6-Methylboronophthalide.—A solution of 4.00 g. of 2,6-dimethylbenzeneboronic anhydride in 40 ml. of reagent grade carbon tetrachloride was boiled for several minutes, and then stirred while 1.78 g. of recrystallized *N*-bromosuccinimide and 8.3 mg. of benzoyl peroxide were added to the solution. The resulting mixture was heated to reflux and irradiated with a 200-watt, unfrosted lamp. After 15 min. the mixture was pale red in color, and a small amount of succinimide had formed. Heating and irradiation were continued for 1.5 hr. after the addition of 3.56 g. more of N-bromosuccinimide and 16.6 mg. of benzoyl peroxide. The succinimide isolated by filtration weighed 2.87 g. (87%). The crude 2-(bromomethyl)-6-methylbenzeneboronic anhydride obtained by concentrating the filtrate weighed 6.29 g. (99%) and contained 39.4% bromine (calcd., 37.9%). It was added portionwise to a stirred, two-phase mixture of 25 ml. of tetrahydrofuran and a solution of 1.43 g. (0.035 mole) of sodium hydroxide in 25 ml. of water. Sufficient heat was evolved during the addition, which required 20 min., to maintain the mixture at 40–50°; the mixture was then stirred overnight under nitrogen. The *p*H was adjusted to 2–3 with 2.5 ml. of 4 *N* hydrochloric acid, and the aqueous layer was extracted with three 20-ml. portions of ether followed by a fourth extraction after the addition of sodium chloride. The ether extracts were combined with the tetrahydrofuran layer and concentrated *in vacuo* (rotary evaporator). The semisolid residue (4.72 g.) was extracted with 130 ml. of boiling 10% ethanol, and the cooled extract was decanted from the oil which had separated and then seeded and stored in the refrigerator. After two days the crystals (1.14 g.) were collected. A second crop of crystals (0.49 g.) and a third crop (0.20 g.) were obtained by concentrating the mother liquor.

The combined crops were sublimed at 45° (0.05 mm.) for 20 hours in a sublimator equipped with a cold finger condenser. The sublimate, 6-methylboronophthalide, weighed 330 mg. (7.4% yield). The crystals sintered at 110° and melted at 115–125° (c). The residue from the sublimation was identified as 2,6-dimethylbenzeneboronic acid. An analytical sample was prepared by resublimation.

Anal. Calcd. for $C_8H_9O_2B$: C, 64.93; H, 6.12; B, 7.32. Found: C, 65.43; H, 6.35; B, 7.09.

URBANA, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS]

Trifluoroacetic Acid as a Catalyst for the Dissociation of an Iodobenzene Dichloride

BY L. J. ANDREWS AND R. M. KEEFER

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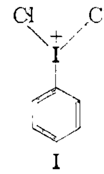
The equilibration of methyl *p*-iodobenzoate dichloride with chlorine and the free iodo compound does not occur at an appreciable rate in carbon tetrachloride, but the reaction in this solvent is markedly catalyzed by trifluoroacetic acid. At relatively low concentrations of the catalyst the reaction is second order with respect to trifluoroacetic acid. The rate of the reaction is not changed when a small quantity of acetic acid, in addition to the catalyst, is included in the medium. In acetic acid solvent the rate of equilibration of the dichloride is markedly enhanced by the addition of trifluoroacetic acid. The order of the catalyzed phase of the reaction is close to unity at 25° and is between one and two at 45°. It is proposed that two molecules of catalyst dimer are incorporated in the activated complex for the reaction in carbon tetrachloride and that these are associated through hydrogen bonding with the two chlorine atoms of the dichloride. It is suggested that when acetic acid is used as the solvent and trifluoroacetic acid is present, any one of three dimers, $(CH_3COOH)_2$, $(CF_3COOH)_2$ and $CF_3COOH \cdot CH_3COOH$, may be coördinated with the two chlorine atoms in the activated complex.

It has been established with considerable certainty that the activation process for the equilibration of iodobenzene dichloride with its components in polar media in the dark is accompanied by a distribution of charge between the iodine and chlorine atoms, as indicated in structure I. Clearly the iodine atom serves as the positive end of the iodine–chlorine dipole since certain substituents (such as $COOCH_3$ and CH_2OH), which are potentially nucleophilic in character and which are properly constituted geometrically, sharply enhance the equilibration rate when they are located *ortho* to the trihalide grouping.[1] These substituents may be presumed to function as neighboring groups in stabilizing the activated complex by coordinating with the iodine atom. Although nitromethane has a much higher dielectric constant than does acetic acid, the dissociation of the dichloride occurs somewhat more rapidly in the latter than in the former solvent at room temperature.[2] The efficiency of acetic acid as a medium can be attributed to its capacity to promote the polarization required for activation by hydrogen bonding to the electronegative chlorine atom of the activated complex.



I

To obtain further information concerning the role of a carboxylic acid in this activation process a study of the kinetics of the trifluoroacetic acid-catalyzed dissociation of methyl *p*-iodobenzoate dichloride in carbon tetrachloride has now been made. Because of its relatively high acidity, trifluoroacetic acid is far superior to acetic acid as a hydrogen bond type solvating agent in polar processes.[2,3] Unlike acetic acid it is a sufficiently effective catalyst at high dilution in carbon tetrachloride so that it has been possible to determine its contribution to the over-all order of the reaction. The iodobenzoic acid derivative rather than iodobenzene dichloride itself has been used to avoid the complication of trifluoroacetic acid-catalyzed chlorination of the aromatic nucleus, a process which can occur rapidly in the absence of substituents which strongly deactivate the ring with respect to electrophilic substitution.[3] A study of the influence of trifluoroacetic acid on the rate of dissociation of methyl *p*-iodobenzoate dichloride in acetic acid, a medium the effective dielectric constant of which should not be strongly dependent on the catalyst concentration, also has been made.

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[1] (a) L. J. Andrews and R. M. Keefer, THIS JOURNAL, **81**, 4218, (1959); (b) R. M. Keefer and L. J. Andrews, *ibid.*, **81**, 5329 (1959).

[2] R. M. Keefer and L. J. Andrews, *ibid.*, **80**, 5350 (1958).

[3] L. J. Andrews and R. M. Keefer, *ibid.*, **81**, 1063 (1959).

Experimental

Materials.—Acetic acid and trifluoroacetic acid were purified before use as described previously.[2] Trichloroacetic acid was recrystallized from benzene and dried over concentrated sulfuric acid *in vacuo* for several days. Eastman Organic Chemicals spectro grade carbon tetrachloride was used without further treatment. Samples of methyl *p*-iodobenzoate dichloride for rate work were freshly prepared from the free iodo compound as described previously.[1a] In rate runs in which the formation of the dichloride from its components was investigated, Eastman Organic Chemicals methyl *p*-iodobenzoate was used without further purification.

The Rate Studies.—To follow the trifluoroacetic acid-catalyzed dissociation of the dichloride, known volumes of stock solutions of the dichloride and of trifluoroacetic acid in carbon tetrachloride were mixed in 1-cm. silica absorption cells at the temperature of the rate studies. It was established by independent measurement that the volumes of trifluoroacetic acid and of carbon tetrachloride were additive on mixing. The initial concentrations of dichloride in the reaction mixtures were established through iodometric analysis of the stock carbon tetrachloride solutions. The total halogen contents of the absorption cells at the end of the reactions were also determined iodometrically. In general the total halogen (the dichloride + chlorine) content of the rate samples remained constant throughout the course of the reaction.

The filled absorption cells were transferred immediately to the temperature controlled housing of a Beckman spectrophotometer, and the reactions followed by noting the drop in optical density of the reaction mixtures with time at 370 mμ. The blank cells contained trifluoroacetic acid in carbon tetrachloride at the same concentrations as were used in the rate runs. In very slow runs the cells were paraffin sealed to prevent chlorine loss. In carbon tetrachloride, dissociation of the dichloride at the concentrations employed (10^{-2}–10^{-3} M) proceeded essentially to completion. The absorption at termination of the reactions resulted almost entirely from the liberated chlorine. The rate constants k_1 for dichloride dissociation were calculated from the slopes of plots of log ($d_t - d_f$) *versus time*, where d_t and d_f are the optical densities of the reaction mixtures at time t and at termination. In the very slow runs, which were not followed to completion, final optical densities were calculated from the initial concentrations of the dichloride and the extinction coefficients of chlorine and methyl *p*-iodobenzoate.

Some runs were conducted in which the formation of the dichloride from its components was followed by noting the increases in the optical densities (370 mμ) of freshly prepared solutions of chlorine and methyl *p*-iodobenzoate with changes in time. In general the iodo compound was initially in considerable excess of the chlorine. The reactions were followed to the equilibration point, and the rate constants, k_1, and the equilibrium constants, K, for dichloride dissociation were evaluated from the measured optical densities and the extinction coefficients of the reactants and the product by procedures described earlier.[2] The extinction coefficient of free chlorine at 370 mμ in carbon tetrachloride was measured separately and was found to vary slightly with the trifluoroacetic acid content of the medium; it ranged from 32.0 to 36.3 as the trifluoroacetic acid concentration was changed from 4.30 to 1.08 M. The extinction coefficient of the dichloride at 370 mμ, as calculated from initial readings in runs in which the dichloride was the starting material, is 168 in carbon tetrachloride and is not noticeably influenced by the trifluoroacetic acid content of the reaction mixture. The absorption of the free iodo compound in carbon tetrachloride was found to be small (ϵ_{370} 0.7). In calculating rate constants for runs in carbon tetrachloride in which acetic acid or trichloroacetic acid was present in the reaction mixtures, it was assumed that the extinction coefficients of chlorine were the same as in solutions of comparable concentrations of trifluoroacetic acid.

It should be noted that methyl *p*-iodobenzoate dichloride does not dissociate at an appreciable rate in carbon tetrachloride. The optical density (370 mμ) of a 0.01 M solution of the dichloride in this solvent in the absence of a catalyst did not change appreciably over a 24-hour period.

The rate runs on the trifluoroacetic acid-catalyzed dissociation of methyl *p*-iodobenzoate dichloride in acetic acid were conducted in essentially the same fashion as were the runs in which carbon tetrachloride was used as the solvent, except that optical densities of the reaction mixtures were measured at 380 mμ. All reactions were followed until equilibrium was reached. At the concentration levels of the rate runs, appreciable quantities of undissociated dichloride were present in the solutions at this point. Procedures described earlier[2] were used to calculate the rate and equilibrium constants for dichloride dissociation. The extinction coefficients of the dichloride, chlorine and the free iodo compound at 380 mμ in acetic acid were found to be 105, 13.3 and 0.3, respectively when the trifluoroacetic acid concentration of the solutions was 1.0 M or less. At higher concentrations of the catalyst the extinction coefficient of the dichloride was somewhat lower and that of chlorine was somewhat higher than the figures given above.

The Recovery of Methyl *p*-Iodobenzoate from the Dichloride.—To ensure that no chlorination of the aromatic nucleus occurs when methyl *p*-iodobenzoate is exposed to chlorine in the presence of trifluoroacetic acid in carbon tetrachloride or acetic acid, two experiments were conducted in which the free iodo compound was recovered from the dichloride as formed in catalyst-containing solutions.

A solution of 200 mg. of the iodobenzoate in 6 ml. of 4.3 M trifluoroacetic acid in carbon tetrachloride was gassed with chlorine and allowed to stand for an hour in the dark. The solution then was poured into aqueous potassium iodide, and the mixture was shaken with aqueous sodium thiosulfate to remove halogen. The carbon tetrachloride phase was dried and evaporated. A residue of 180 mg. of methyl *p*-iodobenzoate was recovered; m.p. and mixed m.p. with an authentic sample, 112–115°.

A solution of 200 mg. of the iodobenzoate in 8 ml. of 3.2 M trifluoroacetic acid in acetic acid was gassed with chlorine. Yellow crystals of the dichloride gradually precipitated; 50 minutes after the start of the reaction these were filtered, washed with carbon tetrachloride and air-dried; wt., 150 mg. The dichloride was dissolved in acetic acid, and the solution was treated with aqueous potassium iodide. The mixture was freed of iodine by washing with aqueous sodium thiosulfate. The precipitated methyl *p*-iodobenzoate was filtered and air-dried; wt., 85 mg.; m.p. and mixed m.p. with an authentic sample, 112–115°.

Results

The Reaction in Carbon Tetrachloride.—The rate law for the equilibration of an iodobenzene dichloride with the free iodo compound and chlorine is given in eq. 1, and the equilibrium constant is defined in eq. 2.

$$-\mathrm{d}(\mathrm{ArICl_2})/\mathrm{d}t = k_1(\mathrm{ArICl_2}) - k_2(\mathrm{ArI})(\mathrm{Cl_2}) \qquad (1)$$

$$K = k_1/k_2 = (\mathrm{ArI})(\mathrm{Cl_2})/(\mathrm{ArICl_2}) \qquad (2)$$

The experimental values of k_1 and K for the dissociation of methyl *p*-iodobenzoate dichloride in carbon tetrachloride containing varying amounts of trifluoroacetic acid are given in Table I.

Because the equilibrium constant of the dichloride is relatively large in carbon tetrachloride, it was evaluated from equilibrium readings of solutions which initially contained free chlorine in the presence of a substantial excess of the free iodo compound. The equilibrium constant was found to decrease slightly as the trifluoroacetic acid content of the medium increased. In general, the iodobenzene dichlorides are subject to more extensive dissociation as the medium polarity decreases.[2]

To establish the order, n, of the dissociation reaction with respect to trifluoroacetic acid (see eq. 3, in which k_u is zero for reactions in carbon tetrachloride)

$$k_1 = k_u + k_c(\mathrm{CF_3COOH})^n \qquad (3)$$

the logarithms of the experimental values of k_1 were plotted against the logarithms of the corresponding trifluoroacetic acid concentrations. The

TABLE I

EQUILIBRIUM AND RATE CONSTANTS FOR THE DISSOCIATION OF METHYL *p*-IODOBENZOATE DICHLORIDE IN CARBON TETRACHLORIDE–TRIFLUOROACETIC ACID MIXTURES

(CF_3COOH),[a] moles/l.	$10^3(ArI)_T$,[b] moles/l.		$10^3(Cl_2)_T$,[b] moles/l.	10^4k_1,[c] sec.$^{-1}$	*K*, mole/l.
		t = 25.2°			
4.30		4.85		6.5	
4.30		2.35		6.9	
4.30		1.23		6.4	
4.30	63.3		12.3	6.9	0.25
4.30	63.3		5.85	6.8	.25
4.30	31.7		11.9	6.6	.23
2.15		5.11		0.91	
2.15		2.55		.90	
2.15		1.25		.85	
2.15	63.3		9.96	.93	.31
2.15	31.7		9.77	.90	.30
2.15	63.3		4.57	.98	.29
1.07^5		5.35		.180	
1.07^5		2.60		.166	
1.07^5		1.30		.170	
1.07^5	63.7		10.0	.214	.34
1.07^5	63.7		4.80	.230	.35
1.07^5	31.9		9.65	.228	.38
0.537		4.70		.038	
.537		2.40		.037	
.537		1.20		.034	
1.43[d]		5.30		.031	
1.43[d]		2.55		.031	
		t = 45.2°			
2.15	66.1		8.15	5.7	.69
2.15	33.0		8.20		.76
1.075		5.15		0.79	
1.075		2.70		.75	
0.537		5.16		.143	
0.537		2.58		.147	

[a] The concentrations which are listed were calculated on the assumption that the acids are monomeric in nature. [b] Where the dichloride, rather than the free iodo compound and chlorine, was the starting material, the initial reactant concentration is listed between the $(ArI)_T$ and $(Cl_2)_T$ columns. [c] Where the formation of the dichloride, rather than its dissociation, was followed, the k_1 values which are reported were calculated from the experimental values of k_2 and K. [d] Trichloroacetic acid was used instead of trifluoroacetic acid in this run.

resultant lines, based on data obtained both at 25.2° and 45.2° (see Fig. 1), are somewhat curved; that is, the apparent order of the reaction increases somewhat as the trifluoroacetic acid is increased. The n-values, based on the minimum slopes of these lines, are 2.27 at 25.2° and 2.46 at 45.2°.

The trifluoroacetic acid concentrations which are reported in Table I are calculated on the assumption that the catalyst is monomeric in nature. It is likely, however, that in carbon tetrachloride the acid is almost completely dimeric in character, since it is largely in the associated form in the gas phase[4] and since other strong carboxylic acids such as trichloroacetic acid are extensively dimerized in non-polar media in the vicinity of room temperature.[5] Thus, it appears that a minimum of two molecules of trifluoroacetic acid dimer are included in the activated complex for the catalyzed dissociation of the dichloride in carbon tetrachloride. The increase in apparent reaction order with respect to the catalyst as its concentration becomes fairly large might be ascribed to the favorable influence of an increase in the dielectric constant of the medium on the rate of a polar process. Some indication that the dielectric effect is of minor significance was obtained by comparing the dissociation rate of the dichloride (initial concentration, 2.6 × 10^{-3} M) in a 1.07 M trifluoroacetic acid solution in carbon tetrachloride (see Table I) with that in a solution which contained both acetic (1.05 M) and trifluoroacetic (1.07 M) acids. The k_1-values (25.2°) for these two runs agreed within 2%. In a 1.05 M acetic acid solution in carbon tetrachloride the dichloride did not dissociate measurably at 25.2° over a 24-hour period. The dielectric constant of acetic acid approaches that of trifluoroacetic acid in magnitude.[6] Therefore the medium in which both acids were present was probably substantially more polar than that which contained only the catalyst acid.

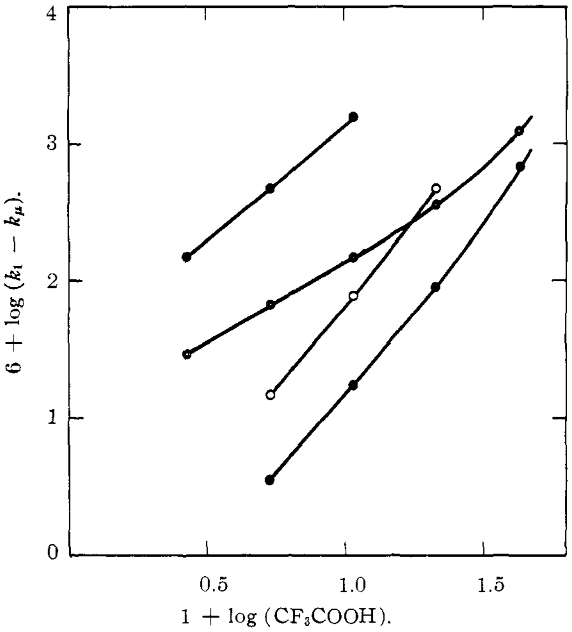

Fig. 1.—Evaluation of the reaction order with respect to trifluoroacetic acid concentration. The symbols ⊙, O, ◎ and ● apply to reactions in CCl_4 at 25.2°, in CCl_4 at 45.2°, in CH_3COOH at 25.2° and in CH_3COOH at 45.2°, respectively.

The fact that the catalytic activity of trifluoroacetic acid was not altered by the presence of an equimolar quantity of acetic acid is of interest from another point of view. It would seem to rule out the possibility that mixed dimers of the two acids are formed in carbon tetrachloride. That is, if the trifluoroacetic acid dimer did not retain its structural identity in the presence of acetic acid, the change should have been reflected in some way in the dichloride dissociation rate.[7] The alternate possibility that a mixed dimer of the two acids is

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(4) J. Karle and L. O. Brockway, THIS JOURNAL, **66**, 574 (1944).

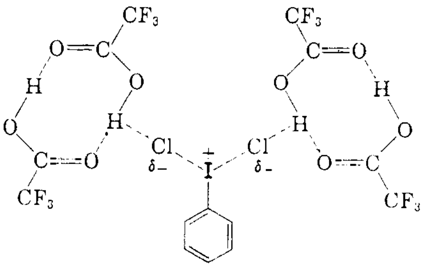
(5) (a) J. T. Harris, Jr., and M. E. Hobbs, *ibid.*, **76**, 1419 (1954); (b) R. Bell and M. H. M. Arnold, *J. Chem. Soc.*, 1432 (1935).

(6) (a) W. Dannhauser and R. H. Cole, THIS JOURNAL, **74**, 6105 (1952); (b) F. T. Harris and C. T. O'Konski, *ibid.*, **76**, 4317 (1954).

(7) Some evidence that mixtures of carboxylic acids do cross dimerize in non-polar media has been reported; (a) B. von Syszkowski, *Z. physik. Chem.*, **131**, 175 (1927); (b) J. N. Brönsted and R. P. Bell, THIS JOURNAL, **53**, 2478 (1931).

formed, which is just half as effective a catalyst as the trifluoroacetic acid dimer, seems far less likely.

Since the evidence that acetic acid can function as a cocatalyst for trifluoroacetic acid is negative, it may reasonably be proposed that the primary function of the fluoro acid dimer in the activated complex for dichloride formation is to solvate the two chlorine atoms, as in structure[8] II. Presumably these two chlorines remain equivalent in the activation process.



II

It is improbable that one of the acid dimers is intimately involved in the solvation of the electropositive center (the iodine atom) since acetic acid is a strong electron donor,[9] relatively speaking, and should function much more effectively in this capacity than its fluorinated analog. Were solvation of the positive center a critical feature of the activation process, a mixture of acetic acid and trifluoroacetic acid, the one to solvate iodine and the other to solvate chlorine, should be a far more potent catalyst than the individual acids. Possibly the steric situation in its vicinity is sufficiently unfavorable so that the iodine atom can only associate in a secondary fashion with the solvent molecules which are coördinated with the chlorine atoms.

The increase in n-values with increasing catalyst concentration is most reasonably ascribed to the development of a secondary solvation sphere in the activated complex. A similar suggestion has been made[10] to explain the fact that the reaction order with respect to phenolic catalysts is higher than unity in the mutarotation of 5α,6β-dibromocholestane in benzene. In this case a second phenol molecule may share its acidic hydrogen with the oxygen atom of the first phenol molecule, which must be significantly polarized through proton bonding to the reactant in the activated complex. The importance of hydrogen bonding capacity (as measured by relative acid strengths) as a criterion of catalyst strength in the dichloride dissociation reaction is clearly indicated by the reactivity order (see Table II) trifluoroacetic acid > trichloroacetic acid >> acetic acid.

The activation energy for the trifluoroacetic acid-catalyzed dissociation of the dichloride in carbon tetrachloride has been approximated from values of $k_1/(CF_3COOH)^2$ at 25.2° and 45.2°, which were obtained by extrapolating plots of $k_1/(CF_3COOH)^2$ *versus* trifluoroacetic acid concentration to zero catalyst concentration. The value E_a = 11.4 kcal. obtained in this way is substantially less than that for the reaction in pure acetic acid. The corresponding entropy of activation, −46 e.u., is much more negative than that for the reaction in acetic acid. This is in accord with the observation made previously that the effects of changes in medium on the energies and entropies of activation for dichloride dissociation are directionally parallel.[2]

The Reaction in Acetic Acid.—The runs conducted to determine the rate constants, k_1, and equilibrium constants for the trifluoroacetic acid-catalyzed dissociation of methyl *p*-iodobenzoate dichloride in acetic acid are summarized in Table II. As was the case with carbon tetrachloride as the solvent, the equilibrium constants were found to increase with increasing concentration of the catalyst.

TABLE II

EQUILIBRIUM AND RATE CONSTANTS FOR THE DISSOCIATION OF METHYL *p*-IODOBENZOATE DICHLORIDE IN ACETIC ACID–TRIFLUOROACETIC ACID MIXTURES

(CF_3COOH),[a] moles/l.	$10^3(ArICl_2)_i$, moles/l.	10^4k_1, sec.$^{-1}$	10^3K, mole/l.
	t = 25.2°		
4.32	7.15	13.6	28.5
4.32	3.60	13.4	30
2.16	7.00	4.7	22.9
2.16	3.50	4.4	23.2
1.08	6.85	2.48	18.9
1.08	3.43	2.48	18.6
0.54	7.43	1.72	16.2
.54	3.70	1.68	15.3
.27	7.49	1.34	16.8
.27	3.68	1.31	15.4
.27	1.85	1.32	..
..	7.55	1.03	14.9
..	5.05	1.05	15.0
..	2.50	1.02	..
1.25[b]	6.83	1.90	17.9
1.25[b]	3.38	1.94	16.2
0.627[b]	6.85	1.50	17.8
.627[b]	3.45	1.54	..
	t = 45.3°		
1.08	7.75	26	..
1.08	3.90	24	..
0.54	7.40	13.9	..
.54	3.70	14.1	..
.27	7.08	10.5	..
.27	3.58	11.1	..
..	8.30	9.2	33.6
..	5.50	9.3	32.3
..	2.78	9.4	..

[a] The concentrations which are listed were calculated on the assumption that the acids are monomeric in nature. [b] Trichloroacetic acid was used in place of trifluoroacetic acid in this run.

The contribution of the catalyzed reaction to the rate constants, k_1, reported for several runs can be obtained by subtracting the k_1-value for the reaction in the absence of catalyst (defined as k_u in eq. 3); some small error may be involved in this calculation because of possible variations in k_u with changes in the catalyst concentration. As shown in Fig. 1 the variation in the logarithms of

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[8] This structure might alternately be formulated as a resonance hybrid based on two equivalent solvated forms of the type depicted by structure I.

[9] R. E. Buckles and J. F. Mills, THIS JOURNAL, **75**, 552 (1953).

[10] H. Kwart and L. Weisfeld, *ibid.*, **78**, 635 (1956).

the resultant values of $k_c(CF_3COOH)^n$ with the logarithms of the corresponding trifluoroacetic acid concentrations for reaction at 25.2° is essentially linear until the catalyst concentration exceeds 2.16 *M*. The minimum slope of this line, which measures the reaction order with respect to the catalyst, is 1:16; the slope of the line for reaction at 45.3° is somewhat larger (1.66). Undoubtedly the two acids in the reaction media are largely dimeric in nature, and it seems reasonable that the trifluoroacetic acid in relatively dilute solution in acetic acid should be largely in the form of a mixed dimer (1:1 $CF_3COOH–CH_3COOH$). Evidence, based on cryoscopic and viscosity measurements, has been obtained that in solutions of acetic acid in trichloroacetic acid solvent–solute adducts are formed.[11] It should be recalled that this type of interaction apparently does not occur in dilute solutions of mixtures of the two acids in carbon tetrachloride.

The simplest explanation for the variation in reaction rate in acetic acid with changes in trifluoroacetic acid content of the medium is based on the assumption that observed k_1-values are related to the concentrations of the various acid dimers in solution as shown in eq. 4. This equation is

$$k_1 = k_I(\mathrm{HOAc{\cdot}HOAc})^x + k_{II}(\mathrm{HOAc{\cdot}TFA})(\mathrm{HOAc{\cdot}HOAc})^{x-1} + k_{III}(\mathrm{HOAc{\cdot}TFA})^2(\mathrm{HOAc{\cdot}HOAc})^{x-2} \quad (4)$$

proposed with the observation in mind that two molecules of trifluoroacetic acid dimer participate in the activation process for dichloride dissociation when carbon tetrachloride rather than acetic acid is the solvent (note that the term TFA represents trifluoroacetic acid monomer). The first term on the right-hand side of the equation corresponds to k_u in eq. 3, which is the contribution of the uncatalyzed reaction to the over-all rate constant. Presumably in acetic acid, solvent dimers (HOAc.·HOAc) can play the same role in the activation process which has been assigned to catalyst dimers for the reaction in carbon tetrachloride (see structure II). The value of x is presumed to be 2 or greater. When the catalyst is present at low concentration in the form of the mixed dimer (TFA·HOAc), it may replace one or two of the acetic acid dimers in the activated complex, with a favorable influence on the over-all reaction rate. At 25.2° the term involving k_{III} in equation 4 must be of negligible importance, at least until the catalyst concentration exceeds 2 *M* (see Fig. 1 and Table II). Since at 45.3° the dependence of $(k_1 - k_u)$ on the trifluoroacetic acid concentration approaches second order even when the catalyst concentration is low (see Fig. 1), one must conclude that k_{III} has a larger temperature coefficient than k_{II}. It should be noted that the apparent reaction order with respect to trifluoroacetic acid increases with temperature both when carbon tetrachloride and acetic acid are used as solvents. A more detailed interpretation of these increases cannot now be made since pertinent information concerning the influence of temperature on dimer–monomer and dimer–mixed dimer content of the reaction mixtures is unavailable.

The activation energy for the uncatalyzed dissociation of the dichloride in acetic acid as calculated from the rate constants at 25.2 and 45.3° (Table II) is 20.6 kcal., and the corresponding entropy of activation is −9.7 e.u. The heat (ΔH^0) and entropy (ΔS^0) of dissociation of the dichloride in acetic acid are 7.3 kcal. and 16 e.u., respectively. These values are similar to those measured previously for other dichlorides in acetic acid.[2]

Values for the energy and entropy of activation for the trifluoroacetic acid-catalyzed reaction have also been approximated from the variation in k_c (eq. 3) with temperature. The k_c-values at 25.2 and 45.3° which were used in this calculation were taken from the intercepts of plots of $(k_1 - k_u)/(CF_3COOH)$ *versus* the corresponding trifluoroacetic acid concentrations. An assumption has been made, which is crude at best, that these intercepts represent $k_{II}(\mathrm{HOAc{\cdot}HOAc})^{x-1}$ (see eq. 3 and 4). The energy (8.1 kcal.) and entropy (−52 e.u.) values thus obtained are both substantially smaller than those for the uncatalyzed reaction in acetic acid.

As is the case for reaction in carbon tetrachloride, trichloroacetic acid also functions as a reaction catalyst in acetic acid although it is less effective than trifluoroacetic acid (see Table II). Again it is clear that the efficiency of various carboxylic acids in promoting dichloride dissociation is determined by their relative acid strengths.

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[11] (a) J. Kendall, THIS JOURNAL, **36**, 1722 (1914); (b) J. Kendall and E. Brakeley, *ibid.*, **43**, 1826 (1921).