

Figure 6.—Linear free energy relationship between k_1 and K_{FeOH} : ○, NaClO_4 (1 M); ◐, KNO_3 (1 M for K_{FeOH} and 0.89 M for k_1); ●, LiNO_3 (1 M for K_{FeOH} and 0.89 M for k_1).

the hydrogen-bonded form of water to accept a proton from $\text{FeCl}(\text{H}_2\text{O})_5^{2+}$ not only with more rapidity⁴ but also to a larger extent than does the non-hydrogen-bonded form. This would explain why substituting the structure-breaking potassium nitrate for lithium nitrate causes the reaction rate to decrease. (With cesium, at low temperatures, where paths 1 and 2 make comparable contributions, the effect on k_2 (see above) seems to cancel that on k_1 when τ is measured.) The effect of enhanced proton transfer thus outweighs the accelerating effect which makes a water molecule in broken-down surroundings more reactive.

The argument is further strengthened by the fact that k_1 is influenced in a similar way as is K_{OH} which is rather analogous to the hydrolysis constant of $\text{Fe}(\text{H}_2\text{O})_6\text{Cl}^{2+}$. In Figure 6 we show a linear free energy relationship plot between K_{OH} and k_1 , taking K_{OH} from our measurements at 18°, k_1 in the presence of LiNO_3 and KNO_3 from our measurements at 19.6°, and k_1 in the presence of NaClO_4 from the results of Yasunaga and Harada⁸ at 25°, using their value of ΔH^\ddagger to correct to 19.6°. The parallelism of the influences on the two constants is obvious, the rate constant being affected by the change of supporting cation more strongly than is K_{OH} .

The slopes of the ΔH^\ddagger vs. ΔS^\ddagger plots lie in a range encountered for many reactions where solvent effects in aqueous media have been studied.^{17,29} This, again, agrees well with our above interpretations.

Whereas the evidence presented in this paper is insufficient to prove our suggestion, the explanation of the observed effects in terms of water structure thus seems to present a consistent picture.

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An Investigation of Iodine-Nitrile Complexes in Different Solvents

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The formation equilibrium constants, K , for the molecular complexes formed between iodine and a series of aliphatic nitriles were studied in several solvents and values of ΔH° and ΔS° determined. The variation in K with nitrile was small but consistent with the Taft σ^* values of the nitriles. The values of K increased in the order aceto- < propio- < butyro- < valero- < pivalonitrile in the solvent carbon tetrachloride. Any change in the thermodynamic parameters with nitrile was masked by the experimental uncertainty and no variation could be detected. The same general behavior was found in *n*-heptane. In addition, K , ΔH° , and ΔS° were determined for the butyronitrile-iodine complex in several other solvents. In these solvents, K increased in the order tetrachloroethylene < carbon tetrachloride \approx carbon disulfide < cyclohexane \approx *n*-hexane < *n*-heptane. This variation could not be ascribed to any systematic change in either ΔH° or ΔS° . There is a compensation between ΔH° and ΔS° in that solvents in which ΔH° is large also have large values of ΔS° . The value of K appears to be more a function of solvent type than any specific solvent parameter.

Introduction

The molecular complexes formed between iodine and a variety of bases have been investigated extensively. Attempts have been made to correlate the stabilities of the complexes with the nature of the base using such parameters as the Taft σ^* value of the base,¹ its ionization potential,² Hammett σ values,³ and more complex parameters such as those proposed by Drago and co-workers.⁴ In addition to the nature of the base, the solvent has been found to have an effect on the stability of a particular complex.⁵ Although the variation in

complex stability with base can be adequately accounted for using one of the above parameters, the influence of solvent is not well understood. To date, very few complexes have been studied in a sufficient number of solvents to allow much correlation. In addition, the reliability of the equilibrium constant K determined by spectrophotometric measurements has been questioned. The determined values of K for a number of complexes have been found to exhibit rather drastic variations with wavelength. These variations have been attributed to either the formation of termolecular complexes⁶ or deviations from Beer's law.⁷ Some of the differences in the values of K ascribed to changes in solvent or base may be due in part to the fact

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TABLE I
VALUES OF THE FORMATION EQUILIBRIUM CONSTANT AND $\epsilon_C - \epsilon_A$ FOR SEVERAL NITRILE-IODINE COMPLEXES AT 25°
IN HEPTANE AND CARBON TETRACHLORIDE^a

Nitrile	Solvent, heptane ^b				Solvent, CCl ₄ ^b			
	465 nm		540 nm		460 nm		535 nm	
	<i>K</i> , l./mol	$\epsilon_C - \epsilon_A$	<i>K</i> , l./mol	$\epsilon_C - \epsilon_A$	<i>K</i> , l./mol	$\epsilon_C - \epsilon_A$	<i>K</i> , l./mol	$\epsilon_C - \epsilon_A$
CH ₃ CN					0.461 ± 0.013	609 ± 14	0.451 ± 0.020	-585 ± 20
C ₂ H ₅ CN ^c	0.953 ± 0.008	614 ± 2	0.947 ± 0.008	-588 ± 2	0.506 ± 0.019	657 ± 17	0.513 ± 0.009	-612 ± 8
<i>n</i> -C ₃ H ₇ CN	1.011 ± 0.012	618 ± 5	0.973 ± 0.011	-601 ± 4	0.508 ± 0.008	685 ± 9	0.506 ± 0.021	-631 ± 8
<i>n</i> -C ₄ H ₉ CN	1.02 ± 0.03 ^{d,e}	683 ± 14 ^{d,e}	1.07 ± 0.08 ^d	-591 ± 25	0.498 ± 0.006	701 ± 7	0.559 ± 0.016	-603 ± 13
C(CH ₃) ₃ CN	1.20 ± 0.06	617 ± 16	1.03 ± 0.02	-632 ± 7	0.595 ± 0.025	657 ± 20	0.576 ± 0.020	-608 ± 16

^a Values of concentrations and absorbances will appear immediately following the article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-3059. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche. ^b Uncertainties are standard deviations. ^c Data from ref 10. ^d Data from ref 9. ^e At 460 nm.

that different spectral regions were used in the investigation.

In an effort to obtain more information on the effect of donor and solvent on the stability of weak complexes, a thermodynamic investigation of complexes of iodine with a series of aliphatic nitriles in several solvents was undertaken. In this investigation, special attention was given to the spectral regions used in the determinations.

Experimental Section

Materials.—Reagent grade iodine was purified by sublimation from potassium iodide before use. The nitriles were the best grades commercially available. Each nitrile was first analyzed using glpc. If a chromatogram showed the presence of isonitrile, the nitrile was treated with cold 1:1 hydrochloric acid according to the procedure recommended by Ferguson.⁸ All nitriles were stirred with calcium hydride, treated with P₂O₅, and then fractionated. The distilled nitriles were stored over a molecular sieve (Linde 3A) until used. Analysis by glpc showed water impurity to be less than 0.2 part per thousand and no other impurity was detectable by this method. The solvents, *n*-heptane (B and A Instrument Grade), cyclohexane (B and A Instrument Grade), tetrachloroethylene (Eastman spectro quality), carbon tetrachloride (Baker GC spectrophotometric quality), carbon disulfide (Baker GC spectrophotometric quality), and *n*-hexane (Eastman, Spectrograde) were used in the determinations. The *n*-heptane, cyclohexane, carbon tetrachloride, and hexane were used without further purification except that dry nitrogen was bubbled through the solvents before use. The tetrachloroethylene was fractionated and the middle fraction (about 50% by volume) was taken for the determination. If unfractionated tetrachloroethylene was used, the solutions were unstable giving absorption spectra that varied with time. Solutions prepared with the fractionated solvent were much more stable. The carbon disulfide was treated with mercury and mercuric sulfate and then fractionated from calcium oxide. Freshly distilled carbon disulfide was used in the determinations. Water content of the solvents was monitored from time to time by glpc.

Preparation of Solutions and Procedure.—All solutions were prepared by weight as described previously.⁹ Mixing and handling of the solutions were carried out in a drybox to ensure against moisture contamination.

The spectra were determined using either a Beckman Model DK2A recording spectrophotometer or a Beckman DU spectrophotometer. The temperatures of the solutions in the spectrophotometers were controlled to within ±0.1° using thermostated cell compartments.

The difference between the absorbance (*A*) of the iodine-nitrile solution and the absorbance (*A*₀) of a reference solution containing the same total iodine concentration in the particular solvent was read directly. The magnitudes of *A* - *A*₀ reached two maxima, one at about 460 nm and the other around 540 nm, irrespective of either the type of nitrile or solvent. Values of *K* were calculated from the values of *A* - *A*₀ using the following equation⁹

$$C_D + C_A = (\epsilon_C - \epsilon_A) \frac{C_D C_A}{A - A_0} - K^{-1} \quad (1)$$

where *C*_D is the total molar nitrile concentration, *C*_A is the total molar iodine concentration, ϵ_C is the molar absorptivity of the complex, ϵ_A is the molar absorptivity of the iodine, and *K* is the formation equilibrium constant. The values of *C*_D ranged from about 0.2 to 1.0 *M* and *C*_A was about 2 × 10⁻³ *M* in all cases. Because of the alterations in the optical properties of the absorbing species with increasing nitrile concentration, eq 1 will yield valid values of *K* only in two spectral regions. One of these is the wavelength at which the complex absorption reaches a maximum; the other is the region in which the absorption of the complex is small compared to that of free iodine.¹⁰ The first of these regions is in the vicinity of the maximum in *A* - *A*₀ at 460 nm and the second region incorporated the maximum of *A* - *A*₀ observed at 540 nm. Therefore, the calculated values of *K* are reported only from the data at the two maxima. In almost all cases the agreement between the two values of *K* is excellent.

In instances where the difference between the two values lies outside of experimental uncertainty, the value of *K* in the 535-540-nm region is considered to be more reliable.¹⁰

In order to check for the possibility of a slow reaction involving iodine with either the nitriles or solvents, time studies were carried out. In addition, the 25° values of *A* - *A*₀ for solutions that had been at elevated temperatures were remeasured. With the exception of pivalonitrile, the solutions seemed to be stable in the solvents heptane and carbon tetrachloride; that is, no systematic changes in the values of *A* - *A*₀ at the wavelengths studied were detected. In the solvent tetrachloroethylene a slow but definite reaction was noted which affected the values of *A* - *A*₀ at 465 nm. Therefore, on this solvent, only data at 535 nm were used and no data were collected at elevated temperatures.

Results and Discussion

Table I lists the values of *K* obtained at 25° for the complexes of iodine with different nitriles in the solvents carbon tetrachloride and heptane. The value of *K* for acetonitrile in carbon tetrachloride agrees with Person, Golton, and Popov's¹ value of 0.42 ± 0.05 *M*⁻¹. Due to the low solubility of acetonitrile in heptane, a reliable value of the formation equilibrium constant for the acetonitrile-iodine complex in this solvent could not be obtained.

As pointed out earlier, the absorbances of the pivalonitrile-iodine solutions varied slowly with time, indicating that some further reaction was occurring. This variation was especially evident in heptane. Therefore, the reliabilities of the values of *K* for the pivalonitrile-iodine complex are less than for the other nitriles.

In either solvent the variation of *K* with nitrile is quite small. However, the increase in *K* noted is consistent with the Taft σ^* values of the nitriles. This is especially evident in carbon tetrachloride. That is,

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TABLE II
 THERMODYNAMIC PARAMETERS OF DIFFERENT NITRILE-IODINE COMPLEXES IN HEPTANE AND CARBON TETRACHLORIDE

Nitrile	Solvent, <i>n</i> -heptane				Solvent, CCl ₄			
	Complete runs ^a		Drago method ^{a,b}		Complete runs ^a		Drago method ^{a,b}	
	-ΔH° ^d	-ΔS° ^e	-ΔH°	-ΔS°	-ΔH°	-ΔS°	-ΔH°	-ΔS°
CH ₃ CN							2.92 ± 0.03	11.31 ± 0.09
C ₂ H ₅ CN			3.93 ± 0.03	13.32 ± 0.09	2.31 ± 0.45	9.2 ± 1.5	2.94 ± 0.05	11.26 ± 0.16
<i>n</i> -C ₃ H ₇ CN	3.20 ± 0.17	10.7 ± 0.5	3.91 ± 0.03	13.07 ± 0.08	2.83 ± 0.17	10.9 ± 0.5	2.97 ± 0.06	11.31 ± 0.18
<i>n</i> -C ₄ H ₉ CN	3.0 ± 0.3 ^c	9.8 ± 0.8 ^c	4.25 ± 0.09	14.12 ± 0.28	2.70 ± 0.35	10.3 ± 1.1	2.93 ± 0.03	10.99 ± 0.15
C(CH ₃) ₃ CN					2.10 ± 0.08	8.2 ± 0.3		

^a Uncertainties are standard deviations. ^b Calculated as described in ref 12. ^c Data from ref 9. ^d In kcal/mol. ^e In eu.

acetonitrile with a Taft σ^* value of zero has the lowest value of K , propio-, butyro-, and valeronitrile with σ^* values that are all about the same (-0.100, -0.115, -0.130, respectively) have intermediate values of K , and pivalonitrile with the most negative σ^* value (-0.32) has the highest value of K .

From the results obtained in the study of halogen complexes of acetonitrile and chloro-substituted acetonitriles in carbon tetrachloride, a linear relationship between $\ln K$ and the Taft σ^* values of the nitriles has been proposed.¹ Our data are consistent with such a relationship. On the basis of this relationship Person, Golton, and Popov have predicted a value of K of 0.53 M^{-1} for the pivalonitrile-iodine complex in carbon tetrachloride. This is close to the experimental value of 0.58 M^{-1} listed in Table I.

It seems, therefore, that the variation in the strengths of the aliphatic nitrile-iodine complexes can be adequately accounted for in terms of inductive effects as measured by the Taft σ^* values. In heptane the correlation between K and σ^* is not as evident as it is in carbon tetrachloride because reliable values of K could be obtained in heptane only for the propionitrile-, butyronitrile-, and valeronitrile-iodine complexes. The experimental uncertainties in K for these three complexes obscure the small change in K predicted by σ^* .

Values of ΔH° and ΔS° , determined for selected nitriles in carbon tetrachloride and heptane, are listed in Table II and were obtained from the slopes and intercepts of $\ln K$ vs. $1/T$ plots, utilizing independent runs at at least three different temperatures. As can be seen from the data in Table II, ΔH° and ΔS° are essentially the same for all the nitriles in a particular solvent. This is not surprising considering the similarities in K . In carbon tetrachloride the average ΔH° for all the nitriles is -2.4 kcal/mol and the average ΔS° is -9.5 eu. These averages are in agreement with the values of ΔH° of -1.9 ± 0.6 kcal and ΔS° of -8.3 ± 2.0 eu reported by Person, Golton, and Popov¹ and a ΔH° of -2.3 ± 0.3 reported by Drago, Wayland, and Carlson¹¹ for the acetonitrile-iodine complex. In heptane, the average value of ΔH° is -3.1 kcal/mol and of ΔS° -10.2 eu.

Since the change in K in going from one nitrile to another in a particular solvent is small, a more precise method of obtaining the thermodynamic parameters was sought. Drago, Carlson, Rose, and Wenz¹² have proposed a method of obtaining values of ΔH° and ΔS° with high precision. This method utilizes an analysis of the spectra of single solutions at various temperatures

at a wavelength at which $\epsilon_C - \epsilon_A$ is essentially temperature independent. Values of ΔH° and ΔS° were calculated using this method at the peak wavelengths. Although the values of ΔH° and ΔS° obtained were much more precise they were appreciably higher (0.5-1.0 kcal in ΔH° and 2-4 eu in ΔS°) than those obtained from independent runs. This discrepancy would indicate that at the wavelengths chosen $\epsilon_C - \epsilon_A$ varies with temperature. From the differences in the thermodynamic parameters calculated by the two methods it is estimated that $\epsilon_C - \epsilon_A$ decreases by about 7 units/10° rise in the 460-nm region and by 8 units/10° rise in the 535-nm region. It is interesting to note that such a small temperature dependence can cause rather large differences in the values obtained from the two methods. It should be pointed out that such a small temperature dependence in $\epsilon_C - \epsilon_A$ is nearly masked by experimental indetermination. The Drago results, however, do reinforce the conclusion that ΔH° and ΔS° do not change significantly in a family of nitriles within a particular solvent. Also, the variation in ΔH° and ΔS° from one solvent to another is about the same as that obtained from independent runs.

The complex formed between butyronitrile and iodine was also investigated in the solvents cyclohexane, hexane, carbon disulfide, and tetrachloroethylene. Table III lists the values of the equilibrium constant

 TABLE III
 EQUILIBRIUM FORMATION CONSTANTS AND THERMODYNAMIC PARAMETERS FOR THE BUTYRONITRILE-IODINE COMPLEX IN DIFFERENT SOLVENTS^a

Solvent	K_C , l./mol (25°)	$-\Delta H^\circ$, kcal/mol	$-\Delta S^\circ$, eu
<i>n</i> -Heptane	0.99 ± 0.01	3.20 ± 0.17	10.7 ± 0.5
Cyclohexane	0.93 ± 0.02	2.89 ± 0.05	9.8 ± 0.3
<i>n</i> -Hexane	0.93 ± 0.02	4.24 ± 0.16	14.4 ± 0.5
Carbon disulfide	0.52 ± 0.02	1.72 ± 0.05	7.1 ± 0.2
Carbon tetrachloride	0.51 ± 0.01	2.83 ± 0.17	10.9 ± 0.5
Tetrachloroethylene	0.41 ± 0.01	3.69 ± 0.11	14.1 ± 0.4

^a The uncertainties are standard deviations using data at both wavelengths using a least-squares analysis.

and ΔH° and ΔS° for the butyronitrile-iodine complex in the different solvents. The value of K decreases by about a factor of 2 in going from heptane to tetrachloroethylene.

The effect of solvent on the stability of molecular complexes has been discussed by a number of investigators. One of the effects that has been considered is the variation in activity coefficient in going from one solvent to another. Attempts have been made to correct for this variation using regular solution theory.^{13,14}

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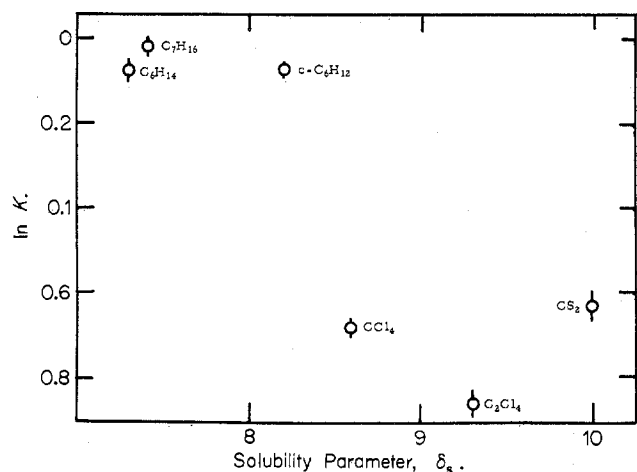


Figure 1.—Plot of $\ln K$ for the butyronitrile-iodine complex vs. the solubility parameter of solvent, δ_s .

From this theory, two equations have been proposed to correlate K with the solubility parameter, δ_s , of the solvent. The simpler of the two, that derived by Buchowski, *et al.*,¹³ has the form

$$\ln K = A + B\delta_s \quad (2)$$

in which A and B are parameters depending only on the donor and acceptor. Figure 1 shows a plot of $\ln K$ vs. δ_s for the butyronitrile-iodine complex in the solvents studied. It is apparent from the plot that δ_s cannot quantitatively account for the variation in K with solvent. There is a general decrease in K with increasing δ_s . However, K seems to be more a function of the type of solvent, that is, hydrocarbon or chlorinated hydrocarbon, rather than any specific value of δ_s . Christian¹⁴ has attempted to correlate K with solvent using a more complex equation that involves not only the solubility parameter of the solvent but also that of the donor and acceptor as well. This equation does not fit the data any better than eq 2 does.

At present, solubility parameters do not seem to describe adequately the influence of solvent on the magnitude of K . This may in part be due to both the un-

certainities in the values of δ_s and the questionable use of solubility parameters for systems involving polar molecules.¹⁵

The values of ΔH° and ΔS° in the different solvents do not show any definite trend. In cyclohexane and hexane the value of K is the same; however, both ΔH° and ΔS° in these two solvents are significantly different. In general, those solvents in which ΔH° is large also have large negative values of ΔS° . That is, there is a compensation between ΔH° and ΔS° . This same type of compensation has been found to exist for many different donor-acceptor complexes. Indeed, linear relationships between ΔH° and ΔS° have been reported.¹⁶

At 25° the greatest difference in K occurs between the solvents *n*-heptane and tetrachloroethylene. This difference represents a change in the free energies of formation of about 0.5 kcal/mol in the two solvents. This change is not far from the experimental uncertainties in ΔH° and $T\Delta S^\circ$. Therefore, it is not possible to ascribe the change in the equilibrium formation constant with solvent to either enthalpy or entropy variation. McKinney and Popov¹⁷ have determined the values of ΔH° and ΔS° for the pyridine-iodine complex in several solvents. The changes in these parameters with solvent were also found to be small and no trend with any specific solvent property was discernible.

Although the influence of solvent on complex stability has been repeatedly demonstrated, there does not seem to be any one solvent parameter that can be used to correlate changes in stabilities. Perhaps when sufficient reliable data become available, this situation will improve.

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