$n^{20}{}_D$ 1.4599 and contained a trace of 4-*t*-butylcyclohexanone. Analysis through the silver nitrate–triethylene glycol column showed no isomeric cyclohexene to be present, however.

1,3-Dimethylcyclohexene.—2,6-Xylenol was hydrogenated in 95% ethyl alcohol over 65% nickel–kieselguhr at an initial pressure of 2680 p.s.i. at 156°. After separation of the catalyst and solvent, 2,6-dimethylcyclohexanol was isolated in 90% yield by distillation; b.p. 173–175° (749 mm.), $n^{23}{}_D$ 1.4595.[29]

With 10% excess acetyl chloride in 3 volumes of pyridine this gave 94% of 2,6-dimethylcyclohexyl acetate, b.p. 110–111° (50 mm.), $n^{23}{}_D$ 1.4376.[29]

When the acetate was dropped onto a 6-inch column of glass beads in a vertical tube furnace maintained at 500° in a stream of nitrogen adjusted to give a residence time of 1 second, 16% of 1,3-dimethyl-cyclohexene (b.p. 127.5–128.0° at 763 mm., $n^{23}{}_D$ 1.4477),[30] was obtained and 75% of the acetate was recovered (b.p. 195° at 761 mm., $n^{23}{}_D$ 1.4371). The 1,3-dimethycyclohexene thus obtained showed a single peak when analyzed on the silver nitrate column and on the tri-*m*-cresyl phosphate column.

4-Methylisopropylidenecyclohexane.[31]—The Reformatsky reaction of ethyl α-bromoisobutyrate and granular zinc in ether–benzene with 4-methylcyclohexanone by the procedure of Hussey and Newman[32] furnished 86% of 4-methyl-1-(2-carbethoxy-2-propyl)-cyclohexanol (8-carbethoxy-4-p-menthanol) as a mixture of isomers, b.p. 90–97° (14 mm.), $n^{20}{}_D$ 1.4402–1.4601.[31] Dehydration was attempted by heating at 145° for 3 hours with 2 parts by weight of anhydrous potassium bisulfate. The distilled product showed hydroxyl bands in its infrared spectrum so the dehydration was repeated by heating with anhydrous potassium bisulfate for 6 hours at 165°. Because of the extra manipulations, the yield of product was only 59%, b.p. 73–78° (1 mm.), $n^{22}{}_D$ 1.4550.[31]

Saponification with potassium hydroxide in ethanol followed by acidification furnished 74% of 4-methyl-1-(2-carboxy-2-propyl)-cyclohexene, m.p. 93.5–95.5° (from ether).[31] This acid liberated carbon dioxide at a smooth rate when heated to 195°. Application of a slight vacuum at short intervals during the 8-hour heating period removed product from the heated reaction zone as formed: yield 92%, $n^{22}{}_D$ 1.4670. Fractionation furnished 3.4 g. (63%) of 4-methylisopropylidenecyclohexane, b.p. 80.5° (35 mm.), $n^{20}{}_D$ 1.4681. This material exhibited a single peak when analyzed through the silver nitrate–triethylene glycol column, but was extensively isomerized by passage through the tri-*m*-cresyl phosphate column. The infrared spectrum (neat) had characteristic bands at 5.62, 10.45 and 10.57 μ.

$\Delta^{9,10}$-Octalin.—The $\Delta^{9,10}$-octalin was prepared essentially by the procedure since described by Dauben[33] except that the regeneration of the olefin from its nitroso chloride derivative was effected by careful warming to 70° of 0.10 mole with 30 ml. of N,N-dimethylaniline. The extracted hydrocarbon distilled at 77.5° at 14 mm. and had $n^{20}{}_D$ 1.4990.[33] Traces of acids, as on the surface of glassware, or the heat of adsorption on activated silica rapidly cause contamination of purified samples of $\Delta^{9,10}$-octalin by an isomerization to $\Delta^{1,9}$-octalin.

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(29) A. Skita and W. Faust, *Ber.*, **72**, 1128 (1939). See R. Cornubert, *et al.*, *Bull. soc. chim. France*, 631 (1950), for discussion of stereochemistry of the several isomers.

(30) G. Chiurdoglu, *Bull. soc. chim. Belg.*, **47**, 241 (1938).

(31) O. Wallach, *Ann.*, **360**, 70 (1908).

(32) A. S. Hussey and M. S. Newman, THIS JOURNAL, **70**, 3024 (1948).

(33) W. G. Dauben, *et al.*, *J. Org. Chem.*, **23**, 1205 (1958).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE LABORATORY FOR NUCLEAR SCIENCE, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASS.]

I. Mechanism of Solvolysis of Triphenylmethyl Chloride in Hydroxylic Solvents[1—3]

BY C. GARDNER SWAIN AND ALEXANDER MACLACHLAN

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Rates of solvolysis of triphenylmethyl (trityl) chloride in nine solvents at 25° are reported. Since these rates are very fast, most of them were determined by extrapolation from measurements at low temperatures, but a few were done in a conductimetric flow system at 25°. Although the $\log (k/k^0) = mY$ equation gives only a fair correlation of these data, the $\log (k/k^0) = c_1d_1 + c_2d_2$ equation gives an excellent correlation using previously determined solvent (d_1,d_2) parameters. The decrease in relative rate of solvolysis in acetic acid in the series *t*-butyl chloride > α-phenylethyl chloride > benzhydryl chloride > trityl chloride suggests that the rate-determining step in acetic acid is nucleophilic attack by acetic acid on the carbonium ion of an ion-pair intermediate.

Table I summarizes new solvolytic data for triphenylmethyl (trityl) chloride in nine solvents, including methanol, ethanol, acetone–water mixtures and acetic acid. The half-lives at 25° range from 5.2 seconds in 95% acetone to 0.0013 sec. in 80% ethanol. The data were obtained by extrapolation from measurements at low temperatures except for 90% and 80% acetone, where a conductimetric flow system at 25° was used, and acetic acid, where a quenching technique at 25° was used. Sodium acetate was added in the solvolyses in acetic acid because they were appreciably reversible without it. Two different concentrations of acetate ion were used to prove that it did not accelerate acetolysis.

TABLE I

RATES OF SOLVOLYSIS OF TRITYL CHLORIDE AT 25°

Solvent[a]	k, sec.$^{-1}$	ΔH^*, kcal.	$\log (k/k^0)$	Y[b]	d_1[c]	d_2[c]
MeOH, 100	159[d]	13.7	−0.53	−1.09	−0.05	−0.73
EtOH, 100	4.89[d]	13.9	−2.04	−2.03	− .53	−1.03
EtOH, 95	35.2[d]	14.0	−1.18	−1.29	....	....
EtOH, 90	81.1[d]	13.9	−0.82	−0.75	− .01	− .54
EtOH, 80	536[e]	..	.00	.00	.00	.00
Me_2CO, 95	0.124[d]	11.9	−3.64	−2.76	....	....
Me_2CO, 90	2.84[d]	13.7	−2.28	−1.86	− .53	−1.52
Me_2CO, 90	1.93[f]	..	−2.44	−1.86	− .53	−1.52
Me_2CO, 80	21.9[f]	..	−1.39	−0.67	− .45	−0.68
AcOH, 100	0.24[g]	..	−3.35	−1.68	−4.82	+3.12

[a] Number after solvent is % by volume based on volumes before mixing; the residue is water; Me, Et, Ac = CH_3, C_2H_5, CH_3CO. [b] Based on *t*-butyl chloride.[4] [c] Solvent parameter based on 25 alkyl halides and esters.[6] [d] Extrapolated from lower temperature data in Table IV. [e] Extrapolated from other EtOH mixtures with eq. 1. [f] From flow system at 25°. [g] From quenching technique discussed in Experimental section; sodium acetate was present (0.0015 and 0.0029 *M* in different runs) to prevent the back reaction.

Comparison of Equations for Correlating Rates of Solvolysis.—Figure 1 shows the correlation ob-

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(1) Supported in part by the research programs of the National Science Foundation and the Atomic Energy Commission and by a National Institutes of Health Research Fellowship to A. M.

(2) For data on triphenylmethyl fluoride and acetate, *cf.* C. G. Swain, T. E. C. Knee and A. MacLachlan, THIS JOURNAL, **82**, 6101 (1960).

(3) For complete experimental data, *cf.* A. MacLachlan, Ph. D. Thesis in Organic Chemistry, M.I.T., August, 1957.

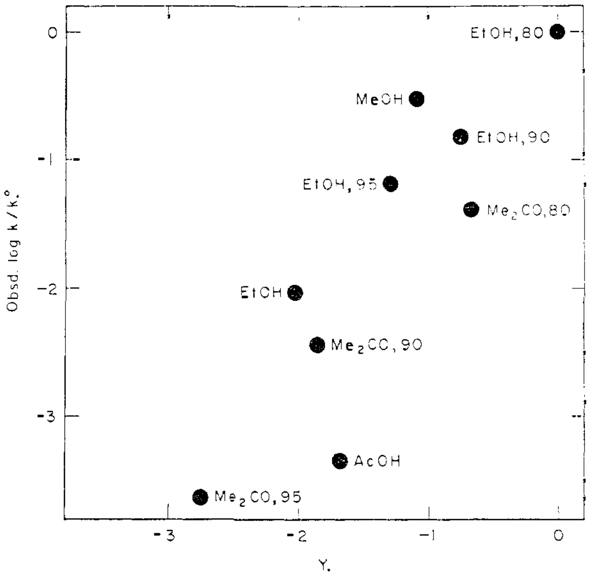

Fig. 1.—Rates of solvolysis of trityl chloride in different solvents at 25° plotted according to eq. 1.

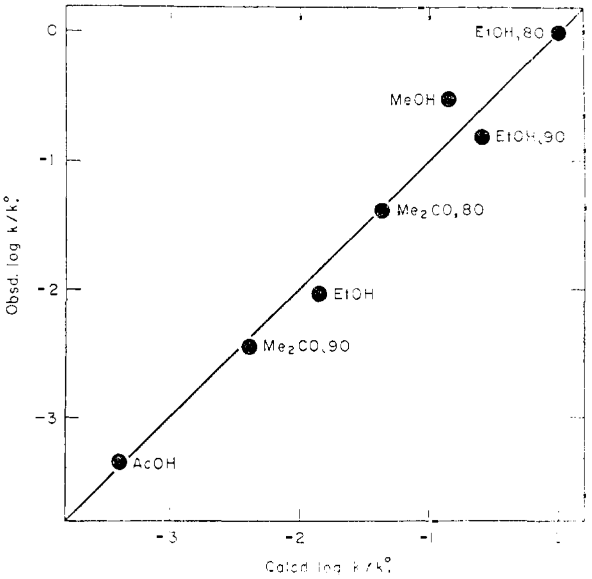

Fig. 2.—Rates of solvolysis of trityl chloride in different solvents at 25° plotted according to eq. 2.

tained using the two-parameter equation[4]

$$\log (k/k^0) = mY \qquad (1)$$

where k and k^0 are solvolytic rate constants for RX in any solvent and in the standard solvent (80% ethanol–20% water), respectively, m depends on RX (defined as 1.00 for *t*-butyl chloride) and Y is a solvent parameter called "solvent ionizing power" (based on *t*-butyl chloride). The point for 80% ethanol in Figs. 1 and 2 is not experimental but was calculated from the three other ethanol–water mixtures with eq. 1. The slope m is 1.32 and our measure of the goodness of fit (Φ)[5] for this equation is 48% (a "fair" fit).

Figure 2 shows the correlation obtained using the four-parameter equation[6]

$$\log (k/k^0) = c_1d_1 + c_2d_2 \qquad (2)$$

where k and k^0 have the same meaning as before but c_1 and c_2 depend on RX and d_1 and d_2 depend on the solvent (and are based on 25 different compounds including methyl bromide and *t*-butyl chloride but *not* including trityl chloride). Here $c_1 = 1.40$, $c_2 = 1.08$, $c_1/c_2 = 1.29$, and Φ is 85% (an "excellent" fit).

The reason for the poorer fit with eq. 1 is a dispersion of the points into lines that are straight only for a given type of solvent pair. This difficulty has also been observed by Fainberg and Winstein in data on α-phenylethyl chloride and bromide and neophyl chloride and bromide.[4] It was concluded that "hydrogen bonding electrophilic assistance to ionization" was the reason for the deviation. They found that "the blend of specific and general solvent influences that make up ionizing power for correlation of rates of solvolysis of chlorides is not quite suitable for correlating solvolysis rates of bromides." They attempted to improve eq. 1 by adding a second term

$$\log (k/k^0) = m_GY_G + m_HY_H \qquad (3)$$

Here m_G and m_H measure the sensitivities of RX to Y_G, the general ionizing power of the solvent, and Y_H, the specific short-range hydrogen-bonding electrophilic solvation function of the solvent. Although the parameters of eq. 3 are still based on *t*-butyl chloride rather than being evaluated from the combined data on all of the compounds and solvents considered, this equation is basically a form of eq. 2.

Changes in the leaving group certainly can produce significant differences in relative reactivity with different solvents. Table II summarizes the striking differences for trityl chloride and fluoride. For example, the ratio of rates in acetic acid and 80% ethanol is 120,000-fold larger for trityl fluoride than for trityl chloride. The four-parameter equations do seem to provide the best way of taking this difference into quantitative account.

TABLE II

COMPARISON OF TRITYL CHLORIDE AND TRITYL FLUORIDE[2] AT 25°

Solvent[a]	$(C_6H_5)_3CCl$ log (k/k^0)	$(C_6H_5)_3CF$ (log (k/k^0))
MeCO, 80	−1.39	−1.79
EtOH, 100	−2.04	−1.73
AcOH, 100	−3.33	+1.76

[a] Same notation as in Table I.

In the following paper[2] it is shown that trityl acetate, trityl *p*-nitrophenyl ether and benzhydryl fluoride are all much closer to trityl fluoride than to trityl chloride in their solvolytic behavior. As discussed there,[2] the reason is at least in part the lower reactivity of the anion formed from the leaving group toward the carbonium ion, which decreases the importance of internal return from ion pairs relative to solvolysis.

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(4) E. Grunwald and S. Winstein, THIS JOURNAL, **70**, 846 (1948); S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951); A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956); **79**, 1597, 1602, 1608, 5937 (1957); S. Winstein, A. H. Fainberg and E. Grunwald, *ibid.*, **79**, 4146 (1957).

(5) C. G. Swain, D. C. Dittmer and L. E. Kaiser, *ibid.*, **77**, 3740 (1955).

(6) C. G. Swain, R. B. Mosely and D. E. Bown, *ibid.*, **77**, 3731 (1955); C. G. Swain and R. B. Mosely, *ibid.*, **77**, 3727 (1955).

In most of the remainder of this paper the leaving group will be restricted to chloride, to focus attention on effects due to changes in the alkyl portion alone.

Evidence for Nucleophilic Attack by Acetic Acid in the Rate-determining Step.—Table III arranges compounds with the same leaving group in order of increasing rate in formic acid relative to 80% ethanol. This is one way of arranging them in order of increasing transition state polarity, since formic acid is the most polar organic solvent commonly studied.[7] Trityl chloride solvolyzes too fast to measure in formic acid. It reacts with the standard solvent (80% ethanol) 300,000 times more rapidly than benzhydryl chloride.

TABLE III

RELATIVE RATES OF SOLVOLYSIS IN FORMIC ACID AND ACETIC ACID AT 25°[a]

Compound[b]	log $(k/k^0)_{HCOOH}$	log $(k/k^0)_{AcOH}$	c_1/c_2[e]
	Bromides		
MeBr[c]	−1.78	−3.01[e]	3.0
EtBr[c]	−1.15	−2.73[e]	2.2
n-BuBr[d]	−1.14	−2.65[e]	2.2
i-PrBr[e]	−0.14	−2.53[e]	1.5
t-BuBr	+1.43	−2.07	..
	Chlorides		
NO_2PhCOCl	−3.37	−4.67	5.2
t-BuCl	+2.08	−1.64	1.0
PhCHClMe	+2.35	−2.05	0.84
Ph_2CHCl	+2.61	−2.36	0.99
Ph_3CCl	....	−3.35	1.29

[a] For references to the papers containing the original measurements, *cf.* Tables I and II of ref. 6, or ref. 4. [b] Me, Et, Pr, Bu, Ph, NO_2Ph = CH_3, C_2H_5, C_3H_7, C_4H_9, C_6H_5 *p*-$O_2NC_6H_4$ respectively. [c] At 50°. [d] At 75°. [e] Calculated from eq. 2. We interpret this quantity as a rough over-all measure of relative sensitivity of rate to variations in nucleophilic reactivity of the solvent compared to sensitivity to variations in its electrophilic reactivity.

The relative rates in formic acid are in accord with a gradual change of mechanism with steadily more polar transition states from methyl bromide to *t*-butyl bromide or from *p*-nitrobenzoyl chloride to *t*-butyl chloride to trityl chloride. This was expected from our earlier hypothesis[6] that *t*-butyl halides are merely intermediate in mechanism between methyl and trityl halides. However, it is not in accord with a "limiting" mechanism for *t*-butyl, α-phenylethyl, benzhydryl and trityl chlorides for the following reason. "Limiting" is defined to mean no covalent bonding of solvent with carbon in the transition state for solvolysis.[4] If that were so, one could no longer explain the increase beyond *t*-butyl chloride as due to a further decrease in sensitivity to the nucleophilic reactivity of the solvent. It would then have to be due to a further increase in sensitivity to dielectric constant, ionizing (solvation) power of the solvent, or special short-range solvation functions of the solvent (dielectric constant, *Y*, and pK_a and d_2 are in fact all higher for formic acid than for 80% ethanol). However, for different chlorides all reacting by a rate-determining ionization, the compound which ionizes easiest (trityl chloride) should be least sensitive to variations in dielectric constant, *Y* or special solvation properties of the solvent. It should be less dependent on help from the solvent than the less easily ionized *t*-butyl chloride. It is generally true that when a highly reactive intermediate is more stabilized internally, it evokes less help from solvent or other external sources for its formation.[9] For example, driving force from participation of a neighboring bromine or other group Z decreases when there are more carbonium-stabilizing substituents on the carbon bearing the leaving group X: $R_2CZCH_2X > R_2CZCH(CH_3)X > R_2CZCH(C_6H_5)X > R_2CZC(CH_3)_2X$.[10] Likewise the effect of one *p*-methyl substituent (factor for increase in rate of solvolysis in aqueous acetone at 25°) decreases when the carbonium ion is better stabilized: $C_6H_5CH(CH_3)Cl$ (60) > $C_6H_5C(CH_3)_2Cl$ (26) > $(C_6H_5)_2CHCl$ (19) > $(C_6H_5)_2C(CH_3)Cl$ (12) > $(C_6H_5)_3CCl$ (3.2).[11] Similarly, we would expect solvation requirements to be more stringent and specific for *t*-butyl cation than for trityl cation. Hammond's postulate[12] applied to this mechanism also predicts that the transition state should more closely resemble the carbonium salt in the *t*-butyl chloride ionization, where it is of higher energy. If a full unit positive charge were forming in the slow step, poor internal distribution of positive charge would make charge development more difficult in the *t*-butyl chloride case, hence that transition state would be of higher energy and especially close to carbonium salt in structure. Therefore *t*-butyl chloride should be accelerated most by formic acid. This is opposite to what is observed. We believe that what is wrong is not the Hammond postulate but the "limiting" mechanism which was assumed.[13] We conclude that

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[7] The dielectric constant of formic acid is reported as 56.1 at 25° by J. F. Johnson and R. H. Cole, *ibid.*, **73**, 4536 (1951). For acetic acid it is reported as 6.2 at 25° by C. P. Smyth and H. E. Rogers, *ibid.*, **52**, 1824 (1930). For a discussion of the physical and chemical differences between acetic acid and all of the other solvents, *cf.* also ref. 8.

[8] C. G. Swain, L. E. Kaiser and T. E. C. Knee, THIS JOURNAL, **80**, 4092 (1958).

[9] However, for subsequent reactions a more stabilized intermediate evokes more help and discriminates more (C. G. Swain, C. B. Scott and K. H. Lohmann, *ibid.*, **75**, 137 (1953)).

[10] S. Winstein and E. Grunwald, *ibid.*, **70**, 828 (1948).

[11] Y. Okamoto, Ph.D. Thesis, Purdue University, January, 1957, p. 96.

[12] G. S. Hammond, THIS JOURNAL, **77**, 334 (1955).

[13] A small change in structure which aids a particular bond cleavage or bond formation may cause that process to be relatively more complete at the transition state provided that the reaction is a polar displacement reaction in solution. Just the opposite is found, in accord with the prediction of Hammond's postulate,[12] in simple free radical reactions. The difference arises because free radical displacements are simple displacements, whereas polar reactions generally involve solvation or desolvation of ions or concerted displacements on more than one atom in the rate-determining step. Aiding one bond change may make that change more complete because there are other difficult bond changes occurring which are affected in the opposite direction. Even in the solvolysis of cumyl chlorides, considered simply to ionize in the rate-determining step, it is evident that ionization is more complete at the transition state with *m*-methyl than with no substituent because the solvent effect (ratio of rates at 25°, methanol to ethanol or ethanol to 2-propanol) is larger for the *m*-methyl compound (and the reverse holds for *m*- or *p*-chloro, *p*-carbomethoxyl or *p*-trifluoromethyl).[14] If solvation bonds could be neglected, Hammond's postulate would predict the reverse, that the transition state would come earlier with *m*-methyl. Evidently nucleophilic solvation is hindered enough to reverse that prediction, hence is not negligible even in this system used for determining σ^+-constants. Solvation bonds are strong bonds.

[14] Y. Okamoto, T. Inukai and H. C. Brown, THIS JOURNAL, **80**, 4975 (1958). *p*-Methyl was not studied, but *p*-phenyl and *p*-fluoro are other groups which behave like *m*-methyl.

nucleophilic reactivity of the solvent is still significant in these reactions (and more important with *t*-butyl chloride than with trityl chloride). This may be either nucleophilic solvation of the transition state in a rate-determining ionization, or rate-determining nucleophilic attack of solvent on carbonium ion in a second step. In either case there is nucleophilic bonding of solvent to carbon in the transition state for solvolysis, and this decreases in importance from *t*-butyl to trityl chloride. Therefore it seems undesirable to classify the reaction of any one of these compounds with formic acid as a "limiting solvolysis."

The order of rates in acetic acid relative to 80% ethanol given in the third column of Table III is even more revealing. Acetic acid, like formic acid, is a stronger electrophilic reagent and weaker nucleophilic reagent than 80% ethanol.[7,8] Accordingly the relative rates simply parallel those for formic acid from primary halides to *t*-butyl chloride. However, for compounds which form still stabler carbonium ions, the relative rates are *abnormally low in acetic acid.* These ratios of rate in acetic acid to rate in 80% ethanol decrease in the order *t*-butyl chloride > α-phenylethyl chloride > benzhydryl chloride > trityl chloride. This is the reverse of the behavior in formic acid, and implies an *increasing* sensitivity to nucleophilic reactivity along this series for solvolyses in acetic acid. An argument against attributing it to an increased sensitivity to dielectric constant or nucleophilic or electrophilic solvating ability of the solvent in a rate-determining ionization step was given in the previous paragraph: trityl chloride should be less, not more, sensitive to these than *t*-butyl chloride because it gives a stabler carbonium ion. It seems hard to escape the conclusion that although the nucleophilic reactivity significant in solvolysis in formic acid may be merely nucleophilic solvation in a rate-determining ionization, that with trityl chloride in acetic acid is something more, namely a rate-determining nucleophilic attack of acetic acid on a triphenylcarbonium chloride ion-pair intermediate rather than rate-determining formation of a carbonium chloride ion pair.

This participation of acetic acid as a nucleophilic reagent in the rate-determining step may be the general rule for solvolyses in acetic acid. A similar abnormally slow rate in acetic acid was observed with *t*-butyldimethylsulfonium perchlorate,[8] suggesting that here the slow step is reaction of acetic acid with a *t*-butyl cation complex, $(CH_3)_3C^+$---$S(CH_3)_2$---ClO_4^-.

In all or nearly all solvolyses of secondary and tertiary halides in acetic acid, it now appears that k_s, the rate constant for reaction of solvent with the ion pair intermediate R^+X^-, is comparable to or smaller than k_{-1}, the rate constant for reversal of the previous step.

$$RX \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} R^+X^- \xrightarrow{k_s} \text{solvolysis products}$$

This makes the k_s step rate-determining. Such a mechanism should not be classified as "SN1" or "limiting."

Trityl fluoride probably comes closer than trityl chloride to the limiting condition that $k_s >> k_{-1}$ because of the much lower nucleophilic reactivity of fluoride ion (in the k_{-1} step). It may therefore be the best available standard for SN1 or limiting behavior. However, a comparison of trityl fluoride and benzhydryl fluoride suggests that even trityl fluoride is somewhat dependent on the nucleophilic reactivity of the solvent. Trityl fluoride is much more reactive than benzhydryl fluoride in polar solvents (rate 1000 times faster in 80% ethanol). However, the relative rate in acetic acid is slightly less for trityl fluoride than for benzhydryl fluoride (log (k/k^0) = +1.76, +2.11, respectively). It appears that nucleophilic attack by acetic acid is again rate-determining.

The conclusion that the solvolysis of trityl chloride in acetic acid solution has reaction of a triphenylcarbonium ion pair with acetic acid as its rate-determining step has another parallel in the methanolysis of trityl chloride in benzene solution, where it was concluded previously that reaction of a triphenylcarbonium ion pair with methanol is rate-determining.[15]

Experimental

Materials.—Trityl chloride was prepared from triphenylcarbinol and acetyl chloride.[16]

Acetone was Fisher reagent grade, stored over Drierite and distilled just before use. Anhydrous ethanol and methanol were obtained by the magnesium method.[17] Acetic acid was obtained by refluxing reagent grade dichromate test glacial acetic acid for 3 days with three times the calculated amount of reagent acetic anhydride equivalent to the water known to be present, then distilling through a column packed with 1 m. of single-turn glass helices.

Sodium ethoxide and sodium methoxide titrating solutions were prepared by dissolving freshly cut sodium in the respective alcohols. Brom phenol blue was the most satisfactory indicator for the kinetics at low temperatures. At 25° brom thymol blue was quite satisfactory. The indicator was always made up in the solvent under study. Sodium acetate was reagent grade, melted in a casserole and held at the melting point until all bubbling had stopped, then used immediately in the preparation of standard solutions in acetic acid.

Kinetics at Low Temperatures.—The method of intermittent titration was used as previously described[18] except that the cell held 10 ml. of solvent, had a mercury-sealed stirrer attached at the top by a glass joint, a stoppered side arm for addition of reagents and solvents, and another opening at the side with a rubber hypodermic stopper through which a 6″ long hypodermic needle (Luer-Lok no. 18, bent in two places) extended from the buret to below the surface of the solution. The cell was flushed with anhydrous, carbon dioxide-free nitrogen before and after addition of solvent to ensure a sharp end-point.

The mixed solvent solutions were all made up by volume at room temperature. To ensure that the same solvent was used throughout a series of runs, the solvents were mixed in a volumetric flask that was capped with a rubber hypodermic stopper. A 10-ml. hypodermic syringe was used to withdraw the sample of solvent for the titration cell. In order to prevent wet air from being introduced as the sample was being withdrawn, another hypodermic needle attached to a drying tower was forced through the stopper to act as a vacuum release.

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(15) C. G. Swain and E. E. Pegues, THIS JOURNAL, **80**, 812 (1958).

(16) W. E. Bachmann, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 841.

(17) H. Lund and J. Bjerrum, *Ber.*, **64**, 210 (1931); L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 3rd ed., 1955, pp. 286, 289.

(18) R. A. Peters and E. Walker, *Biochem. J.*, **17**, 260 (1923); C. G. Swain, R. M. Esteve, Jr., and R. H. Jones, THIS JOURNAL, **71**, 969 (1949); P. D. Bartlett and C. G. Swain, *ibid.*, **71**, 1407 (1949).

Runs at 25° were made in the usual thermostated bath; runs at 0° were made by immersing the reaction cell directly in crushed ice contained in a 1-gal. Dewar flask, and runs at all temperatures below 0° were made in an automatic thermostat constructed as follows. The thermostat bath was in a 1-gal. Dewar containing the titration cell, a stirrer, a toluene–mercury thermoregulator, and a $^3/_8$'' i.d. copper coil through which cold acetone could be circulated from a regulating valve and another 1-gal. Dewar containing a mixture of acetone and Dry Ice by means of a centrifugal pump controlled by the thermoregulator and a vacuum tube relay. Temperature control would easily be maintained to ±0.1° with this device.

The initial concentrations of trityl chloride were 0.0008–0.0025 *M*. One or two drops of a concentrated solution of the reagent in acetone was added by means of a fine-tipped medicine dropper through the side arm and zero time taken when the drops hit the surface of the solvent. Approximately 0.5 ml. of 0.03 *M* sodium hydroxide was used as the titrating agent in all the runs that contained acetone–water mixtures. The titration solution was made up in a solvent that was as close in composition to the medium being titrated as was possible. The solvents where some difficulty was encountered were 5 and 10% water in acetone, since 0.03 *M* sodium hydroxide will not dissolve in these solvents. The titration solution was 80% acetone–20% water, and since good straight lines were obtained, it is assumed that this slight change in solvent composition was negligible. Triethylamine was also used as a base in some of the runs. The titration cell was charged with 10 ml. of solvent and allowed to equilibrate at least 30 min. before each run.

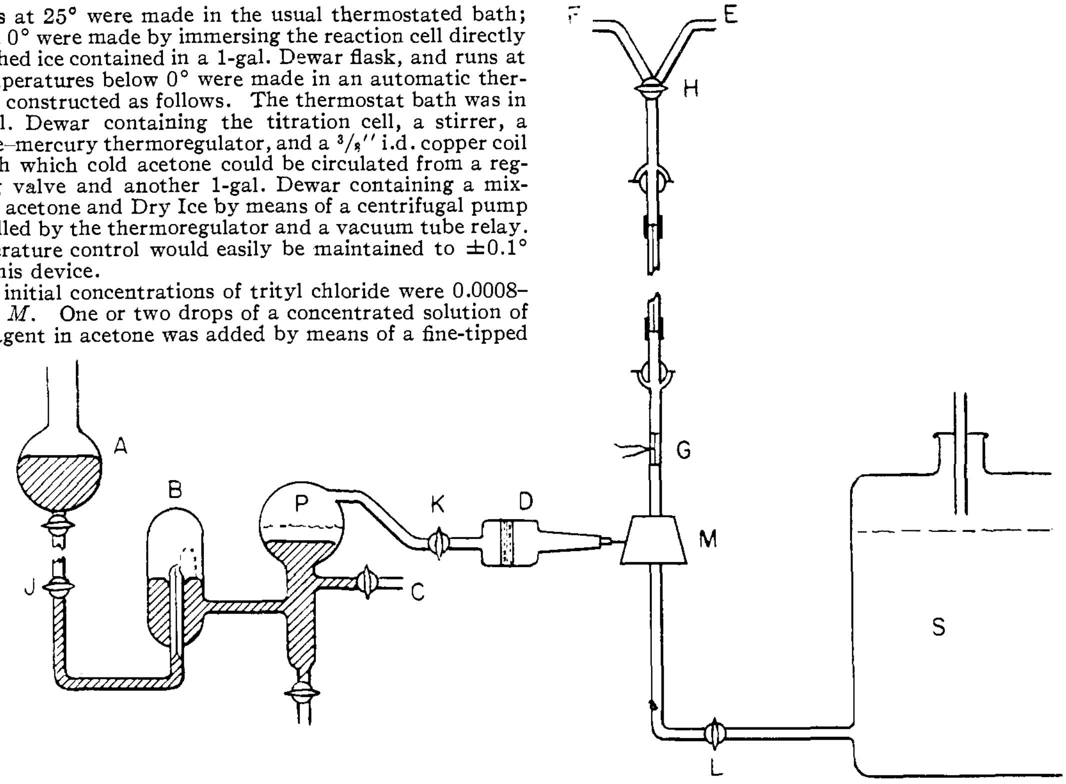

Fig. 3.—Schematic diagram of flow system.

Flow System.—Most of the rates were extrapolated from measurements made below room temperature. However, it was felt that the results obtained would be on a firmer basis if some of the rates could be compared with actual determinations at 25°. Furthermore, some solvents cannot be used at low temperatures because of freezing. A flow system was therefore constructed, tested, used to check one of the extrapolations, and to measure the rate in 80% acetone–20% water. The principle of the flow system is to set up a steady state at a point in a tube, and then to determine the extent of reaction at that point. Trityl chloride, when reacting with a protonic solvent liberates hydrogen chloride, the amount of which may be determined conductimetrically.

It was desired to store the reactant as a concentrated solution in an inert solvent (acetone), and to mix a small amount of the reactant with a large amount of fast-moving solvent completely in a time much shorter than the half-life of the reaction. In the literature there are a large number of designs for mixers for two fast-moving liquids,[19] but designs for mixing a slow and a fast-moving liquid are lacking. Most of the conventional designs were examined for possible adaptiability, but were found unsatisfactory.

The mixer finally constructed (M in Fig. 3) proved to be excellent. A piece of Pyrex capillary tubing for the solvent inlet (8 mm. o.d., 1.4 mm. i.d., 10 cm. long) was carefully ground so that it had a perfectly flat end. By means of a carborundum wheel a radial groove was cut in this section to allow the passage of a Luer-Lok no. 27 hypodermic needle for reactant inlet, when another length of capillary (actual flow tube leading up to the conductivity cell G) was butted against this piece. The two lengths of capillary tubing along with the hypodermic needle were held together firmly within a one-hole Neoprene rubber stopper. Assembly of the mixer was accomplished in the following manner. The needle was forced into the side of the Neoprene stopper so that it pierced the exact center of the hole. Using needle-nosed pliers, and working inside the hole in the stopper from the bottom (solvent inlet side), the needle was bent at a right angle toward this side while it was in the stopper. A piece of 0.010-inch diameter platinum wire about 2 cm. long was made into a fine coil and placed over the needle for the purpose of creating turbulence and enhancing mixing. The inlet length of capillary (bottom section containing the needle channel) was then lubricated with ethylene glycol and forced into the Neoprene stopper until the needle with its turbulence promoter was securely fitted inside the capillary. The final assembly step consisted of inserting the actual flow tube and forcing it firmly against the bottom capillary.

When a dye was added by the reactant pipet, it could be observed visually that mixing was complete as soon as the solution left the mixer (0.5 cm.). Addition of hydrochloric acid instead of reactant also gave the same reading of the conductivity bridge no matter where the cell was placed, thus proving that mixing was complete before the cell was reached. The closest position of the cell was 2.04 cm.

The conductivity cell G in the flow tube was constructed by fusing the two parallel platinum wires into the 1.4-mm. inside diam. capillary tube. The capillary tube was cut off as flat as possible. Two platinum wires (0.010-inch diameter) were stretched across the flat end, parallel and about 0.8 mm. between centers, or 0.5 mm. spacing between the wires, and held in place by a small piece of tape further back on the tube. By careful manipulation of a gas–oxygen flame, the end of the tube was softened and the platinum wires pressed into the glass with the proper spacing. Heating was continued and another piece of capillary butted on. The flame was then adjusted to make it as hot and fine as possible, and the final seal was made by running a fine flame around

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[19] F. J. W. Roughton in A. Weissberger, "Technique of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., Vol. 8, 1953, p. 678.

the newly made seal, causing the glass to flow around the platinum wires. Extreme care had to be exercised here, for if the platinum wires are struck directly by the flame they melt instantly and the cell is useless. The diameter of the capillary tube at the point where the wires were sealed in was slightly less than the diameter of the actual flow tube. About 90% of the circumference of each wire was exposed at the mid-point. The length of each wire exposed was about 75% of its diameter.

Variations in time at the conductivity cell were obtained by inserting lengths of calibrated capillary between the mixer and the cell. To keep the velocity of flow the same for all points, the total resistance to flow was maintained constant by stacking all other lengths of capillary tube, not between the cell and the mixer, above the cell, and holding sections of the flow tube together by means of polyethylene sleeves, which were quite liquid-tight and easily disengaged when necessary. Pyrex $^{18}/_{9}$ ball and socket joints were also used for connections. Since the liquid rose through the whole assembly, the hydrostatic head was always the same.

The pressure pipet P used for metering out the trityl chloride solution at an extremely constant velocity is shown in Fig. 3. By raising the movable reservoir A, as much pressure as desired could be applied to the reactant solution in P. The inertia of the 6 kg. of mercury in A resisted small fluctuations in pressure at the mixer. The reservoir was connected by Tygon tubing ($^{3}/_{16}$-in.) and Pyrex tubing (7 mm. i.d.) to the capillary inlet tube (0.1 mm. i.d.) of side arm B. The capillary nozzle created resistance to the mercury flow and indicated visibly when the mercury was flowing and how rapidly it was being added as it streamed through the acetone, which filled the space above the mercury in B. An acetone solution of trityl chloride was found to react very rapidly with mercury and therefore it was necessary to interpose a thin 2-ml. layer of Nujol (paraffin oil) between the mercury and the 200 ml. of reactant solution. The side-arm D had a sintered glass filter of medium porosity and a hypodermic syringe tip. The extreme stability of the mercury syringe was demonstrated by setting up a steady state of trityl chloride solvolysis in the flow tube and watching for variations in the electrical resistance. Over short periods of time (2 min.) there was no detectable variation with the rate of input that was used. This device is thus an extremely simple yet entirely adequate method of controlling addition of liquids in a very constant manner, even when there is considerable back pressure to overcome. Side-arm B was first filled with acetone, and then mercury was forced in through the capillary nozzle until the proper level was attained. By means of a fine-tipped pipet inserted through side arm C, the layer of Nujol was placed over the mercury. With mercury and Nujol levels still below C, a vacuum was then applied to side arm D, allowing the trityl chloride solution to be drawn in through C. When all the bubbles were removed by applying vacuum to D the pipet was ready to use.

The solvent reservoir S was a 4-liter aspirator bottle with an outlet at the bottom. Nitrogen pressure was applied at the top of S with the aid of a diaphragm valve attached to an ordinary nitrogen cylinder. The valve was set at 20 lb. in.$^{-2}$, but the actual pressure reading was made with a mercury manometer. With the diameter of the flow tube used and the viscosities involved, the pressure was usually in the vicinity of 100 cm. A large flask suitably protected by screening in case of an explosion was used as a ballast tank to smooth out any small fluctuations in nitrogen pressure. This method of solvent propulsion gave extremely constant and reproducible velocities. The velocity of flow was not changed by having the pressure pipet on. By using a standard solution of hydrochloric acid in 80% acetone–20% water it was shown that electrical resistance was slightly dependent on the velocity, decreasing 5% on going from a velocity of zero to that used in the kinetic runs. Therefore all calibrations were carried out at the velocity used in the kinetic runs.

The solubility of trityl chloride in Nujol saturated with acetone and in acetone saturated with Nujol was determined to eliminate the possibility that a significant amount of trityl chloride might dissolve in the Nujol or that a serious concentration gradient might influence the result. The amount of trityl chloride dissolved in each solution was determined by hydrolyzing the trityl chloride present in a 1-ml. aliquot and titrating the acid with sodium hydroxide. Trityl chloride is 3.6 times more soluble in acetone saturated with Nujol (0.86 *M*) than in Nujol saturated with acetone (0.24 *M*). Since there was approximately 100 times more acetone than Nujol in the pipet, concentration gradients were not serious in this system.

The velocity of flow was computed from the time required to fill a 100-ml. buret. The diameter of the capillary tube that was used in all the runs was determined by filling with mercury, and weighing slugs of known length. All measurements were made with cathetometer.[3] The tube was cut into various lengths that would give the desired time intervals for the rate measurements. The lengths of these sections were also measured with a cathetometer.

The operating procedure will be illustrated using Fig. 3. Since the conductivity of a given solution is quite sensitive to the percentage of each solvent in the solution, any one run and its calibration curve were completed on exactly the same solution. Approximately 3 liters of solution was required for each run if 6 or 7 points were desired. Initially stopcock H was in position E (to waste). Stopcock L was opened to flush the system. After 10 sec., J was opened to put mercury pressure on the pipet solution and then K was opened. After a few seconds a conductivity reading was taken. Stopcock H was turned to position F to time the filling of the 100-ml. buret, and meanwhile another conductivity reading was taken. When the volume measurement was complete H was turned back to position E, and then K, L and J were shut off in that order. This procedure was repeated for each point, and also for each calibration, except that in the calibration there was no need for the reactant syringe to be turned on because hydrochloric acid was added in known amounts to the solvent reservoir. The calibration consisted of allowing various concentrations of hydrochloric acid in the solvent to pass through the conductivity cell G at the velocity used in the run. Each resistance reading was taken while a standard volume of the solution was being collected. The solvent solution was titrated with sodium hydroxide solution using brom thymol blue as an indicator. A plot was then made of ml. of base required *vs.* resistance of the solution, and from this, knowing the resistance of the reacting solution at G, one could interpolate from the calibration curve the ml. of base required to titrate this concentration of hydrochloric acid. By collecting the completely reacted solution and titrating it for the total amount of hydrochloric acid liberated, one could calculate the percentage reaction at the time corresponding to the location of the conductivity cell. Calibrations were made before each run, on the same solvent that was to be used. There was never any significant variation of the calibration curves. Initial concentrations of trityl chloride immediately after mixing (before reaction) were 0.0008–0.0016 *M* in 80% acetone and 0.0013–0.0035 *M* in 90% acetone.

Conductivity measurements were made using a Serfass mho-ohm conductance bridge manufactured for A. H. Thomas Co.[20] Measurements were made directly in ohms.

Quenching Method for Determining the Rate in Acetic Acid.—Trityl chloride reaches an equilibrium in acetolysis in pure acetic acid (at approximately 12% reaction with 0.007 *M* trityl chloride). This equilibrium can be shifted to practically complete formation of trityl acetate by adding an equivalent of sodium acetate. The rate of the reaction is inconvenient, *i.e.*, too slow to be measured by the flow technique and too fast to follow by a titration procedure. The best approach short of using a stirred flow reactor was found to be a quenching technique. The apparatus used permitted quenching about 4 sec. after mixing. A 25-ml. round-bottom flask containing a glass propeller with very broad blades was the reaction vessel. A 4-mm. i.d. Pyrex tube with stopcock was sealed to its bottom and down through a glass joint (stopper) of a 300-ml. one-neck round-bottom flask, extending less than half-way to the bottom of the lower flask. The lower flask with 100 ml. of acetone and stopcock closed was submerged in a Dry Ice–acetone-bath to create a partial vacuum. Acetic acid containing the dissolved sodium acetate (10 ml.) was placed in the upper flask. Stirring was commenced and then 1.0 ml. of 0.011 *M* trityl chloride in acetone was added in less than 1 sec. Mixing was almost instantaneous as shown by adding a dye instead of reactant. When the desired time for reaction had elapsed, the stopcock was opened and atmospheric pressure emptied

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[20] H. H. Willard, L. L. Merritt, Jr., and J. A. Dean, "Instrumental Analysis," D. Van Nostrand Co., Inc., New York, N. Y., 2nd ed., 1951, p. 225.

TABLE IV

KINETIC DATA ON THE SOLVOLYSIS OF TRITYL CHLORIDE

Solvent[a]	Temp., °C.	$k \times 10^3$, sec.$^{-1}$	Solvent[a]	Temp., °C.	$k \times 10^3$, sec.$^{-1}$
MeOH, 100	−68.4	3.00	EtOH, 90	−60.3	4.85
MeOH, 100	−67.7	2.92	EtOH, 90	−60.0	4.72
MeOH, 100	−58.0	13.1	EtOH, 90	−52.4	17.8
MeOH, 100	−57.6	13.1	EtOH, 90	−51.8	17.0
MeOH, 100	−56.8	18.7	Me_2CO, 95	−32.5	1.01
EtOH, 100	−50.2	1.33	Me_2CO, 95	−32.3	0.987
EtOH, 100	−50.1	1.38	Me_2CO, 95	−18.0	4.28
EtOH, 100	−40.6	4.75	Me_2CO, 95	−17.6	4.28
EtOH, 100	−40.6	5.02	Me_2CO, 95	− 7.8	12.6
EtOH, 100	−40.3	5.45	Me_2CO, 95	− 7.6	10.2
EtOH, 100	−33.7	12.6	Me_2CO, 95	− 7.5	11.0
EtOH, 100	−33.4	13.8	Me_2CO, 90	−39.6	4.02
EtOH, 100	−33.4	13.9	Me_2CO, 90	−39.0	3.63
EtOH, 95	−59.8	2.23	Me_2CO, 90	−37.8	4.27
EtOH, 95	−59.6	2.20	Me_2CO, 90	−32.3	7.65
EtOH, 95	−50.5	8.88	Me_2CO, 90	−32.3	7.80
EtOH, 95	−50.2	8.75	Me_2CO, 90	−20.6	41.3
EtOH, 95	−40.3	38.5	Me_2CO, 90	+25.0	1833.
EtOH, 95	−40.2	39.8	Me_2CO, 80	+25.0	21700.
EtOH, 90	−70.2	0.94	AcOH, 100	+25.0	240.

[a] Same notation as in Table I.

the upper flask in less than 1 sec., quenching the reaction in the cold acetone. The excess base was then titrated with *p*-toluenesulfonic acid in isopropyl alcohol using the yellow to colorless end-point of brom phenol blue. The titration had to be done slowly near the end-point because of a slow response of the indicator at this temperature. Two different concentrations of sodium acetate (1.5×10^{-3} and 2.9×10^{-3} *M*) were used to show that the rate was independent of acetate ion.

Data and Calculations.—Table IV gives the kinetic measurements. Heats of activation (ΔH^*) were obtained from plots of log k/T *vs.* $1/T$, and extrapolations to 25° made using the equation log $(k_2T_1/k_1T_2) = \Delta H^*(T_2 - T_1)/2.303\ RT_1T_2$ are given in Table I.

The rate of solvolysis of trityl chloride in the standard solvent (80% ethanol–20% water) was expected to be out of the range of either the cooling technique or the flow system. Therefore advantage was taken of the ability of eq. 1 to correlate very well the rates for a single compound in a single type solvent pair. The rates for the three other ethanol–water mixtures determined the straight line for extrapolation to 80% ethanol.

The trityl chloride parameters c_1 and c_2 were obtained from the least squares equations

$$c_1\Sigma d_1^2 + c_2\Sigma d_1d_2 = \Sigma d_1 \log (k/k^0)_{\text{obsd}}$$

$$c_1\Sigma d_1d_2 + c_2\Sigma d_2^2 = \Sigma d_2 \log (k/k^0)_{\text{obsd}}$$

using the d_1 and d_2 solvent parameters previously determined with other compounds and listed in Table I. On Figs. 1 and 2, for 90% acetone only the value determined by the flow method at 25° is plotted. However the figure (0.165 higher) obtained by extrapolation from low temperatures was used as additional datum, and the points for 80% ethanol were omitted (since they must fit), in calculating m, c_1, c_2 and Φ for eq. 1 and 2.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE LABORATORY FOR NUCLEAR SCIENCE, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASS.]

II. Rates of Solvolysis of Triphenylmethyl Acetate and Fluoride[1–3]

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Rates of solvolysis of triphenylmethyl (trityl) acetate in nine solvents at 25° are reported. The rate in acetic acid was measured by using trityl acetate labeled with tritium in the acetate group. The log $(k/k^0) = mY$ equation gives only a fair correlation of the data, but the log $(k/k^0) = c_1d_1 + c_2d_2$ equation gives a good correlation. In its solvolytic behavior, trityl acetate is similar to trityl fluoride previously studied. The hydrolysis of trityl fluoride shows specific hydronium-ion catalysis in water solution. It is accelerated by sodium perchlorate but retarded by sodium chloride.

Table I summarizes the solvolytic data for triphenylmethyl (trityl) acetate in nine solvents. Like trityl fluoride[4] this compound reacts about a million times slower than trityl chloride in the standard solvent (80% ethanol–20% water). Its relative rate in acetic acid (measured by exchange of solvent with trityl acetate labeled with tritium in the acetate group) is also similar to that of trityl fluoride. This rate was not changed by addition of 0.012 *M* sodium acetate. The rates of solvolysis of *t*-butyl chloride and trityl chloride in acetic acid are very abnormally slow by comparison.[2]

TABLE I

RATES OF SOLVOLYSIS OF TRITYL ACETATE AT 25°

Solvent[a]	$k_1 \times 10^5$, sec.$^{-1}$	log (k/k^0)	Y[b]	d_1[c]	d_2[c]
MeOH, 96.7	56	+0.03	−0.72	−0.11	−0.05
MeOH, 69.5	420	+ .90	+1.02	− .06	+1.32
EtOH 100	4.73	−1.05	−2.03	− .53	−1.03
EtOH, 80	52.7	0.00	0.00	0.00	0.00
EtOH, 60	190	+ .56	+1.12	− .22	+1.34
EtOH, 40	912	1.24	+2.20	− .26	+2.13
Me_2CO, 80	1.45	−1.56	−0.67	− .45	−0.68
Me_2CO, 50	72	+0.14	+1.40	− .25	+0.97
AcOH, 100	789	+1.18	−1.68	−4.82	+3.12

[a] Number after solvent is % by volume based on volumes before mixing; the residue is water; Me, Et, Ac = CH_3, C_2H_5, CH_3CO. [b] "Ionizing power," from ref. 5. [c] Solvent constants from ref. 6.

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[1] Supported in part by the research programs of the Office of Naval Research, the National Science Foundation, and the Atomic Energy Commission and by a National Institutes of Health Research Fellowship to A.M.

[2] *Cf.* C. G. Swain and A. MacLachlan, THIS JOURNAL, **82**, 6095 (1960).

[3] For complete experimental data on trityl acetate, *cf.* T. E. C. Knee, Ph.D. Thesis in Organic Chemistry, M.I.T., September, 1956; for trityl fluoride, A. MacLachlan, Ph.D. Thesis in Organic Chemistry, M.I.T., August, 1957.

[4] C. G. Swain and R. B. Mosely, THIS JOURNAL, **77**, 3727 (1955).

[5] E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948); A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

[6] C. G. Swain, R. B. Mosely and D. E. Bown, *ibid.*, **77**, 3731 (1955).