

infrared spectrum identical with an authentic sample, n_D^{20} 1.3826 (authentic sample n_D^{20} 1.3828). *2-Ethylhexanol*: retention time and infrared spectrum identical with an authentic sample, n_D^{20} 1.4271 (authentic sample n_D^{20} 1.4281). *2-Ethylhexyl formate*: infrared spectrum characteristic of formate ester (strong peaks at 8.48 and 5.78 μ), n_D^{20} 1.4168, *Anal.* Calcd. for $C_9H_{18}O_2$: C, 68.31; H, 11.47. Found: C, 68.53, 68.65; H, 11.33, 11.60.

Cobalt Distribution and Determination of K_x .—2-Ethylhexanal (316 mmoles per l. in dihexyl ether) was reduced according to the above described general procedure at 160°, 754 p.s.i. hydrogen partial pressure, 950 p.s.i. carbon monoxide partial pressure and 6.30 mmoles per liter of dicobalt octacarbonyl charged (C_x). When the reduction of aldehyde was 50% complete a liquid aliquot (by wt.) was taken through the cooling coil, at such a rate that the time before cooling to approximately room temperature was approximately 0.02 sec. The depressured and cooled sample was directed into a solution of nickelous chloride-*o*-phenanthroline complex and analyzed for cobalt hydrocarbonyl.¹⁵ Another aliquot (by wt.) was similarly withdrawn, collected in a suitable glass container, and analyzed for total cobalt carbonyls gasometrically.¹⁵ The liquid reaction medium contained 59% of the original cobalt as cobalt hydrocarbonyl and 21% as dicobalt octacarbonyl. Two reactions under conditions identical with the above were conducted in which 15% aliquots of the gas were passed rapidly (5,000 ml./min.) through the cooling coil to a sintered glass filter stick immersed in nickelous chloride-*o*-phenanthroline solution. The precipitate which formed in solution and on the sintered glass was collected and analyzed gasometrically.¹⁵ The gas phase in the autoclave was thus found to contain 24% of the originally charged cobalt as cobalt hydrocarbonyl; over-all cobalt balance, 104%. On cooling, depressuring, and opening the autoclave, a slight color of metallic cobalt was observed on the internal surfaces which were below the liquid level; the amount was too small to be physically recoverable although the color was easily removable by wiping.

The analyses of the liquid samples are believed to be the more accurate; for calculation of K_x the cobalt hydrocarbonyl in the gas phase was taken as the difference between dicobalt octacarbonyl charged and the total cobalt carbonyls in the liquid phase. Four such determinations in separate experiments gave an average value of K_x of 2.8; σ , 0.15.

Determination of K_y .—In experiments at 160° to which no poison was added and which included 4 levels of hydrogen partial pressures from 11 to 770 p.s.i., 3 levels of catalyst concentrations (C_x) from 6.30 to 25.2 mmoles/l., 3 levels of carbon mon-

oxide partial pressures from 500 to 960 p.s.i., and 2 levels of 2-ethylhexanal concentrations 78.5 and 316 mmoles/liter, liquid samples were taken as described above at about 50% completion of aldehyde reduction and analyzed¹⁵ gasometrically for total cobalt carbonyl and cobalt hydrocarbonyl. Concentrations of dicobalt octacarbonyl and cobalt hydrocarbonyl were determined and corrected for thermal expansion of the organic medium on reactor conditions. K_y then was calculated from equation 10 with dicobalt octacarbonyl and cobalt hydrocarbonyl concentrations expressed in moles per liter and hydrogen partial pressure in pounds per sq. in. Eight determinations gave an average value of 8×10^{-5} ; σ 1.8×10^{-5} .

Hydroformylation of Heptenes.—Prior to an experiment all internal surfaces of the three-liter autoclave were cleaned with steel wool and hydrocarbon solvent and polished with clean white cloths. One liter of heptenes prepared by copolymerization of propene and butene²⁸ together with the tabulated quantities of cobaltous oleate and other metal soap was then charged to the autoclave. The free space was flushed with synthesis gas by pressuring twice to approximately 500 p.s.i. and carefully venting. The autoclave was pressure tested at 3000 p.s.i. and then slowly vented to 1500 p.s.i. The autoclave was heated with shaking to 177° over a period of about 1.5 hours. When the reaction started, as evidenced by a sharp drop in pressure, the pressure was raised to 3000 p.s.i. Each time the pressure dropped to 2500 p.s.i. it was raised back to 3000 p.s.i. The first two or three such pressure drops were very rapid and were accompanied by a momentary rise of several degrees in temperature. In these cases the temperature was allowed to subside to 177° before additional gas was added, whereupon the pressure would drop to as low as 1000 p.s.i. The hydroformylations were continued for a total of six hours after the first pressure drop. The autoclave was then cooled to room temperature with an external flow of air. The autoclave was flushed twice with 500 p.s.i. of hydrogen and then pressured to 150 p.s.i. with hydrogen. To decompose the cobalt carbonyls, the contents were then heated to 149° and maintained at this temperature for one hour (no absorption of pressure) before cooling and discharging.

Acknowledgment.—C. L. A. wishes to acknowledge with gratitude financial support from the Robert A. Welch foundation during a major portion of this work.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF IOWA, IOWA CITY, IOWA]

Studies on the Chemistry of Halogens and of Polyhalides. XXII. Halogen Complex Formation and the Taft σ^* Constant¹

BY WILLIS B. PERSON, WILLIAM C. GOLTON AND ALEXANDER I. POPOV²

RECEIVED JULY 24, 1962

Formation constants, standard entropies and standard enthalpies for complex formation were determined for a number of compounds in carbon tetrachloride solutions: acetonitrile and monochloroacetonitrile complexes with ICl, IBr and I₂, dichloroacetonitrile complexes with ICl and IBr and the trichloroacetonitrile complex with ICl. For each halogen log K was found to be a linear function of the Taft σ^* constant. The slopes of log K vs. σ^* plots were -0.60, -0.43 and -0.32 for ICl, IBr and I₂ complexes, respectively. A plot of ΔH° vs. ΔS° for these complexes gave a reasonably straight line, which is characteristic of these donor-acceptor complexes.

Introduction

The classical work of Benesi and Hildebrand³ on the complexing reaction between iodine and benzene provided a strong impetus toward the studies of molecular complexes involving halogen or interhalogen molecules. During the past decade many such complexes have been investigated primarily by spectrophotometric techniques.⁴ It is generally agreed that the halogen

complexes are formed by a Lewis acid-base interaction in which the halogen molecule acts as a Lewis acid (or electron acceptor). A large number of Lewis bases with different donor strengths have been used in the studies of halogen complexes. Among them are various substituted aromatic compounds, aromatic and aliphatic amines, amides and nitriles. Halogen complexes differ considerably in their relative strength as shown by their formation constants whose numerical values range from 0.1 to 10⁵ (in liter mole⁻¹). The strength of a given complex will depend on the relative acid strength of the halogen molecule and on the electron donor strength of the Lewis base which forms the complex.

It is obvious, of course, that the latter property is closely related to the structure of the donor molecule; however, very little work has been done as yet on the relationship between the structure and the chemical properties of the donors on one hand, and the thermo-

(1) Abstracted from the Ph.D. Dissertation of William C. Golton, State University of Iowa, June, 1962.

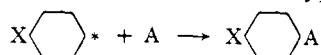
(2) To whom correspondence may be sent. Department of Chemistry, Michigan State University, East Lansing, Michigan.

(3) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

(4) (a) L. J. Andrews and R. M. Keefer in "Advances in Inorganic Chemistry and Radiochemistry," Vol. III, H. J. Emeléus and A. G. Sharpe, Editors, Academic Press, New York, N. Y., 1961, p. 91; (b) previous papers in this series, see *J. Am. Chem. Soc.*, **83**, 3586 (1961), for paper XXI; (c) R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962); (d) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer Verlag, Berlin, 1961.

dynamic properties of the resulting halogen complexes on the other. One of the major studies of this type has been reported by Andrews and Keefer⁵ in which a comparison was made of the stability of various complexes between alkylbenzenes and halogens as the number of alkyl substituents on the aromatic nucleus was changed.

For many years the effects of structure upon chemical reactivity of an organic compound have been interpreted as being due to the sum of approximately independent contributions of polar, steric and resonance effects.⁶ For a series of reactions of the type



where X is a variable substituent and * marks the reaction site, the effect of X can be described by the Hammett equation

$$\log K/K_0 = \rho\sigma \quad (1)$$

Here K_0 is the rate or equilibrium constant for the standard reaction ($X = H$, for example) K is the corresponding rate or equilibrium constant for another substituent, ρ is a proportionality constant which depends on the nature and condition of the reaction and σ is a constant independent of the nature of the reaction, but characteristic of the substituent X. It is thought to consist of three approximately independent terms σ_I , σ_R and σ_S which refer to the inductive, resonance and steric effects, respectively.⁶ Taft⁷ has extended the Hammett sigma relation to include rigid aliphatic compounds, and has defined experimentally a constant, σ^* , in which the resonance and steric effects may be neglected. There seems to be no *a priori* reason why these concepts cannot be applied to the donor-acceptor equilibria and thus take advantage of the fairly extensive set of σ^* values available to enable us to predict formation constants for related series of compounds.

This possibility has been suggested before.⁸⁻¹⁰ Yada, Tanaka and Nagakura⁸ have shown that the heats of formation of complexes between substituted amines and I_2 can be correlated with the Taft σ^* constants, although their studies did not cover a wide range of σ^* values. Recently, Drago, Wenz and Carlson⁹ have shown that ΔH_f for complexes between I_2 and N,N -dimethylamides can also be correlated successfully with the Taft σ^* constants, over a wide range of values for σ^* . In these cases and in the work reported here, the effect of the substituent is expected to be purely inductive, so we should expect fairly good correlation with Taft σ^* constants.

In this work we studied the reaction



with $R = CH_3, CH_2Cl, CHCl_2$ and CCl_3 and $XY = ICl, IBr$, and I_2 . In these reactions the steric effects should be minimal since the geometry of the complexes is expected to remain essentially constant. Moreover, the resonance effect should also be negligible since one would not expect much resonance interaction between the saturated substituents and the reaction site.

Previous work has shown that nitriles form complexes with halogens which, while weak, still are capable of

being detected spectrophotometrically.¹¹ The progressive inclusion of electronegative chlorine atoms into the methyl group was expected to influence strongly the electron donor properties of the nitriles so that there should be a considerable variation in the thermodynamic properties of the resulting complexes. Out of twelve possible combinations of these four donors and three acceptors, nine were actually studied. They were iodine, iodine bromide, and iodine monochloride complexes of acetonitrile, and of chloroacetonitrile, iodine monochloride and iodine bromide complexes of dichloroacetonitrile and the iodine monochloride complex of trichloroacetonitrile. The other three complexes were too weak to be determined by the standard spectrophotometric techniques.

Experimental Part

Reagents.—The source and the purification of iodine, iodine bromide and iodine monochloride were described in previous publications.^{11,12}

Acetonitrile ("spectroquality") was obtained from Matheson, Coleman and Bell. It was purified by refluxing over phosphorus pentoxide for one day and then distilling it through a 38-cm. helices-packed column. The boiling point of the purified solvent was 81.0° at 745 mm. (identical with the literature value¹³). The resulting product had an absorptivity of 0.5 or less in a 1 cm. cell at 205 μ . A sample of this material was analyzed by vapor phase chromatography using a Perkin-Elmer Model 154 chromatograph. It did not exhibit any foreign peaks, but this may be due to the inability of our columns (didecyl phthalate or silicone oil) to resolve impurities in acetonitrile.

Chloroacetonitrile was likewise obtained from Matheson, Coleman and Bell. The original product had a yellow color and showed the presence of several impurities when analyzed in a vapor chromatograph. It was purified by a method analogous to that used for acetonitrile. The middle fraction of the distillate with a boiling point of 123° at 745 mm. (lit.¹⁴ 125° at 760 mm.) was used for subsequent work.

Dichloroacetonitrile could not be obtained commercially and was prepared from chloral hydrate. The first reaction was the conversion of chloral hydrate to dichloroacetamide by treating it in an ether solution with an aqueous solution of ammonia and potassium cyanide¹⁵ and then dehydrating the obtained dichloroacetamide with phosphorus pentoxide in *o*-dichlorobenzene for several hours at 110° , distilling the product under vacuum and then purifying it by several additional fractional distillations. The purity of the product was checked by vapor phase chromatography and by its absorption in the ultraviolet region of the spectrum.

Eastman "White Label" trichloroacetamide was dehydrated with phosphorus pentoxide in xylene solution and purified by fractional distillation. The boiling point of the purified product was 85° at 745 mm. (lit.,¹⁶ 85.7° at 760 mm.). The purity of the product was checked by vapor phase chromatography.

All of these nitriles were stored and handled in a drybox under a nitrogen atmosphere.

Carbon tetrachloride was purified by the previously described procedure.¹¹

Preparation of Solutions.—Stock nitrile solutions of known concentrations in carbon tetrachloride were prepared by direct weighing of the nitrile into a volumetric flask and filling to the mark. These solutions were subsequently diluted to give the necessary series of solutions of variable concentration. Stock halogen solutions in the same solvent were prepared by dissolving the approximate amount of the respective halogen in carbon tetrachloride and then determining the exact concentration by an arsenite titration. All of the solutions were prepared in a drybox under nitrogen atmosphere.

Spectrophotometric Procedure.—Spectrophotometric measurements were made on a Beckman DK-2 recording spectrophotometer using stoppered 1 cm. silica cells. The cell compartment was thermostated by passing through its walls a 50% ethylene glycol solution from a large capacity constant temperature bath. The temperature of the cell compartment was measured through a thermometer well. By the proper adjustment of the reservoir bath temperature and the rate of flow of the ethylene glycol solu-

(5) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **74**, 4500 (1952).

(6) See, for example, J. Hine, "Physical Organic Chemistry," 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(7) (a) R. W. Taft, Jr., in M. S. Newman, ed., "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chap. 13; (b) R. W. Taft, Jr., N. C. Deno and P. S. Skell, *Ann. Rev. Phys. Chem.*, **9**, 287 (1958).

(8) H. Yada, J. Tanaka and S. Nagakura, *Bull. Chem. Soc. Japan*, **33**, 1660 (1960).

(9) R. S. Drago, D. A. Wenz and R. L. Carlson, *J. Am. Chem. Soc.*, **84**, 1106 (1962).

(10) W. B. Person, *ibid.*, **84**, 536 (1962).

(11) A. I. Popov and W. A. Deskin, *ibid.*, **80**, 2976 (1958).

(12) A. I. Popov, J. C. Marshall, F. B. Stute and W. B. Person, *ibid.*, **83**, 3586 (1961).

(13) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Press, New York, N. Y., 1950, p. 528.

(14) J. Vandewiger, *Bull. Soc. Chim. Belge.*, **45**, 251 (1956).

(15) J. R. Clark and W. J. Shibe, "Organic Syntheses," Col. Vol. III, John Wiley and Sons, New York, N. Y., 1955, p. 260.

(16) M. Davies and D. G. Jenkins, *J. Chem. Soc.*, 2374 (1954).

tion it was possible to maintain the temperature of the cell compartment constant to $\pm 0.1^\circ$. Measurements were made at 0, 10, 25 and 40° . In order to prevent condensation of moisture in the cell compartment a stream of dry nitrogen was passed through it when measurements were carried out at 0° and at 10° .

In order to determine the absorbance due to solvents, cells of 0.1 cm. had to be used. In this case the measurements were made on a Cary model 11 recording spectrophotometer.

Formation constants of the complexes were determined by the Ketelaar method.¹⁷ Standard free energy for the complex formation was determined from the formation constant while the standard enthalpy change was determined by the usual manner from the $\log K$ vs. $1/T$ plots. Using these two values the standard entropy was obtained from the usual thermodynamic relationship. In the case of the Ketelaar as well as the $\log K$ vs. $1/T$ plots the slopes of the straight lines were determined by the method of least squares. Concentration units used in calculation were moles/liter. The use of the Ketelaar equation permitted us to evaluate both K and the molar absorptivity of the complex at each temperature. After corrections were made for changing density, the molar absorptivities at the wave lengths studied were found to be essentially constant, within our experimental error.¹⁸

Experimental Results

All of the halogen-nitrile complexes are relatively weak, but in this series their formation constants varied through about two orders of magnitude. Therefore, in order to produce spectral changes which would be adequate for measuring the strength of these complexes, the concentrations of the donor in solution had to be varied over rather wide limits with a relatively large excess of the donor. This was especially true for very weak complexes such as chloroacetonitrile-iodine, dichloroacetonitrile-iodine bromide, and trichloroacetonitrile-iodine monochloride where the concentration of the donor was as high as 6 M . Even under these conditions the spectral changes were not large.

Under these circumstances the measurements inherently contained relatively large errors. In the first place, because of relatively minor changes in the absorption spectra with increasing amounts of the donor molecule, the measurements were reduced to the determinations of small differences between large numbers. In addition, because of the high concentration of donor molecules, one would expect some change in the character of the solvent and the usual assumption that the activity coefficient of the solvent is equal to unity might lead to an additional source of errors.

On the other end of the stability scale, as in the case of the acetonitrile-iodine monochloride complex, the concentration of the donor could always be kept below 1 M . It was noticed, however, that these solutions were relatively unstable and their spectra tended to change with time, possibly due to further reaction of the complex.¹¹ In all cases measurements were made on freshly prepared solutions.

It was observed that in certain cases there was a definite shift in the isosbestic point with increasing concentration of the donor. This was especially noticeable for acetonitrile-iodine and dichloroacetonitrile-iodine monochloride complexes at 0° . To a lesser extent the same observation was made in cases of other solutions at the same temperature.

A shift in the isosbestic point was reported in the study of dimethylacetamide-iodine complexes.¹⁹ In that study it was attributed to the changing character of the solvent with increasing concentration of the donor. It should be added that another possible explanation may be that at higher donor concentrations there is a possibility of forming a second, very weak, complex containing two molecules of donor to the one of the halogen. The precision of our data was insufficient to allow a reasonable differentiation between these two possibilities.

Because of the weakness of our complexes, possible reactivity of the halogen with the donors, and the resulting uncertainties of measurements it was especially necessary to evaluate carefully the obtained data and to do an error analysis. While it is customary to calculate formation constants from data obtained at one wave length, in this case measurements were made at several wave lengths and the results were averaged. Since in this investigation a large number of measurements was made with solutions of different concentrations and at different wave lengths, it was possible to detect spurious results readily. Either individual measurements of an entire set of data at a given wave length were rejected if the value in question was more than three times greater than the average deviation. In such cases these measurements were repeated. Detailed analysis of errors suggested that the relative variation in the value of formation con-

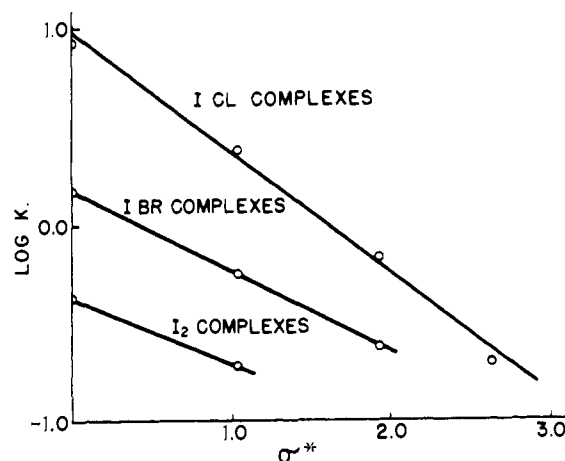


Fig. 1.—Relationship between $\log K$ and σ^* for nitrile-halogen complexes at 25°

stants reported in this work was no greater than 15%. The formation constants obtained at various temperatures as well as the thermodynamic functions for the complex forming reaction are given in Tables I and II. Uncertainties reported in K 's are the average deviations of values from Ketelaar plots at several wave lengths. In Table II, the uncertainties listed are standard deviations calculated from the least squares treatment of the plots of $\log K$ vs. $1/T$.

Discussion

The numerical order of the formation constants follows, in general, the predicted trend. As the electron withdrawing power of the methyl group is increased by progressive chlorine substitution, the complexes become less stable. On the other hand, the stability also is influenced by the relative acidity of the halogens with $\text{ICl} > \text{IBr} > \text{I}_2$ as predicted by Scott.²⁰ Reasonable agreement is found with the values of formation constants of acetonitrile complexes at room temperature determined previously¹¹ (6.9 ± 0.3 , 1.40 ± 0.03 and 0.57 ± 0.02 for ICl , IBr and I_2 complexes, respectively). It should be noted that in previous work no attempt was made to control the temperature and the slight variation in the value for the ICl complex formation constant may be due to this fact. In this case the formation constant varies considerably with temperature (Table I).

TABLE I
FORMATION CONSTANTS FOR NITRILE-HALOGEN COMPLEXES AT VARIOUS TEMPERATURES

	0°	10°	25°	40°
$\text{CH}_3\text{CN}\cdot\text{ICl}$	18.2 ± 0.4	12.4 ± 0.4	8.39 ± 0.77	4.58 ± 0.18
$\text{CH}_3\text{CN}\cdot\text{IBr}$	$2.95 \pm .30$	$2.30 \pm .30$	$1.48 \pm .21$	$1.16 \pm .13$
$\text{CH}_3\text{CN}\cdot\text{I}_2$	$0.59 \pm .06$	$0.43 \pm .01$	$0.42 \pm .05$	$0.35 \pm .03$
$\text{ClCH}_2\text{CN}\cdot\text{ICl}$	$4.38 \pm .17$	$3.55 \pm .30$	$2.41 \pm .24$	$1.23 \pm .22$
$\text{ClCH}_2\text{CN}\cdot\text{IBr}$	$0.92 \pm .02$	$0.76 \pm .03$	$0.55 \pm .03$	$0.46 \pm .05$
$\text{ClCH}_2\text{CN}\cdot\text{I}_2$	$0.26 \pm .02$	$.20 \pm .03$	$.19 \pm .02$	$.18 \pm .02$
$\text{Cl}_2\text{CHCN}\cdot\text{ICl}$	$1.15 \pm .10$	$.82 \pm .07$	$.69 \pm .05$	$.46 \pm .09$
$\text{Cl}_2\text{CHCN}\cdot\text{IBr}$	$0.52 \pm .03$	$.24 \pm .02$	$.23 \pm .08$	
$\text{Cl}_3\text{CCN}\cdot\text{ICl}$	$0.49 \pm .04$	$.39 \pm .02$	$.20 \pm .01$	$.15 \pm .02$

A plot of $\log K$ vs. σ^* for the halogen-nitrile complexes is given in Fig. 1. It is seen that, as predicted by eq. 1, there is a linear relationship between $\log K$ and σ^* . All points for a given series of complexes fall on straight lines within the experimental error of the measurement. Of course there are only a few points for complexes with each halogen, but the data cover a wide range of σ^* values, and there is no reason to doubt that complexes for substituents with intermediate values of σ^* would show deviations in the absence of steric or resonance effects. We believe that our plots support the conclusion of Drago, Wenz and Carlson⁹ that the Taft σ^* values provide a useful cor-

(17) J. A. A. Ketelaar, C. Van de Stolpe, A. Goudsmit and W. Dzcubas, *Rec. trav. chim.*, **71**, 1104 (1952).

(18) For more details see W. C. Golton, Ph.D. Thesis, University of Iowa, 1962.

(19) R. S. Drago, R. L. Carlson, N. J. Rose and W. A. Wenz, *J. Am. Chem. Soc.*, **83**, 3572 (1961).

(20) R. L. Scott, *ibid.*, **75**, 1550 (1953).

relation for extrapolating quantitatively to predict the effect of substituents on the base strength of a donor.

The plots illustrated in Fig. 1 yield empirical equations for the ICl, IBr and I₂ complexes, respectively

$$\log K_{\text{ICl}} = -0.60\sigma^* + 0.96 \quad (2)$$

$$\log K_{\text{IBr}} = -0.43\sigma^* + 0.18 \quad (3)$$

$$\log K_{\text{I}_2} = -0.32\sigma^* - 0.38 \quad (4)$$

TABLE II

STANDARD ENTHALPY AND STANDARD ENTROPY FOR THE FORMATION OF NITRILE-HALOGEN COMPLEXES IN CARBON TETRACHLORIDE

Complex	ΔH° , kcal./mole	ΔS° , e. u. (25°)
CH ₃ CN·ICl	-4.9 ± 0.7	-12.3 ± 2.6
CH ₃ CN·IBr	-4.1 ± .3	-12.8 ± 0.9
CH ₃ CN·I ₂	-1.9 ± .6	-8.3 ± 2.0
ClCH ₂ CN·ICl	-5.3 ± .9	-16 ± 3
ClCH ₂ CN·IBr	-3.1 ± .2	-11.4 ± 0.7
ClCH ₂ CN·I ₂	-1.5 ± .4	-8.4 ± 1.5
Cl ₂ CHCN·ICl	-3.7 ± .4	-13.3 ± 1.3
Cl ₂ CHCN·IBr	-2.0 ± .6	-9.7 ± 3.0
Cl ₃ CCN·ICl	-5.4 ± .6	-21.3 ± 3

On the basis of the above equations it is possible to predict the strength of other nitrile complexes. For example, a value of $K = 10.5$ is predicted for the propionitrile-ICl complex at 25°. This compares rather favorably with the reported value of 14.8 ± 1.2 .²¹ Other predicted formation constants for some nitrile complexes which have not been studied experimentally as yet are given in Table III.

TABLE III

PREDICTED FORMATION CONSTANTS OF NITRILE-HALOGEN COMPLEXES (CARBON TETRACHLORIDE SOLUTIONS AT 25°)

Complex	K
Cl ₂ CHCN·I ₂	0.10
Cl ₃ CCN·IBr	0.11
Cl ₃ CCN·I ₂	0.057
ICH ₂ CN·ICl	2.8
ICH ₂ CN·I ₂	0.22
C ₆ H ₅ CN·I ₂	0.27
<i>t</i> -C ₄ H ₉ CN·I ₂	0.53

The above table includes the formation constants of the missing three members of our series, Cl₂CHCN·I₂, Cl₃CCN·IBr and Cl₃CCN·I₂. The magnitude of these values explains why it was not possible to measure them. Even if pure nitriles could be used as solvents without reaction, none of these complexes would be more than 50% associated! Likewise the spectral shifts would be so small that they could not be measured with any degree of accuracy with presently available instruments.

The predicted magnitudes of K_f for the iodo-substituted nitriles provides the interesting thought that one might expect the iodine atom to compete with the nitrogen atom as the site of donor action in halogen complexes with these donors. Also, one might expect some competition between the nitrogen atom and the π electrons of the benzene ring in a complex between C₆H₅CN and a halogen. (However, the electron-withdrawing character of the nitrile group should weaken the tendency for the benzene ring to donate its π electrons. Also the situation is probably complicated here by resonance effects.²²)

(21) R. E. Buckles and J. F. Mills, *J. Am. Chem. Soc.*, **76**, 4895 (1954).

(22) NOTE ADDED IN PROOF.—While our manuscript was in press, Klabeo (*J. Am. Chem. Soc.*, **84**, 3458 (1962)) reported experimental values for the formation constants of halogen complexes with benzonitrile. His values (at 20°) are higher than predicted from our equations 2-4. (For C₆H₅CN·I₂ he reports $K = 0.8$; cf. 0.27 in Table II.) Both the magnitude and direction of deviation from the predicted values are consistent with the prediction

As expected the ρ^* values decrease with the decreasing acidity of the halogen. Also ρ^* values are negative as expected for a reaction in which the product results in a larger electron demand at the reaction site. These results are in agreement with the usual interpretation of ρ^* .⁷

It is difficult to compare ρ^* values obtained in this investigation with those of other workers due to the scarcity of studies of the same nature. Although Taft^{7a} lists numerous ρ^* values, few of them are comparable to the reaction of halogen complex formation. It may be noted, however, that the ρ^* values for the dissociation of acids are about +1.5 (hence, -1.5 for association) which is the same sign and order as the values reported in this study.

It is interesting to compare our data with other studies of halogen complexes. The data of Yada, Tanaka and Nagakura⁹ for complexes between I₂ and amines give a straight line obeying the equation

$$\log K = -3.65\sigma^* + 4.7 \quad (5)$$

The corresponding equation for N,N-dimethylamide-iodine complexes is

$$\log K = -0.69\sigma^* + 0.84 \quad (6)$$

It would appear that the sign and magnitude of ρ^* found for the halogen complexes with nitriles are approximately what might be expected from these other studies. It is difficult to extend these ideas to the complexes between I₂ and π -donors, since the Hammett and Taft constants apply to reactions of substitution of a σ -bond, rather than to reactions involving the π -electrons. However, the Hammett σ constants do attempt to measure the tendency of a given substituent to withdraw electrons from the ring, both by induction and by resonance effects. It is interesting, therefore, to attempt empirically to correlate the formation constants of complexes with aromatic donors with the Hammett σ constants. Since we could not decide just which σ constants should be preferred *a priori* in such a correlation, we used the σ_p constants. Data from Keefer and Andrews⁵ were plotted as $\log K$ vs. $\Sigma\sigma_p$ (the Hammett σ constant for a *para* substituent) where the sum extends over all substituents on the ring. The resulting straight line equations for ICl and I₂ complexes are, respectively

$$\log K = -1.38\Sigma\sigma_p - 0.17 \quad (7)$$

$$\log K = -0.95\Sigma\sigma_p - 0.83 \quad (8)$$

It is not clear how the slopes of these lines should be related to the values of ρ^* found above. However, the success of this correlation is surprisingly great, and the order of magnitude of the slope found (eq. 7 and 8) is surprisingly close to that for the other complexes, where the application of these ideas is more straightforward.

In a number of previous publications it was observed that a linear relationship exists between the enthalpy and the entropy of halogen complex formation.^{4a} The data reported in this paper are consistent with this observation.

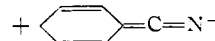
Figure 2 shows a plot of ΔH° vs. ΔS° . A fairly good straight line is obtained which obeys the empirical equation

$$+\Delta S^\circ = 1.85\Delta H^\circ - 5.6 \quad (9)$$

or

$$+\Delta H^\circ = 3.0 + 0.54\Delta S^\circ \quad (10)$$

that resonance effects are important. Thus, resonance structures of the form



will increase the ability of benzonitrile to act as an n-donor. However, it does not seem to be possible to evaluate one parameter, σ_R , such that substitution of ($\sigma^* + \sigma_R$) into equations 2-4 will enable us to predict the experimental formation constants accurately, although the order of magnitude of K is predictable from these equations.

Yada, Tanaka and Nagakura⁹ obtained for amine-iodine complexes the relationship

$$+ \Delta H^{\circ} = -1.667 + 0.545\Delta S^{\circ} \quad (11)$$

The slopes of the two straight lines are essentially identical. This result is perhaps to be expected from the analysis given earlier¹⁰ of the relationship between ΔH and ΔS for amine complexes. Certainly, if the argument given there concerning the slope of the ΔS vs. ΔH plot is correct, the same argument should apply to the plot for the nitrile-IX complexes, since a weak N-I bond is involved in both cases.

Since a linear relationship between ΔS and ΔH for these complexes is apparently found, one of the conditions necessary for a successful linear correlation between $\log K$ and σ^* is fulfilled, in agreement with the empirical finding (Fig. 1). Since

$$\Delta(\Delta F) = 2.3RT\rho^*\sigma^* = \Delta(\Delta H) - T\Delta(\Delta S)$$

and since, from equation 9

$$\Delta(\Delta S) = 1.85\Delta(\Delta H)$$

it follows that

$$\Delta(\Delta H) = \frac{2.3 \times 2.0T\rho^*\sigma^*}{1000} / 1 - \frac{1.85T}{1000}$$

$$\Delta(\Delta H) = 2.5\rho^*\sigma^*$$

at 300° K. Thus, a plot of ΔH vs. σ^* should give a line with greater slope than the corresponding plot of $\log K$. However, when we attempt this plot using our data,

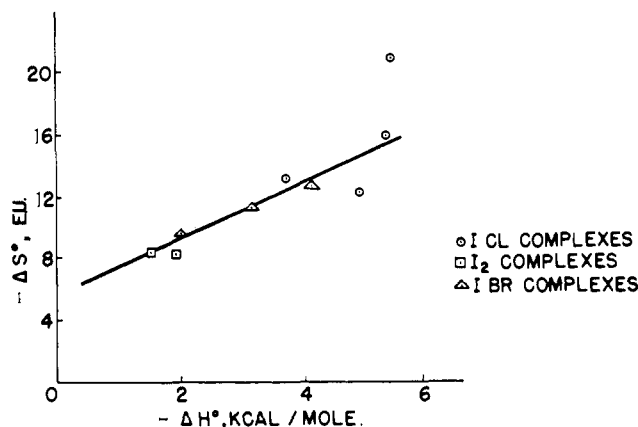


Fig. 2.—Relationship between entropies and enthalpies of formation for nitrile-halogen complexes.

we find considerable scatter, due to the unavoidably large error in the determination of ΔH . Thus, in our case, we find the correlation of $\log K$ with σ^* to be more successful than the correlation of ΔH vs. σ^* .

Acknowledgment.—The authors gratefully acknowledge the support of this research by NSF Grant G-9477. They are also indebted to Professor John Lach of the College of Pharmacy and to Professor Robert Dryer of the Biochemistry Department for the use of Beckman DK-2 spectrophotometers.

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY¹ OAK RIDGE, TENN., AND UNIVERSITY OF MAINE, ORONO, ME.]

Heats of Solution of Solids in Molten Reciprocal Salt Systems

BY M. BLANDER,^{2a} J. BRAUNSTEIN^{2b} AND M. D. SILVERMAN

RECEIVED OCTOBER 29, 1962

The heat of solution of solid AgCl in molten KNO₃, calculated from solubility and e.m.f. measurements by rigorous thermodynamic methods, is 19.2 ± 0.6 kcal/mole. This value is in excellent agreement with a value of 19.6 ± 1.0 kcal/mole estimated from a cycle first proposed by Flood, Förland and Grjøtheim illustrating the usefulness of this cycle in making predictions *a priori*.

In accordance with the considerations of Flood, Förland and Grjøtheim,³ the heat of solution of a solid such as AgCl in a solvent such as KNO₃ may be estimated from a knowledge of the heat changes for the three processes

- (A) $\text{AgCl(sol.)} + \text{KNO}_3(\text{liq.}) \longrightarrow \text{AgNO}_3(\text{liq.}) + \text{KCl(liq.)} \Delta H_A$
- (B) $\text{AgNO}_3(\text{liq.}) \longrightarrow \text{AgNO}_3(\text{infinite diln. in KNO}_3) \Delta H_B$
- (C) $\text{KCl(liq.)} \longrightarrow \text{KCl(infinite diln. in KNO}_3) \Delta H_C$

with processes of the first type usually leading to the largest contribution to the total heat (or excess free energy) of solution in reciprocal systems. This method of estimation of heats of solution in reciprocal molten salt systems is operationally more useful and sound than the Born cycle which has been used previously⁴ to rationalize heats of solution in a similar system but which cycle could not be used for a prediction *a priori*.

This study was undertaken to obtain, for comparison with the above prediction, a reliable value for the heat of solution of solid AgCl in molten KNO₃ which was calculated so as to take into account the known non-ideal behavior of the solution.⁵⁻⁷ None of the previously reported heats of solution^{4,8,9} in similar systems were corrected specifically for non-ideal behavior and hence are invalid, and the apparent heats of solution can only be correct by a fortuitous cancellation of factors.

The heat of solution may be calculated from the thermodynamic equation

$$\frac{d \ln (a_{\text{AgNO}_3} a_{\text{KCl}} / a_{\text{KNO}_3})}{d(1/T)} = \frac{H^{\circ} - \bar{H}^{\circ}}{R} = - \frac{\Delta H_{\text{soln.}}}{R} \quad (1)$$

where the activities (a_i) are in solutions saturated with solid AgCl. If the standard states of AgNO₃ and

(1) Operated for the United States Atomic Energy Commission by Union Carbide Corporation.

(2) (a) North American Aviation Science Center, Canoga Park, Calif. (b) On Sabbatical leave from the University of Maine, August, 1960–August, 1961.

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