The Acetolysis of Triphenylmethyl Chloride in Carbon Tetrachloride

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A spectrophotometric study of the kinetics of acetolysis of trityl chloride in carbon tetrachloride has been conducted using acetic anhydride, which reacts with hydrogen chloride, to shift the equilibrium between the organic halide and trityl acetate. The reaction rate is independent of the anhydride concentration, provided the anhydride is in substantial excess of the trityl chloride. Hydrogen chloride has also been removed with β-bromoallyl-n-hexylamine. When the amine is in considerable excess of the chloride, the reaction is approximately first order in amine. Mechanisms for reaction in the presence of the amine are suggested in which the amine–acetic acid salt functions as a nucleophile in the rate-determining process. The rates of reaction of trityl chloride with several other fatty acids in the presence of the amine have been compared with that for acetic acid. The differences are discussed in terms of differences in the dielectric constants of the media and of the relative strengths of the acids as electrophiles and of the amine salts as nucleophiles.

In discussing the mechanism of solvolysis of triphenylmethyl (trityl) chloride in hydroxylic media a number of investigators have considered the function of the solvent molecules, not only as electrophiles but also as nucleophiles, in rate-determining or pre-rate-determining processes.[1–5] In interpreting the results of a kinetic study of the acetolysis of this halide Swain and MacLachlan[1c] have argued convincingly that the ion pair $(C_6H_5)_3C^+Cl^-$ undergoes nucleophilic attack by acetic acid in the slow step of the reaction, and a similar mechanism has been suggested to explain the kinetics of methanolysis of trityl chloride in benzene.[1b] The assumption that these ion pairs are subject to electrophilic solvation by the hydroxylic reagents has been amply justified.[1–5] An alternate mechanism for the methanolysis has been proposed in which the dual role of the solvent is performed in a concerted rather than a stepwise way.[1a,b]

A study of the kinetics of reaction of trityl chloride with acetic acid and some of its homologs in carbon tetrachloride has now been made. These reactions, like those of trityl halides which occur when pure acetic acid is the solvent,[1c,6] are reversible. However, the reaction kinetics readily can be investigated by a spectrophotometric method if a high molecular weight amine or (when acetic acid is the reactant) acetic anhydride is present in the medium in sufficient quantity to eliminate the hydrogen chloride which is formed. On the basis of the results obtained using the amine it can be concluded that trityl chloride (or its ion pair) is indeed readily susceptible to nucleophilic attack in a slow step in these solvolyses.

Experimental

Materials.—Eastman Organic Chemicals Spectro Grade carbon tetrachloride and trimethylacetic (pivalic) acid were used without further treatment. Acetic acid was purified as described previously.[7] A commercial sample of propionic acid was distilled to remove water, using a Vigreux column, until the boiling point reached 139°; a few crystals of potassium permanganate were added to the boiler and distillation

was continued. A middle cut of b.p. 139.0–139.5° was collected for use in rate work. Valeric acid, b.p. 183.0°, was subjected to a similar purification procedure. Reagent grade acetic anhydride was freshly distilled before use. The authors are indebted to Professor Albert T. Bottini, who provided them with a generous sample of β-bromoallyl-n-hexylamine. This material, the synthesis of which will be described elsewhere by Professor Bottini, is a liquid of b.p. 122–124° (24 mm.) and $n^{26}D$ 1.4711.

The triphenylmethyl chloride (m.p. 111–113°) was prepared from triphenyl-carbinol,[8] recrystallized from a benzene–pentane mixture containing acetyl chloride and dried and stored under vacuum over soda lime and paraffin. Trityl acetate, m.p. 83°, was prepared from trityl chloride and silver acetate[9] and recrystallized several times from ethyl acetate. Trityl propionate was prepared by refluxing a mixture of 3.8 g. of trityl chloride (0.0137 mole) and 5.0 g. of silver propionate (0.0276 mole) in 50 cc. of benzene for 3 hours. The mixture was filtered, and the benzene was stripped from the filtrate under reduced pressure. The crystalline residue was recrystallized from ligroin; wt. 2.03 g., m.p. 77–79°. After a second recrystallization from ligroin the material had m.p. 80–82°.

Anal. Calcd. for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found: C, 83.55; H, 6.55.

Stock solutions of hydrogen chloride in acetic acid were prepared from an anhydrous commercial sample of the gas and were analyzed by gravimetric methods.

The Spectra of Trityl Halides and the Trityl Esters in Carbon Tetrachloride–Carboxylic Acid Mixtures.—The extinction coefficients of the trityl esters in the 280 mμ region are substantially less than that of trityl chloride. It is, therefore, feasible to follow the reactions of the chloride with the fatty acids in carbon tetrachloride solution by spectrophotometric methods. The extinction coefficients of the reactants and products change somewhat with changing carboxylic acid concentration of the medium. In Table I are listed typical values of these constants for trityl chloride and some of its solvolysis products at 278 mμ, the wave length used in the rate and equilibrium measurements subsequently described. Except as noted the extinction coefficients of the chloride and of the trityl esters were calculated from the optical densities of their freshly prepared solutions.

Equilibration of Trityl Chloride with the Trityl Esters.—Although there has been some confusion on this point,[9–11] it has been shown recently that in dilute solution in acetic acid the solvolysis is far from complete[1c]; the equilibrium can, however, be shifted so that trityl acetate formation is essentially quantitative, if sodium acetate is present to react with hydrogen chloride. Actually the synthesis of trityl acetate in high yields has been accomplished by reaction of trityl halide in an acetic acid–ammonium acetate mixture.[12] As in pure acetic acid, acetolysis of trityl chloride is incomplete in carbon tetrachloride solution. This was established by following the reaction spectrophotometrically at 278 mμ (see the section on kinetic studies). The percentages of conversion reported in Table II were calculated using the

(1) (a) C. G. Swain, *J. Am. Chem. Soc.*, **70**, 1119 (1948); (b) C. G. Swain and E. E. Pegues, *ibid.*, **80**, 812 (1958); (c) C. G. Swain and A. MacLachlan, *ibid.*, **82**, 6095 (1960).

(2) H. Hart and F. A. Cassis, *ibid.*, **76**, 1364 (1954).

(3) M. F. Hawthorne and D. J. Cram, *ibid.*, **76**, 3451 (1954).

(4) (a) E. Gelles, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2918 (1954); (b) E. D. Hughes, C. K. Ingold, S. F. Mok and Y. Pocker, *ibid.*, 1238 (1957), and accompanying papers.

(5) R. F. Hudson and B. Saville, *ibid.*, 4130 (1955).

(6) C. G. Swain and R. B. Mosely, *J. Am. Chem. Soc.*, **77**, 3727 (1955).

(7) R. M. Keefer and L. J. Andrews, *ibid.*, **79**, 4348 (1957).

(8) W. E. Bachmann, *Org. Syntheses*, **23**, 100 (1943).

(9) M. Gomberg and G. T. Davis, *Ber.*, **36**, 3924 (1903).

(10) M. Gomberg, *ibid.*, **36**, 376 (1903).

(11) A. G. Evans, A. Price and J. H. Thomas, *Trans. Faraday Soc.*, **51**, 481 (1955).

(12) C. S. Schoepfle, *J. Am. Chem. Soc.*, **47**, 1469 (1925).

TABLE I

EXTINCTION COEFFICIENTS (278 mμ) OF $(C_6H_5)_3CH$ DERIVATIVES IN CCl_4 SOLUTIONS OF CARBOXYLIC ACIDS

[RCOOH, moles/l.	ϵ_{Ph_3CCl}	ϵ_{Ph_3COCOR}	[RCOOH], moles/l.	ϵ_{Ph_3CCl}	ϵ_{Ph_3COCOR}
	R = CH_3-			R = CH_3CH_2-	
0	240	69	2.23	232	70
0.580	..	66[a]	4.47	214	61[c]
2.90	234	56	8.94	169	42
5.80	224	48	R = $CH_3(CH_2)_2CH_2$-		
11.6	204[b]	37	1.52	215	54[d]

[a] Calculated from the final optical density of a rate in which $[Ph_3CCl]_1 = 5.44 \times 10^{-3}$ M and [amine] = 28.1×10^{-3} assuming complete conversion of the chloride to the acetate. This value is in good agreement with that obtained by interpolation of the values which flank it in the table. [b] This value checks that ($\epsilon = 202$) calculated from the optical density of a solution of trityl acetate in a solution of 10^{-2} M hydrogen chloride in 11.06 M acetic acid. [c] This value checks that ($\epsilon = 61.8$) calculated from the final reading of a rate run in which $[Ph_3CCl]_1 = 5.27 \times 10^{-3}$ M and [amine] = 58.7×10^{-3} M. [d] This is the average of two very similar values based on the final readings of two rate runs at [amine] = 59.8×10^{-3} M and $[Ph_3CCl]_1 = 5.4 \times 10^{-3}$ and 2.70×10^{-3} M.

equilibrium optical densities, the initial trityl chloride concentrations and the appropriate extinction coefficients. The values for conversion of the chloride to the acetate seem somewhat large when compared to that (about 12%) reported by Swain and MacLachlan[10] for reaction of 7×10^{-3} M chloride in pure acetic acid and when compared to the corresponding values for reaction with propionic and valeric acids which are also reported. It should be noted, however, that acetic anhydride was employed in the purification of the acetic acid. Traces of this material, which (see below) reacts with hydrogen chloride present in these mixtures, undoubtedly remain in the purified solvent. Even small amounts of the anhydride may produce a measurable shift

$$(C_6H_5)_3CCl + RCOOH \rightleftarrows$$
$$(C_6H_5)_3C-OCOR + HCl \quad (1)$$

of the equilibrium (eq. 1) to the right.

The values for the percentage conversion of chloride to ester which are presented in Table II can be used to estimate equilibrium constants ($K = [Ph_3COAc][HCl]/[Ph_3CCl]$). The constants thus obtained for reaction at 11.6 M acetic acid have an average value of 0.44×10^{-3} mole/l. In one experiment equilibrium was approached from the opposite direction ($[Ph_3COAc]_1 = 4.75 \times 10^{-3}$ M and $[HCl]_1 = 5.53 \times 10^{-3}$ M in 11.6 M acetic acid). From the equilibrium optical density of the solution a K-value of 0.50×10^{-3} mole/l. was calculated. The two constants are in surprisingly good agreement considering the possible influences of traces of acetic anhydride on the equilibrium position.

TABLE II

PERCENTAGE CONVERSION OF TRITYL CHLORIDE TO ESTER (CCl_4, 25.1°)

10^3 [ArCl]$_1$, moles/l.	[RCOOH], mole/l.	Conversion, %	10^3 [ArCl]$_1$, moles/l.	[RCOOH], moles/l.	Conversion, %
Acetic acid			Propionic acid		
7.53	2.90	22	5.27	0.447	8
3.45	2.90	20	5.26	2.23	12
1.73	2.90	28	2.63	2.23	21
7.53	5.80	24	1.32	2.23	33
3.45	5.80	24	5.59	4.47	8
1.73	5.80	34	5.27	4.47	14
5.18	11.60	33	1.40	4.47	25
3.61	11.60	30	Valeric acid		
1.73	11.60	39	5.40	1.52	12

The Kinetic Studies.—To remove hydrogen chloride from the reaction mixtures either acetic anhydride (when acetic acid was used) or, more generally, β-bromoallyl-n-hexylamine, in substantial excess of the initial trityl chloride,

were included in the rate samples. In the presence of the former the shift of equilibrium 1 to the right may be ascribed[13] to the establishment of equilibrium 2. That a rather

$$(CH_3CO)_2O + HCl \rightleftarrows CH_3COCl + CH_3COOH \quad (2)$$
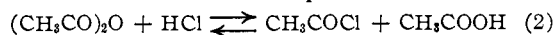
substantial excess of the anhydride is required to shift equilibrium 2 far to the right is suggested by the fact, most apparent for runs at the lowest anhydride concentration, that the final optical densities of the rate samples were higher than the values predicted using the known extinction coefficients of the reaction product (Table I). In such cases the first-order rate constants k (eq. 3), which were calculated

$$kt = 2.303 \log [Ph_3CCl]_i/[Ph_3CCl] =$$
$$2.303 \log [(d_i - d_t)/(d_t - d_f)] \quad (3)$$

from the slopes of plots of log $(d_t - d_f)$, drifted downward with time. The subscripts i and t refer, respectively, to initial time and time t; d_f is the final optical density, predicted on the assumption that ester formation is complete. Rate constants, k, which are later reported for acetolyses in the presence of acetic anhydride are, in cases where their values drifted during a run, based on initial phases of the reactions. In connection with the reversibility of the reaction of the anhydride and hydrogen chloride (eq. 2), it is interesting to note that when acetyl chloride (in addition to the anhydride) was included in a reaction mixture in relatively small quantity, only a very small percentage of trityl chloride was converted to acetate when equilibrium was attained.

The equilibrium optical densities from runs in which acetic anhydride was present could not always be accurately measured. The final readings tended to drift somewhat, sometimes up and sometimes down. For this reason it has not been possible to make a reliable estimate of the equilibrium constant for the anhydride reaction (eq. 2).

The carboxylic acid salts of β-bromoallyl-n-hexylamine (R_1R_2NH) and the amine hydrochloride formed (eq. 4) as trityl chloride reacted were soluble in

$$R_1R_2NH_2^+OCOR^- + HCl \longrightarrow$$
$$R_1R_2NH_2^+Cl^- + RCOOH \quad (4)$$
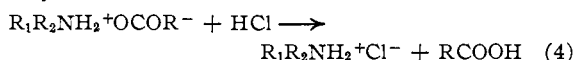
the various media at the concentration levels of the rate runs. Sodium acetate, guanidinium acetate and amines of lower molecular weight (e.g., pyridine) were unsatisfactory for hydrogen chloride removal since the sodium chloride and amine hydrochlorides produced precipitated during the reactions in the carbon tetrachloride-containing media. Ester formation seemed to proceed to high percentages of completion in the presence of even a moderate excess of β-bromoallyl-n-hexyl-amine, as evidenced by the close correspondence of final optical densities of the rate samples with those estimated using the data of Table I. For example, the final optical density of a reaction mixture of initial concentrations, $[Ph_3CCl] = 5.44 \times 10^{-3}$ M, [amine] = 28.1×10^{-3} M and [HOAc] = 0.580 M was found to be 0.460 as compared to a calculated value of 0.462 for a solution 5.44×10^{-3} M in trityl acetate. In some instances, particularly in runs of long duration, the reaction mixtures or the blanks containing the amine underwent some changes which were reflected in the optical densities of the rate samples and which were not characteristic of the reaction under investigation. These changes, which occurred rather erratically, usually were accompanied by the development of a brownish color in the sample or the blank. When such changes took place, the final readings were very noticeably different from predicted values. Rate constants for runs with added amine again were evaluated graphically (eq. 3 using predicted rather than actual d_f values). Except in cases in which the erratic changes mentioned above occurred or in which the amine concentration was not in large excess of that of the trityl chloride, plots of log $(d_t - d_f)$ were linear to high percentages of completion. When deviations from linearity were observed, the rate constants were evaluated from data taken in initial phases of the reaction.

For use in experiments to determine whether the acetolysis of trityl chloride was subject to a salt effect, an amine hydrochloride sample was prepared by gassing a dilute carbon tetrachloride solution of β-bromoallyl-n-hexylamine with anhydrous hydrogen chloride. The mushy white solid which separated was washed with carbon tetrachloride and

(13) For evidence of an analogous reaction of hydrogen bromide and acetic anhydride see H. W. Underwood and G. C. Toone, J. Am. Chem. Soc., 52, 393 (1930).

dried in a vacuum desiccator over paraffin. A stock acetic acid solution of the white waxy product thus obtained was prepared and used to introduce the hydrochloride into rate samples.

Rate runs were started by mixing a known volume of a stock solution of trityl chloride in carbon tetrachloride with known volumes of the appropriate stock solutions of the amine or of acetic anhydride. The solutions, which had been prepared and stored at the temperature used in the kinetic studies, were mixed directly in 1-cm. absorption cells. These were placed in the temperature-controlled (± 0.1°) housing of a Beckman spectrophotometer and measured frequently, until reaction was complete, against a blank which was identical with the original reaction mixture except that it contained no trityl chloride.

Results

The Kinetics of Acetolysis.—As has been discussed in detail in the Experimental section, the acetolysis of trityl chloride in carbon tetrachloride proceeds essentially to completion if acetic anhydride is present in large excess of the chloride. As illustrated in Table III, the reaction under these conditions is first order in trityl chloride, and the rate constants k (eq. 3) increase with the acetic acid content of the medium but are independent of changes in the acetic anhydride concentration.

TABLE III

RATE CONSTANTS FOR ACETOLYSIS OF TRITYL CHLORIDE IN THE PRESENCE OF ACETIC ANHYDRIDE (CCl_4, 25.1°)

$10^3[ArCl]_i$, moles/l.	[HOAc], moles/l.	$10^3[Ac_2O]$, moles/l.	10^4k, sec.$^{-1}$
4.81	16.3	351	73
a	11.6	351	14.8 ± 0.7
b	11.6	141.4	15.5 ± 0.4
c	11.6	70.7	15.9 ± 1.5
c	5.8	351	2.5 ± 0.6
4.93	5.8	70.7	2.5
c	2.9	351	1.00 ± 0.03

^{a} The rate constant reported is the average for two runs at $10^3[ArCl]_i$ = 5.00 and 2.50 M. ^{b} The rate constant reported is the average for two runs at $10^3[ArCl]_i$ = 2.50 and 1.25 M. ^{c} The rate constant reported is the average for three runs at $10^3 [ArCl]_i$ = 5.00, 2.50 and 1.25 M.

When the acetolysis is carried out using β-bromo-allyl-n-hexylamine rather than acetic anhydride as a hydrogen chloride trap, the individual runs generally follow a first-order rate law (eq. 3) to high percentages of completion provided the amine is in substantial excess of the chloride. When the amine and initial trityl chloride contents of the reaction mixtures are of the same order of magnitude, the experimental k-values fall off sharply with time even though trityl acetate is formed quantitatively. The first-order rate constants for reactions in the presence of even moderate amounts of the amine are substantially larger than those observed when acetic anhydride is present. This is evident from a comparison of the k-values of Tables III and IV for reactions at an acetic acid concentration of 2.90 M. Also the rate constants for acetolysis in the presence of the amine (including initial k-values for runs at relatively low amine concentration) increase in approximate proportion to the amine concentration of the medium. The same relationship between rate constant and amine concentration is apparent in the reaction of trityl chloride with propionic acid at 4.5 M acid concentration (see Table IV).

TABLE IV

RATE CONSTANTS FOR THE ACETOLYSIS OF TRITYL CHLORIDE IN THE PRESENCE OF β-BROMOALLYL-n-HEXYLAMINE (CCl_4, 25.1°)

$10^3[ArCl]_i$, moles/l.	[RCOOH], moles/l.	$10^3[amine]$, moles/l.	10^4k, sec.$^{-1}$
		Acetic acid	
5.47	5.80	27.1	210
5.47	5.80	27.1	150^a
b	2.90	28.2	37 ± 3
5.63	2.90	16.0	21
5.63	2.90	6.6	12
c	1.51	59.3	31 ± 3
5.40	1.51	29.7	16
b	1.16	56.4	15 ± 1
b	1.16	28.3	4.92 ± 0.05
5.40	0.755	59.3	5.75
b	0.580	28.1	2.0 ± 0.1
		Propionic acid	
5.27	4.47	113.7	38.5
b	4.47	58.7	21.4 ± 0.7
b	4.47	28.7	9.7 ± 0.5
5.37	2.23	59.8	5.8 ± 0.6^d
. .	1.52	59.8	3.0^e
b	1.12	60.3	1.62 ± 0.08
		Valeric acid	
b	1.52	59.8	1.19 ± 0.02
b	0.76	61.0	0.58 ± 0.03
		Trimethylacetic acid	
5.37	1.51	59.3	0.17
5.37	0.75	59.3	0.12

^{a} The rate sample also contained the amine hydrochloride at a concentration of 0.020 M. ^{b} The rate constant reported is the average for three runs at $10^3[ArCl]_i$ = 5.40, 2.70 and 1.35 M. ^{c} The rate constant reported is the average for two runs at $10^3[ArCl]_i$ = 5.40 and 2.70 M. ^{d} The rate constant reported is the average for two runs at 10^3 [amine] = 59.0 and 60.6 M. ^{e} This value of k has been obtained by interpolation from the other values recorded for propionic acid.

Since the amine is present in these reaction mixtures as the salt, $R_1R_2NH_2^+OCOR^-$, its influence on k-values might reasonably be characterized as a "salt effect." It seems likely, however, that such an effect is of only minor importance as a rate-controlling factor since when the hydrochloride prepared from the amine is added to the reaction mixtures it produces no rate enhancement. In fact if anything, the hydrochloride causes a slight rate deceleration (compare the results of the two runs at 5.80 M acetic acid concentration in Table IV).[14]
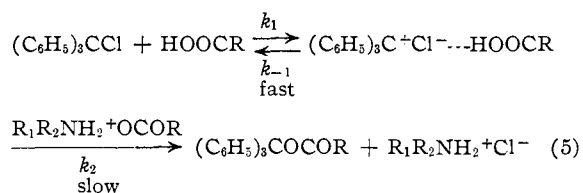
Unless the somewhat questionable assumption is made that the carboxylic acid salt of the amine has a much larger salt effect than the hydrochloride,[15]

(14) It seems improbable that this deceleration can be ascribed to a "common ion" (chloride ion) effect in view of the relatively low polarity of the reaction medium and the consequent unlikelihood of free ion intermediates. Also it has been established semi-quantitatively that the sharp diminution in first-order rate constants during acetolyses in which the amine concentration is comparable to that of the initial trityl chloride concentration (6 × 10^{-3} M) occurs whether or not the amine hydrochloride is initially present in appreciable quantity (0.02 M). That is, the drop in k-values must be ascribed to a drop in acetate ($R_1R_2NH_2^+OAc^-$) concentration rather than to a build-up of the hydrochloride content of the medium.

(15) W. G. Young, S. Winstein and H. L. Goering, J. Am. Chem. Soc., **73**, 1958 (1951), have, for example, shown that in the acetolysis of γ,γ-dimethylallyl chloride, in which ionization of the chloride

the rate increases produced by increasing the amine concentration must be attributed to the capacity of the carboxylates to participate as nucleophiles in the rate-determining process. Apparently only when the amine concentration of the medium is very small is any appreciable fraction of the product (trityl ester) formed by a reaction which is kinetically independent of the amine. Presumably, although this cannot be stated unequivocally, in the absence of the amine the carboxylic acid takes over the role played by the carboxylate as a nucleophile in the rate-determining stage of the reaction. As noted previously, the solvent appears to function as a nucleophile in the slow step of the reaction of trityl chloride in pure acetic acid. It would seem useful in this connection to know something about the order of the reactions in carbon tetrachloride with respect to the carboxylic acid. Not much significance can, however, be attached to the apparent order in acetic acid (>1) found for reaction in the presence of acetic anhydride (see Table III). The kinetic consequences of changing the concentration of acetic acid in a carbon tetrachloride medium hinge on a combination of factors some of which must, for the moment, be classified as intangible (e.g., the influence of changes in the acetic acid monomer–dimer ratio on rate). It is interesting to recall that trityl chloride reacts in 100% acetic acid in the presence of sodium acetate of no higher than $3 \times 10^{-3} M$ in concentration at a rate which is independent of the salt concentration. That is, under such conditions the solvent rather than the acetate functions as the nucleophilic reagent. Also the acetolysis of trityl fluoride[6] and the exchange reaction of labeled trityl acetate in acetic acid[16] are independent of the presence of sodium acetate in the medium in relatively high concentration.

The Mechanism of Acetolysis.—Two reasonable mechanisms for the formation of the trityl esters in the presence of an appreciable quantity of the amine can be suggested. The first of these, eq. 5, is analogous to that which seems most likely to apply to the solvolyses of trityl chloride in pure acetic acid.[1c] In the present case the carboxylic acid may be presumed to contribute as an electrophile to the establishment of an equilibrium between the starting chloride and a triphenylcarbonium chloride ion pair. This is followed by reaction of the ion pair with the carboxylate.

$$(C_6H_5)_3CCl + HOOCR \underset{\substack{k_{-1} \\ \text{fast}}}{\overset{k_1}{\rightleftarrows}} (C_6H_5)_3C^+Cl^-\text{---}HOOCR$$

$$\xrightarrow[\substack{k_2 \\ \text{slow}}]{R_1R_2NH_2{}^+OCOR} (C_6H_5)_3COCOR + R_1R_2NH_2{}^+Cl^- \quad (5)$$

must be the rate-determining process, the salt effects of potassium acetate, lithium acetate and lithium chloride are all very similar.

(16) C. G. Swain, T. E. C. Knee and A. MacLachlan, J. Am. Chem. Soc., **82**, 6101 (1960).

Alternately the attack of carboxylate on carbon and the electrophilic solvation of departing chloride by the carboxylic acid may be concerted in character. Both of these processes are qualitatively at least in accord with the observed enhancement of reaction rate with increases in the amine and carboxylic acid concentrations.

It is of interest to consider the effect on reaction rate of changing the structure of the carboxylic acid (see Table IV). The rate constants for reaction at fixed concentration of the amine and of the several acids which were investigated vary with the acid in the order $CH_3COOH > CH_3CH_2COOH > CH_3CH_2CH_2CH_2COOH > (CH_3)_3CCOOH$. These four acids have very similar dissociation constants in water (ranging from about 1.8×10^{-5} for acetic to about 1.0×10^{-5} mole/l. for trimethylacetic acid[17]). The dielectric constants of acetic, propionic and n-valeric acids are[18] $6.15(20°)$, $3.30(10°)$ and $2.66(20°)$. A value for the dielectric constant of trimethylacetic acid apparently has not been obtained, but it most certainly is close to that for n-valeric acid. Since the k-values for the reactions of propionic and n-valeric acid in the presence of the amine are comparable in magnitude, it can reasonably be assumed (considering that the dielectric constants of the two acids are about the same) that the two amine salts are of similar reactivity as nucleophiles and also that the two acids are about equally electrophilic in character. It seems reasonable to conclude that the electrophilic reactivities of all four of the acids, which must hinge on their capacities to hydrogen bond to departing chloride in the reaction with trityl chloride, are related to the acid dissociation constants and are therefore about equal. Then if it is assumed that the nucleophilic reactivities of the amine salts of acetic, propionic and valeric acids are about the same, the relatively high reactivity of the chloride in the amine–acetic acid mixture can be attributed to the fact that acetic acid has a substantially larger dielectric constant than its higher homologs. Although the change in medium dielectric constant which occurs when trimethylacetic acid is substituted for n-valeric acid must be small, an appreciable reduction in rate is observed, probably because of the difference in the strength of the salts of the two acids as nucleophilic reagents. The low reactivity of the trimethylacetate must be associated with the shielding of the carboxylate group (COO^-) of the amine salt by its bulky t-butyl substituent. It is much less likely that the electrophilic character of the free acid (hydrogen bonding capacity) is subject to the steric influence of the t-butyl group.

(17) J. F. J. Dippy, J. Chem. Soc., 1222 (1938).
(18) A. A. Maryott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids," National Bureau of Standards Circular 514, August 10, 1951.