peptides with either nickel(II) or cobalt(II). As before, the k_2 for glycine is appreciably greater. Increasing the ligand size does not appreciably decrease k_2, indicating therefore that the larger glycine k_2 cannot be ascribed to less blocking of coordinating sites by the bound ligand.

Consequently, it may be concluded that glycine complexation of nickel and cobalt is normal and may be compared with other ligands[10] and with the H_2O^{17} nmr studies on these two ions.[11] Chelation by the simplest peptides of identical charge derived from glycine is a slower process. Special intramolecular processes required by the peptides to form the stable chelate species may be the source of this relative kinetic inefficiency.

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Iodine as a Reference Soft Acid in Nonaqueous Solvents

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It is well known that empirical sequences showing relative hardness or softness of Lewis acids or bases are often altered by changing from one reference reactant to another. Drago and Wayland[1] proposed a double-scale enthalpy equation (eq 1) allowing a quantitative

$$-\Delta H = E_A E_B + C_A C_B \qquad (1)$$

basis for rationalizing such variations by resolving the molar enthalpy for adduct formation into electrostatic and covalent contributions. (The quantities E and C refer to the electrostatic and covalent parameters, respectively, for a given acid (A) and base (B) forming a 1:1 addition compound in a poorly solvating medium.) Iodine was selected as the reference soft acid and was assigned equal values (unity) of E_A and C_A. Since the electronic spectrum of iodine shows sizable solvatochromic effects, the study reported herein was undertaken to examine the correspondence between the spectral energetics of I_2–B adducts and the Drago–Wayland enthalpy parameters. The comparison of the magnitude of this spectral shift to other solvent properties was surveyed, as well.

The relationship between the Mulliken charge-transfer model[2] and the double-scale enthalpy equation was developed by Drago and Wayland, and the major consequence of this is that both electrostatic and covalent terms contribute significantly to the ground-state energy for the complex, even though the energies of interaction for such acids and bases are small. For specific complexes with I_2, Mulliken assigned the blue shift of the 520-mμ band (gas phase) of iodine in complexing solvents to repulsive exchange interactions between the iodine and the donor, and, therefore, the strength of the charge-transfer interaction proportionately raises the energy of the iodine excited state. However, since the total wave function for the ground state for the donor–I_2 complex involves the weaker London and dipole–dipole forces as well as the larger exchange forces, the Mulliken treatment does not preclude small blue shifts in poorly complexing aprotic solvents. Voigt[3] has attributed the latter effect to contact-charge-transfer perturbations and has observed a degree of correlation to the ionization potential of the solvent. The magnitude of the blue shift relates in a regular manner to the solvent ionization potential only for those liquids containing the same donor atom, and no correspondence between these variables is found for solvents having different donor atoms. The same conclusion applies when the dielectric constant of the base is plotted against λ_{max} of iodine. (Graph is not included here.)

Examination of the frequency shift in terms of both E_B and C_B should assist in clarifying which exerts the larger influence in specific I_2–donor interactions. The data required for such correlations are summarized in Table I and include the basic solvents for which Drago–Wayland parameters have been determined. Iodine transition energies ($E_T = 2.859 \times 10^{-3}/\lambda_{max}$) were calculated from the absorption maxima reported by Voigt.[3] Although not included herein, plots of the change in transition energy [$\Delta E_T = (E_T)_{soln} - (E_T)_{vap}$] as a function of E_B or $-\Delta H$ were completely scattered with no general trends being apparent.

The shift in the I_2 transition energy with C_B of the solvent is shown in Figure 1. For each of the curves, it is clear that the magnitude of the I_2 blue shift increases with the increasing covalent parameters of the donor. In contrast to the solvent ionization potential, the C_B *vs.* ΔE_T function places the donors largely into two major groups: aprotic solvents (curve A) and hydrogen-bonding solvents (curve B). However, one important aprotic base, pyridine, falls well away from the curve, in contrast to the reasonably close fit for the other nitrogen bases. In terms of Pearson's HSAB principle,[4] the aromatics and aprotic oxygen, sulfur, and nitrogen bases on curve A usually show predominantly soft characteristics, and the hydrogen-bonding oxygen and nitrogen bases of curve B are hard. For the latter, increased stabilization of the ground state through hydrogen bonding in I_2–B may be responsible for raising E_T to a higher value than that for the aprotic base having the same donor atom.

The Kosower Z value[5] for a coordinating solvent has been useful in the estimation of the solvation energy for inorganic species in nonaqueous media, and in a number

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TABLE I
IODINE ABSORPTION MAXIMA AND BASE PARAMETERS

No.	Donor	E_T, kcal/mol	C_B	Z^a
1	i-C_8H_{18}	54.88	...	60.1
2	CCl_4	55.30	...	60.0
3	$CHCl_3$	55.84	...	63.2 (59.3^b)
4	CH_2Cl_2	56.50	...	64.2
5	C_6H_6	56.95	1.36	60.0
6	$C_6H_5CH_3$	57.64	1.91	...
7	Tetrahydrofuran	64.10	4.69	75.0^b
8	CH_3OH	64.98	1.12	83.6
9	C_2H_5OH	64.54	...	79.6
10	n-C_3H_7OH	64.25	...	78.3
11	i-C_3H_7OH	63.96	...	76.3
12	n-C_4H_9OH	63.82	...	77.7
13	$(C_2H_5)_2O$	61.35	3.55	65.2
14	p-Dioxane	63.25	3.82	71.4^b
15	C_6H_5Br	56.84	...	59.2
16	CS_2	54.98	...	58.5
17	Pyridine	67.75	6.92	66.0^b
18	$(C_2H_5)_2S$	65.72	7.78	...
19	NH_3	66.49	3.42	...
20	CH_3NH_2	68.40	6.14	...
21	$(CH_3)_2NH$	69.39	8.68	...
22	$(CH_3)_3N$	69.06	11.61	...
23	$C_2H_5NH_2$	68.56	6.14	...
24	$(C_2H_5)_2NH$	69.73	8.76	88.6^b
25	$(C_2H_5)_3N$	69.06	11.35	89.2^b
26	Quinuclidine^c	71.48	13.40	...
27	$(CH_3)_2SO$	63.53	3.42	71.1

[a] Solvent Z values are from E. M. Kosower, *J. Am. Chem. Soc.*, **80,** 3253 (1958). [b] Additional experimental values were measured with 4-carbomethoxy-1-ethylpyridinium iodide. [c] Based on data of A. Halpern and K. Weiss, *J. Am. Chem. Soc.*, **90,** 6297 (1968), which were used to calculate C_B from $-\Delta H$ (13.9 kcal).

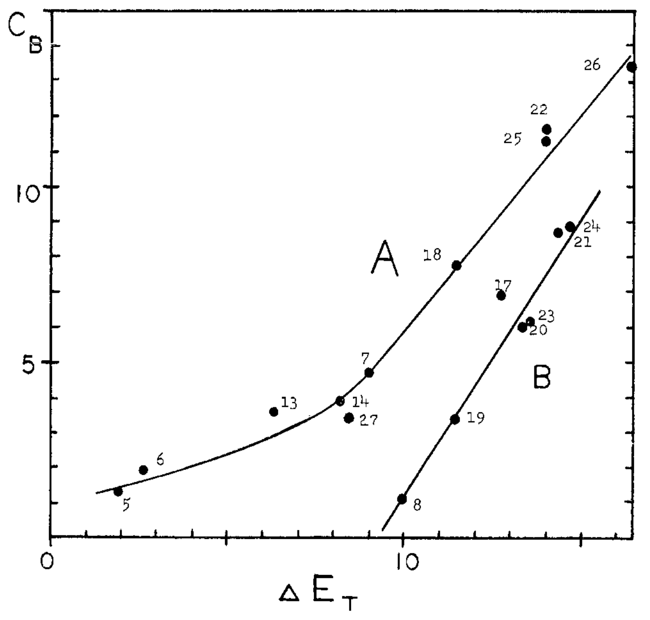

Figure 1.—Shift in λ_{max} of I_2 as a function of the C_B value of the donor. Numbered points correspond to the bases listed in Table I.

of instances this quantity is superior to the dielectric constant for assessing the roles of different aprotic solvents in dissociative equilibria.[6] Therefore, it is appropriate to compare the blue shift in the electronic spectrum of iodine with the corresponding shift in the charge-transfer transition of the 4-carbomethoxy-1-ethylpyridinium iodide ion pair. The function of the solvent upon the charge-transfer interaction in the pyridinium iodides appears to involve primarily the ground state, either through (a) stabilization of the ground state by H bonding to the anion or (b) lowering of the ground state by strongly solvating the cation. There is some evidence that Z values correlate with $\pi \rightarrow \pi^*$ transitions in nitrones[7] and the nitrate ion,[8] as well as with carbonyl shifts;[5] however, no correspondence is observed with solvent-induced red shifts for π-bonded merocyanines[9] and Nile Blue A oxazone.[10]

Donor Z values *vs.* the change in transition energy for iodine are plotted in Figure 2. The continuous nonlinearly increasing function includes only the very soft basic hydrocarbons and the oxygen and sulfur bases. Points for most of the alkyl and aryl halides, as well as those for the nitrogen bases, are widely scattered from the curve. It should be noted that the uncertainties in the Z values for the amines and pyridine are large, because of a sizable shift in λ_{max} with changes in concentration of the pyridinium iodide. Similar limitations must apply to E_T values for the I_2–N complexes, because of the possibility of other iodine-containing species absorbing in the same spectral area.

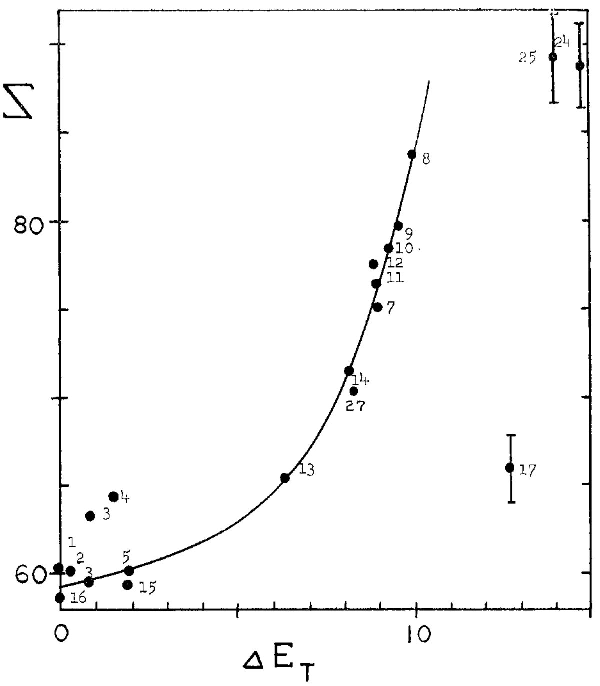

Figure 2.—Blue shift of λ_{max} for I_2 as a function of the donor Z value. Numbered points are the solvents in Table I.

Although the quantitative correspondence is inexact, the same qualitative order for decreasing base hardness is found with respect to both iodine and the pyridinium

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iodides, that is, alkyl amines > alcohols > ethers > aromatics > alkanes. The low solubility of the pyridinium salts in poorly solvating liquids requires indirect methods for the assignment of Z values to the very soft donors. By contrast, iodine is particularly attractive as a reference soft acid for determining comparative softness of nonpolar and aprotic donors.

Experimental Section

The 4-carbomethoxy-1-ethylpyridinium iodide (Eastman Organic Chemicals) was recrystallized by dissolving the solid in warm chloroform containing a minimum of added absolute methanol. The filtered solution was allowed to concentrate and crystallize at room temperature, giving yellow-orange crystals (mp 114°). Acetone[5] was not as suitable as a solvent, since it was quite difficult to free the solid product completely from adsorbed solvent, and the solute tended to separate as an oil.

All donor solvents were Spectro-Analyzed reagents with the exception of the amines (Eastman White Label). Solvent Z values were obtained by the procedure of Kosower.[5] However, those for pure *p*-dioxane and tetrahydrofuran were graphically extrapolated from Z *vs.* v/v fraction in binary mixtures with water. Experimental values for chloroform and the amines were measured in binary solutions with added methanol (20% v/v), because of the low solubility of the pyridinium salt. Absorption maxima were determined on a Beckman DU spectrophotometer.

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Preparation of Chlorodifluoramine, $ClNF_2$

BY KARL O. CHRISTE

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The synthesis of $ClNF_2$ was first reported in 1960 by Petry.[1] Since then, numerous papers dealing with the preparation of this interesting compound have been published.[2-9] The majority of these preparations are based on the reaction of HNF_2 with chlorine or chlorine-containing compounds.[1,4-6,9] With the exception of the reactions between HNF_2 and ClF[9] or inorganic hypochlorites,[6] the yields of $ClNF_2$ (based on HNF_2) are only about 50% or lower. The remaining methods based on N_2F_4,[7,8] NaN_3,[3] or NH_4^+-containing salts[2] result in only moderate yields of $ClNF_2$ or are hard to control. This paper reports a new, more convenient synthesis of $ClNF_2$ from HNF_2 and *t*-butyl hypochlorite.

This reaction produces $ClNF_2$ in quantitative yield (based on HNF_2). In contrast to the reaction between HNF_2 and ClF,[9] it does not require the use of a metal–Teflon vacuum system but can be carried out in a standard all-glass vacuum line. Aqueous solutions of inorganic hypochlorites have previously been used[6] to convert NHF_2 into $ClNF_2$. However, in aqueous solutions proper control of the pH value and use of a flow reactor are essential to suppress the competing reaction resulting in the formation of N_2F_4.

Experimental Section

Caution! Difluoramine is highly explosive[4] and protective shielding should be used during handling operations. The compound was always condensed at −142° and the use of a −196° bath should be avoided.[4]

Materials and Apparatus.—Difluoramine was prepared from difluorourea as reported by Lawton, *et al.*[10] *t*-Butyl hypochlorite was prepared from *t*-butyl alcohol.[11] Both compounds were purified by fractional condensation and their purity was determined by infrared spectroscopy. All reactions were carried out in a Pyrex high-vacuum line having stopcocks lubricated with Halocarbon grease (from Halocarbon Products Corp.). Infrared spectra were taken on a Perkin-Elmer Model 337 spectrophotometer using a 5-cm Pyrex cell fitted with AgCl windows.

Preparation of $ClNF_2$.—Difluoramine (1.06 mmol) and *t*-butyl hypochlorite (1.08 mmol) were combined at −142° in a U trap. The mixture was allowed to warm to room temperature and a smooth reaction took place. After 90 min the mixture was separated by fractional condensation at −54, −95, −142, and −196°. An infrared spectrum of the material trapped at −196 and −142° showed the presence of only $ClNF_2$ (1.06 mmol). The large bulk of the organic material was trapped at −54°.

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A Crystalline Molybdenum(V)–Histidine Complex

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Interest in the implication of molybdenum in enzyme function has prompted recent research on the coordination chemistry of molybdenum ions with α-amino acids, notably cysteine and its esters.[1-3] With respect to other α-amino acids Spence and Lee[4] carried out spectrophotometric, electron paramagnetic resonance, and

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