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Kinetic and Spectrophotometric Evidence for Acid–Salt Interaction in a Non-polar Medium. A Further Study of Trityl Chloride Solvolysis

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The reaction of trityl chloride with chloroacetic acid in carbon tetrachloride to form trityl chloroacetate is strongly accelerated when an amine (β-bromoallyl-*n*-hexylamine or tri-*n*-butylamine) is added to the medium. Qualitatively speaking the rate is dependent both on the free acid and the amine salt concentration. If, however, it is assumed that the salt is a 1:1 amine–acid adduct, the reaction rates are observed to reach a maximum and then to diminish rather than to increase continuously as the apparent salt concentration is increased and the apparent acid concentration is held constant. This unusual rate effect is explained on the assumption that when sufficient acid is available the salt is in the form $R_3N(ClCH_2COOH)_2$. Supporting spectrophotometric evidence has been obtained.

The acetolysis of triphenylmethyl (trityl) chloride in carbon tetrachloride proceeds to completion if acetic anhydride or an acetic acid salt is present to remove hydrogen chloride.[1] When the salt of β-bromoallyl-*n*-hexylamine is used and the free acetic acid concentration is of the order of 0.5 *M* or larger, the reaction (eq. 1) is rapid enough at room temperature so that kinetic measurements can conveniently be made. Under these conditions the

$$(C_6H_5)_3CCl + R_2\overset{+}{N}H_2\overset{-}{O}COR \longrightarrow (C_6H_5)_3COCOR + R_2\overset{+}{N}H_2\overset{-}{Cl} \quad (1)$$

reaction is first order with respect to the salt and has an apparent order of higher than first with respect to acetic acid. Presumably the salt serves as a nucleophile in the rate-determining process, while the acid promotes reaction through electrophilic solvation of departing chloride ion. Because relatively high concentrations of acetic acid have been used in rate studies of this acetolysis, the observed order of the reaction with respect to the electrophile may, to some extent, reflect changes in the dielectric constant of the medium.

In an attempt to obtain a more reliable estimate of the contribution of the acid species to the experimental rate law, a more reactive electrophile, chloroacetic acid, which effectively induces reaction when its concentration is small, has been substituted for acetic acid. That is, a kinetic study has been begun of the reaction of trityl chloride in carbon tetrachloride with chloroacetic acid and certain of its amine salts. Insofar as the original objective of the investigation is concerned, no totally satisfactory conclusions have been reached. However, in confirmation of previously reported spectroscopic evidence that more than one acid molecule may associate with a base in a non-polar medium,[2,3] it has been demonstrated kinetically that chloroacetic acid interacts with its amine salts in carbon tetrachloride.

Experimental

Materials.—The sources of carbon tetrachloride, triphenylmethyl chloride and β-bromoallyl-*n*-hexylamine were the same as stated previously.[1] Reagent grade chloroacetic acid was recrystallized from carbon tetrachloride and stored under vacuum. Eastman Organic Chemicals white label chloroacetyl chloride and redistilled (reduced pressure) tri-*n*-butylamine were used.

Several unsuccessful attempts were made to obtain a sample of chloroacetic anhydride which was free of chloroacetic acid. A sample of m.p. 46–52°, prepared from chloroacetyl chloride and potassium nitrate,[4] was used for rate work. The neutral equivalent of this material was found to be 89.7, which corresponds to a 50–50 weight % mixture of the acid and the anhydride.

Trityl Chloroacetate.—An attempt was made to obtain a pure sample of this ester so that its ultraviolet absorption spectrum, required for interpretation of the rate runs, could be investigated. Silver chloroacetate, prepared by the method of Hill and Simmons,[5] was dried under vacuum over sulfuric acid. A mixture of 9 g. of freshly recrystallized trityl chloride and 30 g. of the silver salt in 100 ml. of dry benzene was shaken mechanically for 24 hours. The mixture was then filtered, and the filtrate was concentrated under reduced pressure. The yellow oil thus obtained changed to sticky crystals of wide melting range (*ca.* 60–100°) after 2 days in a vacuum desiccator. Numerous unsuccessful attempts to obtain a highly purified sample of the ester were made. The product proved to be appreciably soluble at room temperature in both polar and non-polar media. Also it was readily susceptible to hydrolysis even on relatively brief exposure to atmospheric moisture, and triphenylcarbinol, m.p. 165°, was frequently obtained as the product of recrystallization. The best sample was obtained by cooling a petroleum ether solution of the crude product in an ice-bath. The colorless oil thus formed was separated from the solvent by decantation. This material solidified after standing 2 days under vacuum over sulfuric acid (m.p. 59–67°). It was analyzed for chlorine by treating a hydrolyzed sample with excess standard silver nitrate and back-titrating with standard potassium thiocyanate solution.

Anal. Calcd. for $C_{21}H_{17}O_2Cl$: Cl, 10.5. Found: Cl, 11.2.

The molecular extinction coefficient of this product in carbon tetrachloride solution *versus* a carbon tetrachloride blank was 65.9 at 278 mμ, the wave length used in the kinetic work. To check this value for the extinction coefficient of trityl chloroacetate two solutions of the ester were prepared directly by shaking 25.0-ml. samples of 1.43×10^{-3} *M* solutions of trityl chloride in Drierite-dried carbon tetrachloride with 1.0-g. portions of silver chloroacetate. The stoppers of the reaction flasks were paraffin sealed. One flask was shaken for 5.5 hours and the other for 11 hours. After the solids in each had settled, samples of the liquid phases were transferred to 1-cm. absorption cells for spectrophotometric measurement. Values of ϵ_{278} of 69.6 and 68.5, in reasonably good agreement with that found for the carbon tetrachloride solution of the crystalline sample of the ester, were thus obtained. It was established by a separate experiment that the spectral properties of a sample of carbon

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(1) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **83**, 3708 (1961).

(2) (a) G. M. Barrow and E. A. Yerger, *ibid.*, **76**, 5211 (1954); (b) E. A. Yerger and G. M. Barrow, *ibid.*, **77**, 4475, 6206 (1955); (c) G. M. Barrow, *ibid.*, **78**, 5802 (1956).

(3) L. E. I. Hummelstedt and D. N. Hume, *ibid.*, **83**, 1564 (1961).

(4) O. Diels and H. Okada, *Ber.*, **44**, 3333 (1911).

(5) A. E. Hill and J. P. Simmons, *J. Am. Chem. Soc.*, **31**, 821 (1909).

tetrachloride were not significantly altered when it was shaken for several hours with silver chloroacetate.

The Rate Runs.—The reaction rates were determined spectrophotometrically using the same general procedures which have been described for studying the kinetics of reaction of trityl chloride and acetic acid.[1] A wave length of 278 mμ, at which the extinction coefficients of trityl chloride and trityl chloroacetate are respectively 240 and 69 in dilute solutions in carbon tetrachloride, was used in following the conversion of the halide to the ester. In most instances the concentrations of chloroacetic acid and the amines which were included in the reaction mixtures were much larger than that of trityl chloride. The optical measurements were made using a blank which was identical with the original reaction mixture except that it contained no trityl chloride. The reactions in the presence of the amines proceeded to completion under the conditions of the runs, as evidenced by the fact that the final optical densities of the rate samples were generally in good agreement with values predicted using the known extinction coefficient of the ester. In a few runs in which the terminal readings showed a slow downward drift with time, probably because of hydrolysis of the ester by traces of moisture in the medium, the predicted d_f values were used in calculating rate constants. Rate constants k, as defined in eq. 2, were calculated from

$$kt = 2.303 \log [(C_6H_5)_3CCl]_i/[(C_6H_5)_3CCl] = 2.303 \log (d_i - d_f)/(d_t - d_f) \quad (2)$$

the slope of the linear plots of log $(d_t - d_f)$ *versus* time. The symbol d represents the optical density of the reaction mixture at 278 mμ and the subscripts i, f and t apply, respectively, to initial and final times and to time t. In those cases in which the salt concentration varied appreciably during the course of the runs (that is, in runs in which the initial amine concentration was not substantially greater than that of trityl chloride), curved plots were obtained. The k-values reported for such runs were calculated from initial slopes of these lines.

In the absence of the amines the conversion of trityl chloride to the chloroacetate occurs relatively slowly and reaches an equilibrium (eq. 3) just as does the corresponding reaction of trityl chloride and acetic acid. Using

$$(C_6H_5)_3CCl + ClCH_2COOH \rightleftharpoons (C_6H_5)_3COCOCH_2Cl + HCl \quad (3)$$

the equilibrium optical density of a carbon tetrachloride solution, initially 2.4×10^{-3} M in trityl chloride and 0.1 M in chloroacetic acid, it was estimated that the reaction to form ester was 14.5% complete at 25°. A crude estimate of the rate constant for ester formation in the absence of amine was made by using chloroacetic anhydride as a trap for hydrogen chloride (eq. 4), on the assumption that it would shift equilibrium 3 to the right without affecting the forward reaction rate.

$$(ClCH_2CO)_2O + HCl \rightleftharpoons ClCH_2COOH + ClCH_2COCl \quad (4)$$

Acetic anhydride was used successfully in a similar fashion in the acetolysis kinetic studies.[1] Because of solubility limitations, the amount of the chloro anhydride which could be included in the reaction mixtures was insufficient to produce a quantitative conversion of trityl chloride to ester, although the equilibrium (eq. 3) was favorably shifted. Therefore plots of log $(d_t - d_f)$ *versus* time for runs with added anhydride were found to curve with time. The rate constant later reported for reaction with anhydride rather than with amine in the medium is calculated from the initial slope of such a plot. As should be the case if eq. 4 correctly accounts for the effect of chloroacetic anhydride in shifting equilibrium 3, it was found that the equilibrium concentration of ester formed in the reaction of trityl chloride with chloroacetic acid in the presence of the anhydride was sharply reduced when chloroacetyl chloride was initially included in the reaction mixture.

It was established by a separate spectrophotometric experiment that trityl chloride (2.5×10^{-3} M) did not react with β-bromoallyl-*n*-hexylamine in carbon tetrachloride over a several hour period.

Spectrophotometric Studies of Amine–Chloroacetic Acid Interaction in Carbon Tetrachloride.—A series of solutions of 0.04 M chloroacetic acid in carbon tetrachloride were prepared in which the concentration of added tri-*n*-butylamine varied from 0 to 0.08 M. The infrared spectra of these solutions from 2–15 μ were recorded using a Beckman IR-4 infrared spectrometer and 1-mm. sodium chloride cells (double beam operation with a carbon tetrachloride blank). Another series of carbon tetrachloride solutions, in which the amine concentration varied from three times to less than half that of the acid, were subjected to spectrophotometric study over a wave length range of 300–340 mμ using the Beckman DU spectrophotometer and 1-cm. absorption cells with carbon tetrachloride as the blank.

Tri-*n*-butylamine was used in preference to β-bromoallyl-*n*-hexylamine in the investigation of the salt spectra because it had a spectrum suitable for both the ultraviolet and infrared work. The unsaturated amine was not suitable for the ultraviolet studies since the absorption of its salts overlapped that of the free amine rather strongly.

Results

The Effect of Amines on the Rate of Reaction of Trityl Chloride with Chloroacetic Acid.—It has been demonstrated semi-quantitatively that the reaction of trityl chloride with chloroacetic acid in carbon tetrachloride is relatively slow in the absence of added amines. From the results of a rate run at a concentration of 0.42 M chloroacetic acid and an initial trityl chloride concentration of 2.5×10^{-3} M (with chloroacetic anhydride added to remove hydrogen chloride, as described in the Experimental section) a first-order rate constant (eq. 2) of $k_{25°} = 0.3 \times 10^{-3}$ sec.$^{-1}$ has been calculated. The rate constant for another run in which β-bromoallyl-*n*-hexylamine was in the reaction mixture (presumably in the form of a salt) at a concentration equal to that of the acid (0.100 M) is $k_{25°} = 0.15 \times 10^{-3}$ sec.$^{-1}$. When both the amine salt and free acid are present, the reaction is much more rapid. A value of $k_{25°} = 13.0 \times 10^{-3}$ sec.$^{-1}$ has been obtained for a run in which the amine and acid concentrations were, respectively, 0.027 and 0.131 M. These results are in accord with those of the earlier work on the acetolysis of trityl chloride. In the presence of both the acid and the amine salt the favored reaction path must be one in which both substances are included in the transition state for formation of the trityl ester.

In all of the rate samples the molar quantity of acid was equal to or greater than that of the amine. In a preliminary attempt to account more quantitatively for the effects of changes in the amine and acid concentrations on the reaction rate, the assumption was made that the amine in these samples was totally converted to the 1:1 amine–chloroacetic acid salt. It was anticipated that, as in the case of the reaction of trityl chloride and acetic acid, the rate constant k should increase with increases in the concentration of the free acid [HA] or of the salt. A summary of the results of a number of runs at varying acid and amine concentrations is presented in Fig. 1, in which k is plotted against the amine (presumably in the form Am.HA) concentration. Each dotted line corresponds to a series of runs in which the concentration of the free acid [HA] is the same, assuming that the free acid concentration is the difference between the total acid $[HA]_t$ and total amine $[Am]_t$ concentration of the medium. The free acid concentrations are recorded next to the lines to which they apply. At any fixed concentration of amine $[Am]_t$ the k-values do, as expected, increase with [HA]. However no value for

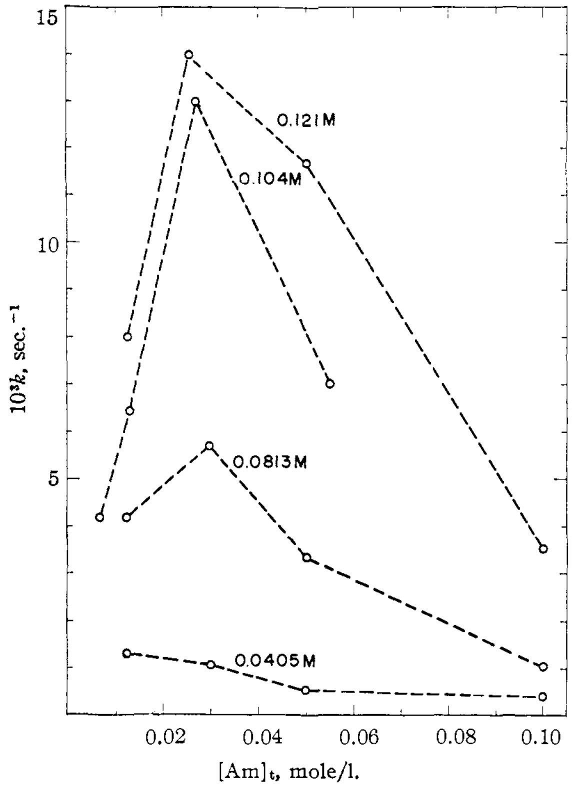

Fig. 1.—Rate constants for trityl chloroacetate formation at 25.0° in carbon tetrachloride. The initial trityl chloride concentrations in the runs varied over a range of 2–5 × 10^{-3} *M*. The abscissa values represent the total amine ($CH_2{=}CBrCH_2NHC_6H_{13}$-*n*) content of the medium and the figures beside each line correspond to values of $[HA]_t - [Am]_t$.

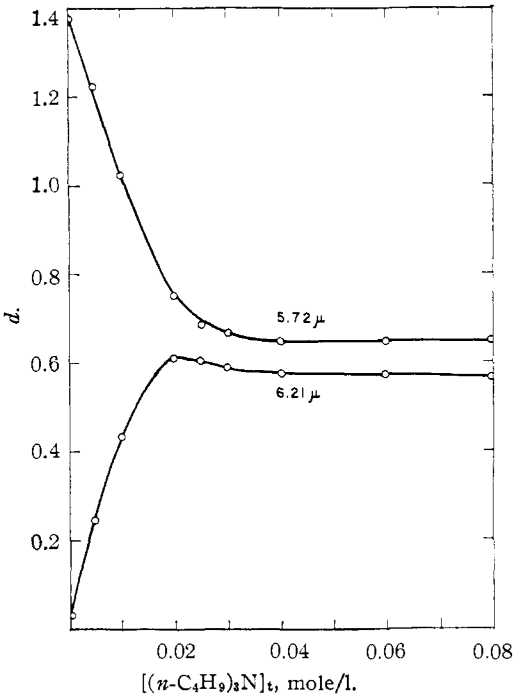

Fig. 2.—The optical densities of 0.04 *M* chloroacetic acid solutions in carbon tetrachloride (1-mm. cells) as a function of their tri-*n*-butylamine concentrations.

the order of the reaction with respect to [HA] can be assigned which is even approximately applicable over the entire range of acid and amine concentrations of the rate runs. Only when the amine concentration $[Am]_t$ is relatively low as compared to the free acid concentration do the *k*-values for reaction at a fixed value of [HA] show an increase with increasing salt concentration (see the points for values of $[Am]_t < 0.04$ *M* on Fig. 1). As the salt concentration becomes appreciable *k* values actually diminish with increases in $[Am]_t$, and this phenomenon is most pronounced in cases in which the free acid concentration is low.

This rate depression is not peculiar to reaction in the presence of β-bromoallyl-*n*-hexylamine. The results of pertinent runs in which tri-*n*-butylamine was substituted for the unsaturated amine are summarized in Table I. Again the rate constant diminishes rather than increases with increasing salt concentration when the free acid concentration calculated as described above, is constant and not substantially greater than $[Am]_t$.

The apparent anomaly concerning the relationship between amine concentration and rate constant is satisfactorily explained on the basis that the salt Am.HA interacts with the acid to form $Am(HA)_2$. As a result, the free acid concentration in a number of the runs must have been much lower than indicated in Fig. 1 and Table I, and it is for these runs that the inverse relationship between *k* and $[Am]_t$ has been noted.

In these cases the favorable effect on rate of increasing the salt content (Am.HA) of the medium is more than offset by the reduction (eq. 5) in the actual concentration of free acid[6] available for participation in the reaction

$$Am{\cdot}HA + HA \longrightarrow Am(HA)_2 \qquad (5)$$

The results of this investigation constitute very striking support for the conclusion,[2] based on the results of infrared spectrum measurements of solutions of various amines and acetic and other acids in non-polar media, that 1:2 amine–acid adducts are formed if sufficient acid is available. Indeed this type of salt, which in reality is formed from an acid dimer and the amine, is apparently sufficiently stable in a number of cases so that it exists in appreciable concentration even in solutions in which the acid and the amine are present only in equimolar quantity.

Infrared and Ultraviolet Spectra of the Salts.—The infrared spectra of a series of 0.04 *M* chloroacetic acid solutions in carbon tetrachloride which contained varying amounts of tri-*n*-butylamine were taken as described in the Experimental section in an attempt to establish the relative stabilities of the species $Am(ClCH_2COOH)_2$ and $Am(ClCH_2COOH)$. In Fig. 2 the optical densities of these solutions at 5.72 and 6.21 μ, wave lengths at which the absorption of the amine is low, are plotted against the corresponding amine concentrations (*cf.* ref. 2). The intensity of the 5.72 μ band of the free carboxylic acid was found to diminish rapidly

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[6] The free acid undoubtedly is largely dimeric in nature. For purposes of simplification it is represented as the monomer throughout this discussion.

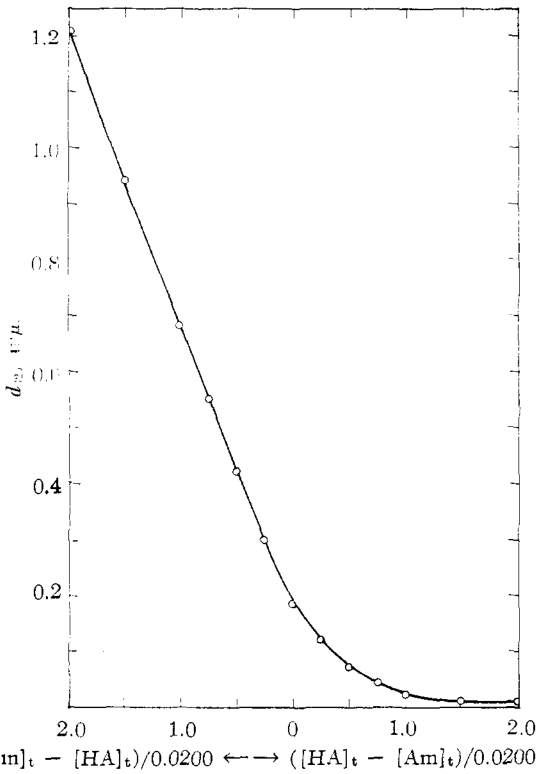

Fig. 3.—Optical densities (320 mμ, 1-cm. cells) of carbon tetrachloride solutions of $ClCH_2COOH$ and $(n\text{-}C_4H_9)_3N$. The point corresponding to an abscissa of zero is for a solution which is 0.0200 M in both the acid and the amine. Points to the right of this one apply to solutions in which $[\text{Am}]_t = 0.0200\ M$ and $[\text{HA}]_t > 0.0200\ M$. The points to the left apply to solutions in which $[\text{HA}]_t = 0.0200\ M$ and $[\text{Am}]_t > 0.0200\ M$.

until the acid to amine mole ratio was about 2:1. On further lowering of the ratio to 1:1 the intensity of the 5.72 μ band decreased much more slowly and approached a constant value. Thus it is probable that only small amounts of free acid are present when the acid to amine ratio is < 2. At the same time a new band developed at 6.21 μ, which reached a maximum intensity at the 1:2 amine to acid mole ratio. At this point, as in similar situations involving other acids and amines,[2] the conversion of the free acid to Am(HA)_2 must have been quantitative or almost so. The absorption intensities of the 1:2, Am(HA)_2, and 1:1, Am.HA, salts must be very similar at these wave lengths, since the optical densities of Fig. 2 do not change markedly as the acid to amine ratio is decreased below 2:1.

No infrared wave length was discovered which was well suited for following the transformation of Am(HA)_2 to Am.HA. This change was more obviously reflected in the ultraviolet spectra of the acid–amine solutions. In Fig. 3 a plot is shown of the optical densities at 320 mμ of a series of carbon tetrachloride solutions all of which were 0.0200 M both in chloroacetic acid and in tri-n-butylamine and in which there was either additional acid or amine. The acid itself is non-absorbent in the wave length region of this plot, but the pure amine has a substantial near-ultraviolet absorption which results from a tailing off of the far-ultraviolet amine[7] peak. It is assumed in this discussion that the absorption of the acid-amine solutions at 320 mμ can be ascribed entirely to free amine and that any absorption of the salt or solvated salt is negligible. Thus the concentration of free amine in a particular solution may be estimated from the optical density and the known extinction coefficient of the amine (28.4 at 320 mμ). Values for the free amine concentration of one acid–amine solution, which were calculated from the optical densities and extinction coefficients at several wave lengths around 320 mμ, were found to be in close agreement, indicating that very likely the absorption of the salts in this region is indeed negligible.

TABLE I

THE FORMATION OF TRITYL CHLOROACETATE IN THE PRESENCE OF $(n\text{-}C_4H_9)_3N$ (CCl_4, 25.0°)[a]

$[\text{ClCH}_2\text{COOH}]$,[b] mole l.$^{-1}$	0.0817	0.0817	0.120	0.120	0.120
$[\text{Am}]_t$, mole l.$^{-1}$	0.0250	.0500	0.0128	0.0255	0.051
10^3k, sec.$^{-1}$	3.22	.79	7.5	8.6	4.65

[a] In all runs $[(C_6H_5)_3CCl]_i$ was 2.4–2.5 × $10^{-3}M$. [b] The free acid concentration assuming that the amine was totally converted to a 1:1 amine–acid salt.

The observed changes in optical density of solutions of amine and acid (in the region in which the acid to amine ratio is less than or does not greatly exceed unity) are explained on the assumption that equilibrium 6 is established.

$$2\text{Am}\cdot\text{HA} \rightleftharpoons \text{Am} + \text{Am(HA)}_2$$

$$K = [\text{Am(HA)}_2][\text{Am}]/[\text{Am}\cdot\text{HA}]^2 \quad (6)$$

As analysis of the infrared data indicates (see above), the concentration of free acid is negligible under these conditions. Equations 7 and 8 may then be used to estimate the 1:1 and 1:2 salt concentrations. Equilibrium constants (eq. 6)

$$[\text{HA}]_t - ([\text{Am}]_t - [\text{Am}]) = [\text{Am(HA)}_2] \quad (7)$$

$$[\text{Am}]_t - [\text{Am(HA)}_2] = [\text{Am}\cdot\text{HA}] \quad (8)$$

were evaluated from the appropriate data of Fig. 3 and measurements at other wave lengths using eq. 7 and 8 and the known extinction coefficient of the amine. Representative K-values are listed along with the total acid and amine concentrations of the media in Table II. The agreement in the series of values reported is good considering the complexity of the system and the assumptions involved. Like the corresponding triethylamine–acetic acid adduct[2a] (K = 0.6, CCl_4), the 1:2 tri-n-butylamine–chloroacetic acid adduct can exist in appreciable quantity in carbon tetrachloride even in the presence of a moderate amount of the free amine.

The existence of a few 1:2 amine–acid adducts has been demonstrated by other than spectrophotometric methods. For example the 1:2 pyridine–phenol complex in carbon tetrachloride was detected by vapor pressure measurements.[8] The formation of a similar complex has been suggested to explain the results of a study of the heat of reaction of 2-picoline with excess methanesulfonic acid.[9] A

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[7] C. Tannenbaum, E. M. Coffin and A. J. Harrison, *J. Chem. Phys.*, **21**, 311 (1953).

[8] C. G. Swain and J. F. Brown, *J. Am. Chem. Soc.*, **74**, 2691 (1952).

[9] H. C. Brown and R. R. Holmes, *ibid.*, **77**, 1727 (1955).

TABLE II

VALUES OF K (EQ. 6) FOR INTERCONVERSION OF THE 1:1 AND 1:2 SALTS (CCl_4, 25.0°) OF $(n\text{-}C_4H_9)_3N$

$[HA]_t$, mole/l.	$[Am]_t$, mole/l.	$[Am]_{calcd}$, mole/l.	K
0.1027	0.1027	0.0316	0.64
.0608	.0507	.0115	.80
.0514	.0514	.0160	.70
.0302	.0300	.0093	.70
.0302	.0400	.0174	.58
.0300	.0200	.0022	.85
.0257	.0257	.0082	.77
.0250	.0200	.0040	.73
.0200	.0200	.0065	.86
.0200	.0250	.0107	.82
.0200	.0300	.0150	.75
.0200	.0350	.0196	.77
.0200	.0400	.0241	.71
.0200	.0500	.0334	.65
.0200	.0600	.0428	.58
.0128	.0128	.0041	.79
.0064	.0064	.0021	.91

seemingly satisfactory explanation for the incorporation of more than one acid molecule in the product of acid–base interaction, which is apparently a rather general phenomenon, has been given by Van Looy and Hammett.[10] In the absence of a properly constituted solvent the extra acid molecules are presumed to function as solvating agents for the anionic moiety of the acid–base interaction product.

The Influence of Salt and Acid Concentration Changes on Reaction Rate.—In Table III the rate constants for a few of the runs on the reaction of trityl chloride and chloroacetic acid in the presence of β-bromoallyl-*n*-hexylamine are resurveyed in terms of the estimated concentrations of free acid and of 1:2 acid–amine salt present in the mixtures. As can be seen from the first three entries on the left side of the table, *k*-values for reactions at constant salt concentration are approximately proportional to the acid concentration. When the acid concentration is fixed and the salt concentration is doubled, the rate constant increases by a factor of about 2 so long as the salt content of the mixture is relatively small (see the right side of Table III). However, as the salt concentration increases to higher levels the apparent reaction order with respect to $[Am(HA)_2]$ appears to diminish, possibly because the salt is beginning to aggregate in the non-polar medium. These results are, in a broad sense, in accord with those of the earlier investigation[1] of the reaction of trityl chloride with acetic acid in carbon tetrachloride, although no evidence of kinetic complications resulting from salt aggregation was obtained in the rate work on acetolysis. The previous study was, however, conducted using solutions which contained acetic acid in high enough concentration to provide for ready solvation rather than for clustering of the salt molecules. In the light of the results of the present work it can be stated with some assurance that this acetic acid salt, which was previously described as $AmH^+OCOCH_3^-$, should have been identified as $Am(CH_3COOH)_n$ with $n \geq 2$.

TABLE III

THE VARIATION IN RATE CONSTANT WITH FREE ACID AND 1:2 SALT CONCENTRATION (CCl_4, 25.0°)[a]

$[Am(HA)_2]$, mole/l.	$[HA]$,[b] mole/l.	10^3k, sec.$^{-1}$	$[Am(HA)_2]$, mole/l.	$[HA]$,[b] mole/l.	10^3k, sec.$^{-1}$
0.0135	0.0121	0.52	0.00625	0.094	3.0
.0135	.0270	1.1	.0135	.091	6.4
.0135	.0376	1.7	.027	.077	13.0
.041[c]		0.4	.054	.108	13.9
.081[d]		1.0			

[a] In all runs $[(C_6H_5)_3CCl]_i = 2.5 \times 10^{-3}M$. The amine was $CH_2{=}CBrCH_2NHC_6H_{13}\text{-}n$. [b] The concentration of free acid calculated as the monomer. [c] A mixture of 1:1 and 1:2 salt in which the minimum concentration of the former is 0.059 M and the maximum concentration of the latter is as shown in the table. [d] A mixture of 1:1 and 1:2 salt in which the minimum concentration of the former is 0.019 M and the maximum concentration of the latter is as shown in the table.

The 1:2 salt of chloroacetic acid, even in the absence of free acid, does react with trityl chloride at a measurable rate (see the last two runs at the left of Table III). Comparatively speaking, a 1:1 amine–acid mixture and also the free acid alone are much less effective as reactants. Very likely this relatively high reactivity of the 1:2 salt, which in reality is both a salt and an acid, can be attributed to its capacity to function both as a nucleophile and as an electrophile. Further work concerning the role of this salt as a kinetically identifiable species in promoting the conversion of trityl chloride to its chloroacetate is planned.

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[10] H. Van Looy and L. P. Hammett, *J. Am. Chem. Soc.*, **81**, 3872 (1959).