ate. The mechanism for the formation of SiH_4 or GeH_4 is unknown; no evidence for production of these compounds *before* the addition of alkyl halides was observed.

This work has led to the preparation of CH_3, C_2H_5, and CH_3OCH_2 derivatives of SiH_4 and GeH_4 in good yields, as shown in Table I. An investigation of the relative merits of lithium, sodium, and potassium for the reactions leading to $CH_3OCH_2GeH_3$ showed that the use of lighter alkali metals resulted in lower yields (Li, 9%; Na, 19%; K, 41%). This may, in part, be ascribed to the slower dissolution of sodium and lithium in HMPA, which could lead to more extensive decomposition of the GeH_3^- ion. It is also possible that the stability of the GeH_3^- (and SiH_3^-) ion in solution is dependent upon the nature of the counterion.

TABLE I

ALKYLSILANES AND -GERMANES SYNTHESIZED FROM HMPA SOLUTIONS OF POTASSIUM SILYL AND POTASSIUM GERMYL

Compd	% yield	Retention time,[a] min
CH_3GeH_3	94	3.70[b]
$C_2H_5GeH_3$	65	8.30[b]
$CH_3OCH_2GeH_3$	41	26.40[c]
CH_3SiH_3	90	2.51[b]
$C_2H_5SiH_3$	70	4.75[b]
$CH_3OCH_2SiH_3$	22	13.13[c]

[a] Column temperature, 30°; He flow rate, 100 cc min^{-1}; sample introduced through a commercial gas-sampling valve. [b] Column used was $^1/_4$ in. × 15 ft of 20% squalane on 60–80 Chromosorb W. [c] Column used was $^3/_8$ in. × 20 ft of 20% Carbowax 400 on 60–80 Chromosorb W.

Further work is planned both on spectroscopic studies and preparative reactions involving the solutions of alkali metal derivatives of the group IV hydrides in HMPA.

Experimental Section

All manipulations of volatile compounds were carried out in a Pyrex glass vacuum system of conventional design. Stopcocks were lubricated with Apiezon hydrocarbon greases in preference to fluorocarbon greases which were found to be attacked by alkali metal solutions. Alkali metals were weighed under xylene and pressed into thin plates before reaction. HMPA (Fisher) was dried and stored over 4A molecular sieves. SiH_4 and GeH_4 were prepared by well-known methods.[15,16] Alkyl halides were commercial products, used as received. The vapor-phase chromatography was carried out on a Varian-Wilkins Aerograph A90-P3 gas chromatograph.

Preparative Reactions.—A typical preparation will be described in some detail since variations in technique can result in very low yields. For the other compounds studied, similar procedures were used with suitable adjustment of quantities.

Preparation of CH_3GeH_3.—HMPA (10 ml) was degassed, first at room temperature and then at ~110° (reflux temperature) under ~10^{-4} torr. The reaction vessel was then cooled to about 10°. Potassium (90 mg, 2.30 mmoles) was added and the vessel was rapidly reevacuated. The metal began to dissolve at once to give a blue solution. When the vessel was completely evacuated, GeH_4 (2.76 mmoles) was condensed into a side arm and allowed to expand into the entire vessel. On stirring or shaking, a rapid reaction occurred and the potassium completely dissolved in ~15 min. The solution at this stage was a very pale yellow (an orange or green tint at this stage indicates decomposition of the anion or solvent, respectively). The volatile matter [permanent gas + excess GeH_4 (0.45 mmole)] was removed and CH_3I (2.45 mmoles) was added. This reacted rapidly with the yellow solution with effervescence; no precipitate was formed and the solution became colorless. The volatile products (2.37 mmoles) were removed after 10 min. This material was fractionated under vacuum at −120° to remove excess CH_3I and finally was analyzed by gas chromatography. The product was found to contain 2.16 mmoles of CH_3GeH_3. (An independent sample of CH_3GeH_3 was synthesized from CH_3GeCl_3 and $LiAlH_4$ for the retention time comparison.) The yield of CH_3GeH_3 based on the potassium used (or GeH_4 used) was 94%.

The solutions should be kept below room temperature at all times, especially during dissolution of the alkali metal. Failure to observe this precaution results in attack on the solvent and evolution of volatile matter thought to contain $(CH_3)_2NH$. The characteristic deep blue color of the alkali metal solution is replaced by a dirty brown color in this case.

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The Iodine–Valeronitrile Charge-Transfer Complex

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Various attempts have been made to correlate the stabilities of the complexes formed between iodine and different organic bases with empirical parameters such as the Hammett σ and the Taft σ^* values. Drago, Wenz, and Carlson[1] have shown that ΔH° values for complexes of iodine with N,N-dimethylamides can be correlated with σ^* values. However, these investigators noted that deviations were encountered when the equilibrium formation constants were compared with σ^* values. Arzamanova and Gur'yanova,[2] in an investigation of the complexes of iodine with amines, ethers, and sulfides, have found a relationship between the heats of formation and the dipole moments of the intermolecular bonds. Person, Golton, and Popov[3] have determined the equilibrium constants and ΔH° and ΔS° values for some of the complexes formed between the Lewis acids ICl, IBr, and I_2 and the bases acetonitrile and mono- and dichloro-substituted acetonitriles.

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[2] I. G. Arzamanova and E. N. Gur'yanova, *Dokl. Akad. Nauk SSSR*, **166**, 1151 (1966).

[3] W. B. Person, W. C. Golton, and A. I. Popov, *J. Am. Chem. Soc.*, **85**, 891 (1963).

For each acid they found that a linear relationship exists between $\log K_c$ and the σ^* values of the bases, where K_c is the formation equilibrium constant. This relationship permitted the values of K_c for yet unmeasured nitrile–halogen complexes to be predicted. It would be expected from this relationship that the value of K_c would change only slightly in the iodine–nitrile family with increasing length of the nitrile aliphatic chain.

In the course of an investigation of the solvent properties of valeronitrile, the thermodynamic constants for the charge-transfer complex between iodine and valeronitrile were measured. The correlation of these data with the Taft σ^* value has been examined.

Experimental Section

Materials.—Reagent grade iodine was purified by sublimation from potassium iodide. B and A Instrument Grade *n*-heptane (Allied Chemical Corp.) was used without further purification. Eastman valeronitrile was purified using the method of Ferguson.[4]

Preparation of Solutions.—Stock solutions of about 5×10^{-3} *M* iodine in heptane were prepared by weight. Solutions prepared by diluting the stock solutions followed Beer's law and gave a molar absorptivity of 917 ± 3 at 520 mμ, in good agreement with the value reported by De Maine at 25°.[5] Solutions used for the spectrophotometric determinations were prepared by mixing weighed amounts of the iodine stock solutions and valeronitrile in volumetric flasks and diluting with heptane. The iodine concentration in the solutions decreased slowly with time and with exposure to light. To minimize this effect the solutions were protected from light and measured immediately after preparation.

The solutions studied in the visible region were approximately 8×10^{-4} *M* in iodine while the valeronitrile concentrations ranged from 0.2 to 0.9 *M*. The solutions studied in the ultraviolet region were about 1.6×10^{-3} *M* in iodine and from 0.1 to 0.4 *M* in valeronitrile. At 25° ten different valeronitrile concentrations were used in the investigation in the visible region and six in the ultraviolet region. At higher temperatures five different valeronitrile concentrations were used.

Concentrations at temperatures other than 25° were calculated using literature values of the densities of heptane and valeronitrile at the different temperatures.[6]

Visible and Ultraviolet Spectra.—Visible spectra were determined using a Beckman Model DU spectrophotometer equipped with thermal spacers through which water from a constant-temperature bath was circulated. Ultraviolet data were obtained on a Beckman Model DK2A recording spectrophotometer in which the temperature was maintained at 25 ± 0.1° with a specially designed water-cooled cell compartment.

To obtain the spectra, the iodine–valeronitrile solutions were run against an iodine–heptane reference. Using this reference, values of $A - A_0$ were read directly from the spectrophotometer, where A is the absorbancy of the iodine–valeronitrile solution at a particular wavelength, and A_0 is the absorbancy of the iodine reference solution. Readings were taken at intervals of between 15 and 20 mμ in the range from 445 to 560 mμ. An isosbestic point was observed at 498 mμ for all valeronitrile concentrations. The wavelengths used for the equilibrium constant calculations in the visible region were 560, 540, 520, 475, 460, and 445 mμ. In the ultraviolet region a continuous plot of $A - A_0$ was recorded between 230 and 270 mμ at 25°. Values of $A - A_0$ obtained at 237.5 mμ were used in equilibrium constant calculations.

Results and Discussion

A modification of the method of Rose and Drago[7] was used for the calculation of the equilibrium constants. The final equation is in the form

$$C_D = C_D C_I \frac{\epsilon_C - \epsilon_I}{A - A_0} - K_C^{-1} \qquad (1)$$

where C_D is the total valeronitrile concentration, C_I is the total iodine concentration, and ϵ_C and ϵ_I are the molar absorptivities of the complex and iodine, respectively.

Equation 1 differs from that of Rose and Drago in that the terms $(A - A_0)/(\epsilon_C - \epsilon_I)$ and $-C_I$ have been dropped in eq 1. The magnitudes of $\epsilon_C - \epsilon_I$ found for the iodine–valeronitrile system range from 421 to 606. Using these values and the data listed in Table I, it is obvious that the omission of $(A - A_0)/(\epsilon_C - \epsilon_I)$ and C_I would introduce no appreciable error in the calculation of K_c. A plot of C_D *vs.* $C_D C_I/(A - A_0)$ gives a straight line of slope $\epsilon_C - \epsilon_I$ and an intercept of $-K_c^{-1}$. Figure 1 shows a plot of C_D *vs.* $C_D C_I/(A - A_0)$ at different wavelengths for the system at 25°. The best straight lines were determined by the method of least squares with the aid of a computer.

Tables I and II list representative data for two wavelengths in the visible and one in the ultraviolet region at 25°.

TABLE I

VISIBLE SPECTROPHOTOMETRIC DATA FOR VALERONITRILE–IODINE IN HEPTANE AT 25°[a]

		560 mμ		460 mμ	
$10^4 C_I$	C_D	$A - A_0$ (exptl)	$A - A_0$ (calcd)	$A - A_0$ (exptl)	$A - A_0$ (calcd)
8.046	0.2735	−0.081	−0.081	0.120	0.120
8.240	0.3109	...	...	0.133	0.135
8.014	0.3479	...	...	0.144	0.144
7.800	0.3674	−0.097	−0.097	0.143	0.145
7.646	0.3759	−0.101	−0.097	0.144	0.144
7.815	0.4662	−0.114	−0.115	0.175	0.172
8.072	0.5383	−0.129	−0.131	0.195	0.195
7.708	0.6267	−0.137	−0.137	0.205	0.205
7.821	0.6998	−0.151	−0.149	0.222	0.222
7.799	0.9556	−0.176	−0.175	0.262	0.262
		$K = 1.04$		$K = 1.03$	

[a] Material supplementary to this article has been deposited as Document No. 9514 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

Table III gives the values of K_c at the different temperatures. Also given in Tables I and II are values of $A - A_0$ calculated from the values of K_c and $\epsilon_C - \epsilon_I$. The close agreement between the experimental and calculated $A - A_0$ values must be viewed in the light of the sensitivity of these values to changes in K_c as measured by the sharpness of fit criterion proposed by Conrow, Johnson, and Bowen.[8] The sharpness of fit

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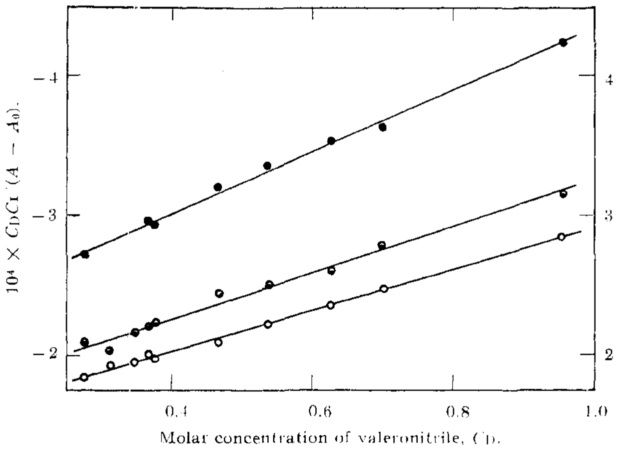

Figure 1.—Plots of $C_DC_I/(A - A_0)$ *vs.* C_D at 25° for 560 (●), 540 (◒), and 460 (○) mμ. The left-hand ordinate is for 560 and 540 mμ; the right-hand ordinate is for 460 mμ.

TABLE II

DATA AT 237.5 mμ FOR VALERONITRILE–IODINE IN HEPTANE AT 25°

C_D	10^3C_I	$A - A_0$ (exptl)	$A - A_0$ (calcd)
0.1200	1.628	−0.302	−0.300
0.1936	1.627	−0.453	−0.455
0.2495	1.623	−0.556	−0.559
0.3053	1.625	−0.656	−0.654
0.3470	1.630	−0.727	−0.724
0.4078	1.640	−0.818	−0.819
		$K = 0.99$	

for 560 and 460 mμ, for example, is 6 and 13, respectively, while at 237.5 mμ, a sharpness of 25.5 is obtained. Although the sharpness of fit in the visible region is lower than hoped for, the consistency of the results at the different wavelengths in this region together with the agreement with the result found at 237.5 mμ substantiates the reliability of the values of K_c listed in Table III. Plots similar to Figure 1 were drawn for the other temperatures and wavelengths.

TABLE III

VALUES OF THE FORMATION CONSTANT, K_c, AT DIFFERENT TEMPERATURES

Temp, °C	K_c,[a] l. mole^{-1}
25.0	1.02 ± 0.03
35.0	0.94 ± 0.08
45.0	0.80 ± 0.10
50.0	0.71 ± 0.08
55.0	0.65 ± 0.02

[a] Each K_c listed is the average of the K_c values at the different wavelengths.

From the data in Table III, a $\Delta H°$ value of −3.0 ± 0.3 kcal/mole and a $\Delta S°$ value of −9.8 ± 0.8 eu were obtained. The uncertainties are the standard deviations estimated by the least-squares method. The value of 1.02 obtained for K_c at 25° is considerably larger than the value of 0.46 predicted for iodine complexes from the equation of Person, Golton, and Popov.[3] This difference is considered to be well outside the range of experimental indetermination and indicates that simple inductive effect considerations, as reflected by the Taft σ^* values, while effective in predicting the variation in K_c with halogen substitution, are of quite limited use when a different kind of substitution is involved. It should be pointed out that any contribution due to steric effects would be expected to make the value of K_c smaller than that predicted from σ^* rather than larger as observed.

Another correlation which is often made in charge-transfer complexes involves a linear variation of $\Delta H°$ with $\Delta S°$. Person, Golton, and Popov[3] have found that for the substituted acetonitriles and halogens the equation $\Delta S° = 1.85\Delta H° - 5.6$ can be written. It is interesting to note that the values of $\Delta H°$ and $\Delta S°$ found by us for the valeronitrile–iodine system fit this equation quite well.

The equilibrium formation constants have been measured for only three aliphatic nitriles with iodine (acetonitrile,[3,9] propionitrile,[10] and chloroacetonitrile[3]). The value for acetonitrile–iodine has been determined with good agreement by two different investigators and can be regarded with some confidence. In the case of chloroacetonitrile, however, the high nitrile concentration (6 *M*) used to obtain measurable amounts of complex formation could cause an appreciable change in the dielectric constant of the system and affect the value of K_c observed. As yet there are not sufficient data available for the iodine–nitrile systems to permit more than semiquantitative evaluation of the influence of substituent groups on the value of K_c, but it seems that other than simple inductive and steric arguments must be considered.

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The Binding of Mercury(II) by Glycine. A Raman Spectral Study

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Raman spectroscopy is a convenient technique for studying complexes of d^{10} ions, which do not possess spectral or magnetic properties that allow their characterization by other methods. Furthermore, the low Raman intensities of water bands permit study of these complexes in aqueous solution, free from the strong