4d] it is reasonable from Bjerrum or Born theories to expect that the thermodynamic parameters for solvation be proportional to $\Delta H^\circ_{\mathrm{int}}$ as expressed in eq 4 and 5.[9,11] From a comparison of other available gas-phase and solution-phase data, this appears to be a rather general phenomenon.[4d,12] The signs of h and s are in accord with predictions from such electrostatic theory,[13] i.e., $\Delta H^\circ_{\mathrm{ext}}$ effects oppose the $\Delta H^\circ_{\mathrm{int}}$ effects and $-T\Delta S^\circ_{\mathrm{ext}}$ tends to compensate the $\Delta H^\circ_{\mathrm{ext}}$ term.

The aminopyridines are exceptional among substituted pyridines because they are much more basic in solution than expected from the $\Delta G^\circ_{\mathrm{prot,s}}$ or $\Delta H^\circ_{\mathrm{prot,s}}$ correlations. Such behavior could be rationalized as resulting from strong solvation at a site of high positive charge density in the amino substituents. Interestingly, the dimethylamino derivatives also show such a deviation, suggesting that hydrogen bonding effects alone do not explain the deviation of the aminopyridines.

From a comparison of the proton affinity of 2,6-di-*tert*-butylpyridine and its estimated $\Delta G^\circ_{\mathrm{prot,s}}$ in water[14] with those of pyridines in Figure 2, an interesting deviation of ca. 3.5 kcal/mol is evident. Although $\Delta G^\circ_{\mathrm{prot,s}}$ of 2,6-dimethylpyridine shows rather normal behavior in solution, the 2,6-di-*tert*-butylpyridinium ion appears to be less well solvated than expected from these correlations, perhaps because of steric hindrance to solvation. Further studies on analogously substituted pyridines are in progress to clarify the solvation factors involved in these exceptional cases.

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Isomerization on Metals. Correlation between Metal Particle Size and Reaction Mechanisms

Sir:

Hydrogenolysis of methylcyclopentane and isomerization of hexanes on platinum belong to the class of catalytic reactions wherein the selectivity of the reaction depends upon the metal particle size. Previous work has shown that platinum-alumina catalysts of extremely high and low dispersion ($\bar{d}$ = 15 and 180 Å, respectively) behave in a very different way in these reactions. For example, nonselective hydrogenolysis of methylcyclopentane takes place on highly dispersed 0.2% Pt-Al_2O_3 catalyst with an almost equal chance of breaking all five cyclic carbon-carbon bonds (Figure 1a). On the other hand, the CH_2-CH_2 bonds are selectively ruptured on 10% Pt-Al_2O_3 of low dispersion (Figure 1b).[1] Moreover, labeling experiments have shown that isomerization of 2-methylpentane to 3-methylpentane proceeds almost exclusively according to a "cyclic" mechanism (CM) on the 0.2% Pt-Al_2O_3 catalyst, while the contribution of the alternative "bond shift" (BS) mechanism is predominant on 10% Pt-Al_2O_3 (Figure 2).[2]

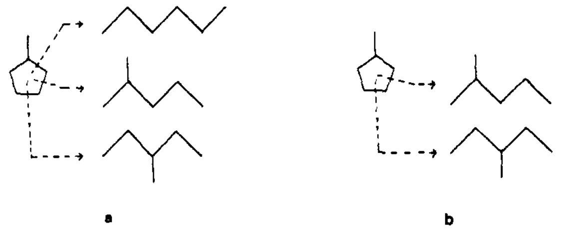


Figure 1.

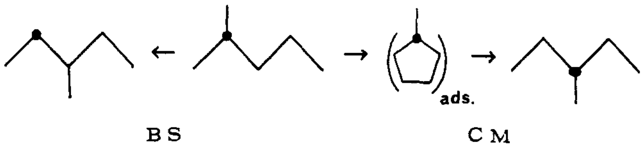
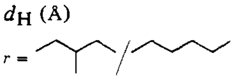
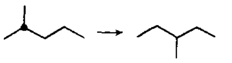
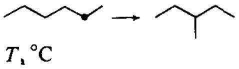


Figure 2.

We report in this note some preliminary results concerning the existing correlation between the metal particle size and the relative contributions of the various mechanisms (cyclic or bond shift for isomerization, selective or nonselective for methylcyclopentane hydrogenolysis). A set of seven Pt-Al_2O_3 catalysts with a mean metal particle size (d_H) ranging from 10 to 200 Å was prepared. The continuous change of metal dispersion, *a*, defined by the ratio between superficial and total platinum atoms and obtained from hydrogen chemisorption measurements, was effected by changing (1) the metal content of the catalyst from 0.2 to 10% and (2) the dehydroxylation state of the alumina; calcinating an extremely pure alumina described elsewhere[3] at 600 °C during 1-200 h modified the concentration of the superficial hydroxyl groups and also the size of the metal particles in the supported catalysts obtained by impregnation with chloroplatinic acid and reduction.

The following three reactions were studied as a function of d_H. (1) Hydrogenolysis of methylcyclopentane, from the ratio *r*, 3-methylpentane over *n*-hexane, are calculated the relative contributions of the selective and nonselective mechanisms. (2) Isomerization of 2-methylpentane-*2*-^{13}C

Table I

Catalysts	Pt %	2.25	8.5	8.4	7.1	4.1	2.5	0.2
	on Al_2O_3[a]	A	A	B' 10 h	B' 210 h	B' 210 h	B' 210 h	A'
	Cl %	0.5	0.85	0.6	0.75	0.6	0.6	0.2
Characterization	a = H/Pt	0.05	0.07	0.12	0.35	0.55	0.70	1.0
	d_H (Å)	170	120	70	24	16	12	8.5
Methylcyclopentane	r = 	3.2	2.4	1.3	0.7	0.4	0.4	0.4
Hydrogenolysis at 220 °C	Selective mech %	85	80	64	37	0	0	0
% of cyclic mechanism in isomerization		25	16	20	16	30	62	84
		48	55	—	67	—	83	100
	T, °C	285	254	254	254	254	254	300

[a] A and A' represent two batches of commercial alumina with decreasing superficial OH content. B'_{nh} an alumina A' which has been calcinated at 600 °C in air during *n* hours.