from 1 to 4 × 10^{-3} dynes and thus not significant. Precision in bound water determination varied from 1 to 5% depending on the amount of water bound. The field factor for the balance, $H\left(\frac{\partial H}{\partial S}\right)$, was 5.41 × 10^6 gauss^2/cm.

NOTE ADDED IN PROOF.—Using the auto-oxidation and carbon-monoxide-binding tests the OCy preparations were found to contain 95% native form. The oxidation–reduction titration behavior was that to be expected for a one-electron process and the standard half-cell potential had the accepted value. Although no tests for the presence of "modified" form after the hydration experiments were made, the complete reproducibility of the susceptibility experiments made on the same sample indicates that little modified form was produced by drying and rehydration.

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[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY, EMERYVILLE, CALIFORNIA]

Solvent Effects on $n \rightarrow \sigma^*$ Transitions; Complex Formation Between Amines and Halomethanes

BY D. P. STEVENSON AND G. M. COPPINGER

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By means of measurements of the ultraviolet absorption spectra of isoöctane solutions of triethylamine with added, (1) chloroform, (2) fluorotrichloromethane, (3) carbon tetrachloride and (4) bromotrichloromethane, it is shown that amines (B) form complexes with halomethanes, (A), that are either 1:1 charge transfer complexes or interact (in 1:1 pairs) to give rise to so-called contact charge-transfer spectra. The complex formation (or contact interaction) accounts for the photochemical instability of solutions of aliphatic amines in carbon tetrachloride solution. The photo reactivities of the amines in the three tetrahalomethanes in the ultraviolet increase in the order, $FCCl_3 < ClCCl_3 < BrCCl_3$.

In connection with our survey of the use of solvent effects on the spectral location of $n \rightarrow \sigma^*$ transitions as means of studying specific solvation of the hydrogen bonding type, it seemed to be of interest to compare by this technique the hydrogen bonding power of chloroform toward amines with that of the previously studied water[1] and simple alcohol[1b] solvent systems. To this end we undertook the comparison of the ultraviolet absorption spectrum of triethylamine in chloroform solution with that of this base in water, isooctane and diethyl ether. In line with out previous experience, we expected to find a blue shift of the chloroform solution spectrum of the ethylamine relative to that of the ether or isooctane spectrum only slightly less than the blue shift that is found in tertiary butyl alcohol solution.[1b] As may be seen in Fig. 1, curves VI and V, respectively, the chloroform solution spectrum shows a large red shift relative to the isooctane solution spectrum, in complete contradiction to our expectation.

This observation immediately suggested the existence of an interaction between the amine and chloroform that is quite independent of any hydrogen bond complexing that these molecules may undergo. As may be seen in curves VII and VIII, the spectra of solutions of triethylamine in fluorotrichloromethane and in carbon tetrachloride show even larger red shifts from the isooctane solution spectrum than does that of the chloroform solution. Interaction here cannot involve hydrogen bonding by solvent. This spectral behavior of triethylamine in the halomethane solutions is that which would be expected if the amine forms a complex with the halomethanes of the type that have become known as "charge transfer complexes."[2,3,4] In the following paragraphs we will present spectroscopic evidence that triethylamine (B) does form a one to one molecular complex with each of the halomethanes (A), chloroform, fluorotrichloromethane, carbon tetrachloride and bromotrichloromethane, of the type AB. We will also cite photochemical evidence that shows such, AB, complex formation is not limited to B = trialkylamine and that the electronic absorption spectra of these complexes are indeed very probably of the charge transfer type.

The method employed to establish the existence of triethylamine–halomethane complexes and to determine the stoichiometry of the complexes was the observation of the absorption spectra of dilute isooctane solutions containing different ratios of amine to halomethane. In concentration units of moles/liter, the ratio B/A of the solutions measured were approximately 0.75/0.25; 0.50/0.50; 0.25/0.75 and 0.25/0.25. Through the use of calibrated quartz inserts in the 1 cm. cells it was

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(1) (a) D. P. Stevenson, G. M. Coppinger and J. W. Forbes, *J. Am. Chem. Soc.*, **83**, 4350 (1961); (b) D. P. Stevenson, *ibid.*, to be submitted for publication.

(2) H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949).

(3) R. S. Mulliken, *J. Chem. Phys.*, **19**, 514 (1951).

(4) The reviewer of this paper has suggested that the data to be presented below are better interpreted as indicating that amines and the halomethanes undergo "contact interaction," of the type described by L. E. Orgel and R. S. Mulliken [*J. Am. Chem. Soc.*, **79**, 4839 (1957)] to give rise to the new absorption bands as contact charge-transfer spectra, rather than as actual charge-transfer complexes with finite formation constants. The authors believe their experimental data are adequate to establish the stoichiometry of the interaction, 1:1, be it ordinary charge-transfer complex formation or a case of contact interaction. However, they also feel that it requires over interpretation of the present data to reach a conclusion with respect to the question, is the formation constant of the "complex" very small, but finite, or identically zero? The authors feel that the important aspect of the present paper is their evidence that the halomethanes constitute a hitherto unrecognized class of "acceptors" (albeit weak) for strong donors of the amine type. It should be noted in this connection that interaction of the type reported here is either non-existent or hardly observable in the case of the diethyl ether–carbon tetrachloride system (unpublished observations of one of the present authors (DPS)).

TABLE I

ABSORBANCES D AT 2700 Å.

Et_3N	Isoöctane, moles/liter $CHCl_3$	$CFCl_3$	CCl_4	$CBrCl_3$	D (1 cm.)	δD	$\delta D/A^0B^0$	~K, liter/mole
1.000	0.000	...	...	...	1.195	.....	.....	...
0.672	.260	...	...	...	1.730	0.928	5.31	
.448	.520	...	...	...	1.730	1.195	5.14	0.085
.224	.260	...	...	...	0.595	0.327	5.61	
.224	.780	...	...	...	1.220	0.952	5.00	
.527	...	0.122	...	...	2.020	1.390	21.6	
.351	...	.243	...	...	2.360	1.940	22.8	.074
.176	...	.122	...	...	0.653	0.443	20.6	
.176	...	.365	...	...	1.668	1.456	22.6	
.753	...	...	0.234	...	23.2	22.3	126.6	
.502	...	...	.467	...	30.7	30.1	128.2	.096
.261	...	...	.243	...	8.91	8.60	135.6	
.251	...	...	.701	...	22.8	22.5	127.7	
.535	...	...	...	0.239	184.7	168.0	1310	
.358	...	...	...	.478	240.8	208.2	1216	
.179	...	...	...	.717	211.0	162.5	1264	
1.000	In $CHCl_3$	...	...	...	61.4			
1.000	In $CFCl_3$	...	...	...	297			
1.000	In CCl_4	...	...	...	1345			

possible to vary (in steps) the optical path so that measurements could be made over a sufficient range of wave length that the absorbance varied over a factor of 10^3 for each solution. Spectra were obtained with the use of a Cary Model 14 spectrophotometer. Representative samples of the spectral data on the various isooctane solutions, the absorbance of 1.00 cm. solution D at 2700 Å. are shown in column 6 of Table I.

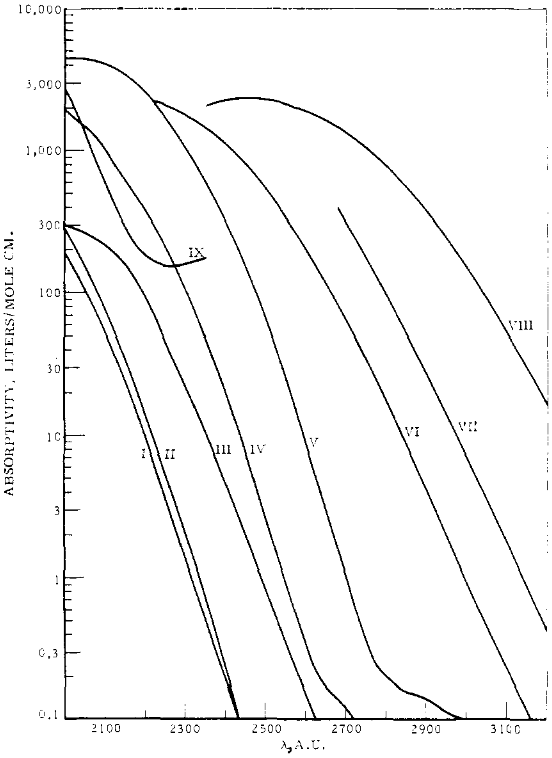

Fig. 1.—Curves I, II, III, IX are $CHCl_3$, $CFCl_3$, CCl_4 and $CBrCl_3$, respectively, in isoöctane solution, IX continued in Fig. 2. Curves IV, V, VI, VII and VIII are for triethylamine in water, isooctane, chloroform, fluorotrichloromethane and carbon tetrachloride, respectively. All measurements made with a "Cary" Model 14 ultraviolet spectrophotometer.

If two solutes A and B react in solution to form a complex AB

$$A + B \rightleftarrows AB \tag{1}$$

with an absorptivity ϵ_c then the equilibrium constant

$$K = \frac{(AB)}{(A)(B)} \tag{2}$$

will be related to the absorbance D of the solution by the expression

$$K = \frac{\delta D/\epsilon_c}{(A^0)(B^0)} \tag{3}$$

where

$$\delta D = D - A^0\epsilon_a - B^0\epsilon_b$$

if $K\sqrt{A^0B^0}$ is sufficiently small compared to unity that the concentration of the complex (AB) is small compared to the initial concentrations of A and B, (A^0) and (B^0), respectively. The quantities ϵ_a and ϵ_b are the absorptivities of A and B, respectively, in the solvent.

There are shown the quantities δD for the various solutions in column 7 of Table I, and in column 8 there are shown, $\delta D/A^0B^0$, that will equal the constant $K\epsilon_c$ if the various restrictions enumerated in the preceding paragraph are satisfied. It will be seen that $\delta D/A^0B^0$ is essentially constant for the approximately nine-fold variation of A^0/B^0 for each of the four systems, triethylamine in isooctane, plus (1) $CHCl_3$, (2) $CFCl_3$, (3) CCl_4 and (4) $BrCCl_3$. This result unambiguously establishes the existence in isooctane solution of the complexes, $[(C_2H_5)_3N \cdot XCCl_3]$ (X = H, F, Cl and Br). The fact that $\delta D/A^0B^0$ increases by less than 10% with two-fold dilution of the $A^0/B^0 \sim 1$ solutions shows that $K\sqrt{A^0B^0} \leq 0.1$.

The small magnitude of the quantity, $K\sqrt{A^0B^0}$, for these systems precluded our separately determining K and ϵ_c for each of the complexes from dilution measurements at constant A^0/B^0. We do not feel the accurate knowledge of the equilibrium constants to be of sufficient interest to justify the effort that would be required to obtain the accuracy of measurement necessary for the resolution of K from ϵ_c by the dilution technique. The approximate values of the association constant K for three of the complexes, shown in the last column of Table I, were estimated by aid of the assumption that the amine is completely associated when in pure halomethane solution and that the absorptivity of the complex in halomethane equals that of the complex in isoöctane.[5]

There are shown in Fig. 2 the quantities $K\epsilon_c$ *vs.* wave length λ for isoöctane solutions of the four complexes of triethylamine computed from the data of which that shown about in Table II are representative samples.

There is also shown in Fig. 2 the isoöctane solution absorption spectrum of bromotrichloromethane for comparison with that of its amine complex and the spectra of the other three halomethanes (Fig. 1, curves I, II and III).

The chemically significant feature of the observations recounted above is the fact that the absorptivities of the complexes of the amine with CCl_4 and $BrCCl_3$ are quite large at wave lengths greater than 3000 A. It is this fact that accounts for the instability of solutions of aliphatic amines in carbon tetrachloride that has been the subject of a number of recent publications.[6,7] On standing in a Pyrex or soft glass flask, solutions of amines with carbon tetrachloride in isoöctane, as well as solutions of amines in carbon tetrachloride, rather rapidly develop white crystalline precipitates if the solutions are not protected from light. The precipitates have been identified by means of their infrared spectra as amine hydrochlorides, and it has been found that chloroform is formed simultaneously in amount that is comparable with that of the amine hydrochloride. When bromotrichloromethane is substituted for carbon tetrachloride, the products are amine hydrobromide plus chloroform. The formation of triethylamine hydrochloride from CCl_4 and triethylamine has been reported by Foster,[8] which we confirm. We have further identified the products mentioned above for systems containing either di-*n*-propyl or tri-*n*-propyl amine. The latter two amines also form hydrochlorides by this photochemical reaction with fluorotrichloromethane.

That the reaction forming the amine hydrohalide is truly photochemical can be convincingly demonstrated in the following fashion. If the solution of an amine in carbon tetrachloride in a narrow bore tube is exposed to a "sun lamp" through a grid, there is quickly developed in the tube a "negative" of the grid, *i.e.*, the white crystalline amine hydrochloride is formed in the illuminated sections of the tube and not in the dark sections.[9]

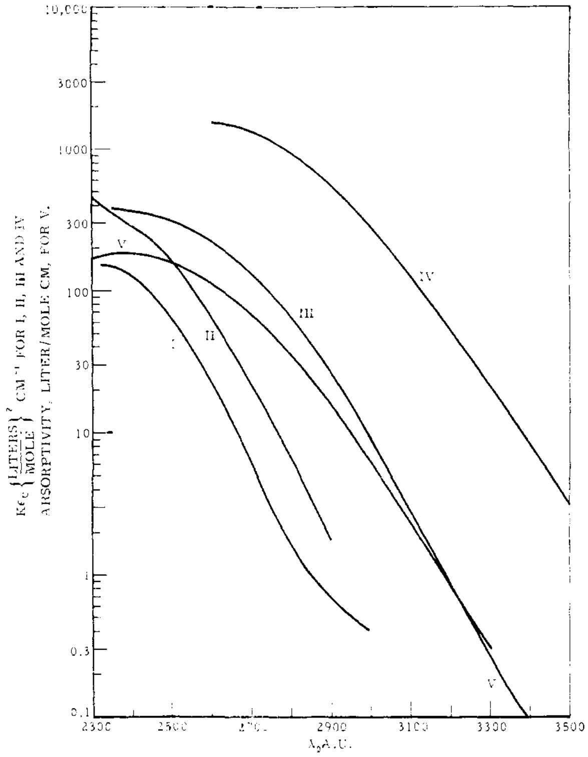

Fig. 2.—Absorption spectra in isoöctane solution. $K\epsilon_c$ for $(C_2H_5)_3N\cdot XCCl_3$ complexes; I, $HCCl_3$; II, $FCCl_3$; III, $ClCCl_3$; IV, $BrCCl_3$; Curve V, ϵ_A for $BrCCl_3$, see also IX of Fig. 1.

Such photochemical instability of the amine-halomethane systems is readily understood in terms of a charge transfer character of the absorption bands (Fig. 2). The reaction

$$e^- + XCCl_3 \longrightarrow X^- + \cdot CCl_3$$

is exothermic for X = Cl or Br. Hence, if the light absorption process involves a transfer of an electron from the amine portion of the complex to the halomethane portion in the fashion that has been suggested for charge transfer, spectra,[10,11] it might be expected that this excited molecule (now, B^+A^-) will dissociate to $B^+X^- + CCl_3$. The trichloromethyl radical so formed will abstract a hydrogen atom to form the chloroform while the trialkyl ammonium halide, B^+X^-, can lose HX to form alkenyl amine, or the trichloromethyl radical may initiate a chain reaction as suggested by Kurz, Hutton and Westheimer.[12] Alternatively, the absorption of light by the complex may result in the reaction

$$(C_3H_7)_3N\cdot XCCl_3 \xrightarrow{h\nu} R_2N{-}CH{=}CH_2CH_3 + HCCl_3 + HX$$

by a non-chain, non-free radical process.

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[5] These association constants are only to be interpreted as upper limits to the association constants if the phenomenon here reported is due to real complex formation. As indicated in footnote 4, the present data are not of adequate quality to distinguish between very small, but finite, association constants, from the identically zero association constants associated with the contact interaction of Orgel and Mulliken.[4]

[6] (a) R. F. Collins, *Chem. and Ind.* (London), 704 (1957); (b) N. H. Cromwell, P. W. Foster and M. M. Wheeler, *ibid.*, 220 (1959).

[7] (a) G. J. Beichl, J. E. Colwell and J. G. Miller, *ibid.*, 203 (1960); (b) H. Williams, *ibid.*, 900 (1960).

[8] R. W. Foster, *ibid.*, 1354 (1960).

[9] An experiment performed by Dr. R. Gersmann in these Laboratories.

[10] R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

[11] R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

[12] J. L. Kurz, R. Hutton and F. H. Westheimer, *ibid.*, **83**, 584 (1961).

A more detailed account of the studies of the photolysis of the various amine-halomethanes will be separately reported by one of the present authors (G.M.C.). At this point we will note but one other observation on this photolysis, namely that the order of reactivity of the three tetrahalomethanes considered in the present paper increases in the order

$$FCCl_3 < ClCCl_3 < BrCCl_3,$$

and CBr_4 is even more reactive than $BrCCl_3$ as might be expected.

Finally, it should be noted that to the extent that we associate charge transfer character with the absorption bands of these amine–halomethane complexes, it is not appropriate to describe their spectral location in terms of a red shift from the $n \rightarrow \sigma^*$ band of the amine. The absorption band is a new one, characteristic of neither of the components of the complex.[13] However, the spectral location of the absorption band of the complex should be related to the difference between the ionization potential of the base component and the electron affinity of the "acid" component.[11,14] If we accept the result shown in Table I, the essential equality of the constants for formation of the complexes of triethylamine with each of the halomethanes, then the $K\epsilon_c$ curves become essentially ϵ_c curves for the complexes. No relation between red shift and electron affinity is revealed in the results.

(13) A. B. F. Duncan, "Annual Reviews of Phys. Chem.," Vol. V, Stanford, California, 1954, pages 185–194.

(14) H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

[Contribution from the Department of Chemistry, University of Southern California, Los Angeles, California]

The Effect of Pressure on the Rate and Equilibrium Constants of Chemical Reactions. The Calculation of Activation Volumes by Application of the Tait Equation[1]

By Sidney W. Benson and Jerome A. Berson

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By a detailed analysis of the effect of pressure changes on rate and equilibrium constants, it is shown that the usual assumption that the volume change or volume of activation is independent of pressure is seriously in error. An explicit expression for the pressure-dependence of the above constants in non-ionic systems is derived by use of the Tait Equation. With this expression, it is possible to evaluate independently the volume of activation at zero pressure and the coefficient of compressibility of the transition state. In addition, a simple analytical procedure is developed for obtaining the Tait constants from P*-V*-T data. For ionic systems, corrections for the pressure-dependence of the activity coefficients are shown to be negligible in water solution but important in systems of lower dielectric constant. The most important effects in ionic systems arise from the electrostriction of the solvent, and these can overshadow the normal compressibility effects. An explicit analysis of ionic systems involves a knowledge of ionic sizes; further, the pressure-dependences of both the activity coefficient and electrostriction terms are different from that of the short-range molar volume term. It is therefore doubtful that the data for ionic systems can be uniquely interpreted. Data from the literature on the rates of decomposition of azo-bis-isobutyronitrile and the Diels–Alder dimerization of isoprene are re-examined and shown to yield interpretations quite different from those of the original authors. Attention is called to the importance of adiabatic heating and temperature gradients in producing significant errors in the study of the pressure-dependence of reaction rates.

The interpretation of reaction rates by the transition state theory, involving thermodynamic treatment of activation parameters, implies the concept of an activation volume.[2-4] For a reaction $aA + bB + \cdots \rightleftarrows X^{\ddagger} \rightarrow$ Product in solution, the rate constant k is given by

$$k = \frac{RT}{Nh} K^{\ddagger} \frac{\gamma_A \gamma_B}{\gamma_x^{\ddagger}} = \frac{RT}{Nh} K^{\ddagger} K_\gamma \qquad (1)$$

where $K^{\ddagger}$ is the thermodynamic equilibrium constant at infinite dilution for the conversion of the reactants to the transition state $X^{\ddagger}$, and the γ's are activity coefficients of the species in question. The pressure-dependence of the rate constant is

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = \left(\frac{\partial \ln K^{\ddagger}}{\partial P}\right)_T + \left(\frac{\partial \ln K_\gamma}{\partial P}\right)_T \qquad (2)$$

By substituting $\ln K^{\ddagger} = -\Delta F^{\ddagger}/RT$ and using the thermodynamic relationship $(\partial F/\partial P)_T = V$, we can convert equation 2 to

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = \frac{-\Delta V^{\ddagger}}{RT} + \left(\frac{\partial \ln K_\gamma}{\partial P}\right)_T \qquad (3)$$

$\Delta V^{\ddagger}$ and $\Delta F^{\ddagger}$ represent the change in partial molar quantities; $\Delta V^{\ddagger}$ is the difference in partial molar volume $(V_t - \Sigma V_r)$ between the transition state and the reactants, and $\Delta F^{\ddagger}$ is the corresponding difference in standard partial molar free energies. The interpretation of the pressure-dependence of the reaction rate constant (or equilibrium constant, which is expressible by the same formalism) requires the separate evaluation of both $\Delta V^{\ddagger}$ and $(\partial \ln K_\gamma/\partial P)_T$. The present paper offers an explicit solution to this problem.

The Contribution of Ionic Activity Coefficient Effects to the Pressure-dependence of Rates and Equilibria.—According to the Debye–Hückel limiting law,[5a] the molal activity coefficient of an

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(2) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **31**, 875 (1935).

(3) (a) *Cf.* S. D. Hamann, "Physico-Chemical Effects of Pressure," Academic Press, Inc., New York, N. Y., 1957, Chapter 9. (b) *Ibid.*, pp. 54–57.

(4) *Cf.* S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp. 510–518.

(5) *Cf.* (a) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Company, Inc., New York, N. Y., 1958, pp. 164–170. (b) Ref. 4, pp. 521–528.