Table III

Thermochemical Properties of Polyacetylenes

Structure	M.p., °C.	Density, g./ml. (°C.)			Heat of combustion[a] −ΔH^0c at (°C.) Kcal./mole	Cal./g.	Cal./ml.
$HC{\equiv}C[(CH_2)_4C{\equiv}C)]_2{-}H$	−3	0.865(25)		0.807(105)	2025(25)	10887(25)	9417(25), 8786(105)
$CH_3(CH_2)_{12}CH_3$	6[b]	.769(25)[c]		....	2262(25)	11402(25)	8654(25), ...
$HC{\equiv}C[(CH_2)_4C{\equiv}C]_3{-}H$	19	.883(25)		.834(105)	2898(25)	10896(25)	9621(25), 9087(105)
$CH_3(CH_2)_{18}CH_3$	37	.785(25)[d]	0.777(40)	.735(105)	3206(25)[d]	11350(25)[d]	8819(40), 8342(105)
┌C≡C┐ $(CH_2)_5$ $(CH_2)_5$ └C≡C┘	100	1.040(25)[d]		.872(105)	1906(25)[d]	10140(25)[d]	10546(25),[d] 8842(105)
┌$(CH_2)_{14}$┐ └────┘	58	0.942(25)[d]	0.834(60)	.809(105)	2215(25)[d]	11302(25)[d]	9426(60), 8613(105)

[a] Herron Testing Laboratories, Cleveland, Ohio. [b] R. R. Dreisbach, "Physical Properties of Chemical Compounds. Vol. II," Advances in Chem. Series, No. 22, Am. Chem. Soc., 1959. [c] F. D. Rossini, *et al.*, "Selected Values of Properties of Hydrocarbons," Circular C461, National Bureau of Standards, 1947, pp. 40, 41, 57, 143–155. [d] Solid.

mm. When heated at atmospheric pressure it did not decompose below 316°.

The triple bonds in the polyacetylenes are responsible for the higher densities of these compounds compared with the corresponding saturated hydrocarbons. Some thermochemical properties of representative polyacetylenes are listed in Table III. Three saturated compounds tetradecane, eicosane, and cyclotetradecane are included for comparison purposes. Since some of the polyacetylenes are solids at room temperature, density measurements were also made near the melting points and at 105°.

An examination of heat of combustion data (kcal./mole and cal./g.) shows lower values for acetylenes than the corresponding saturated hydrocarbons. This is due to the fewer hydrogen atoms in the acetylene molecules. However, since the densities of the polyacetylenes are greater than those of saturated hydrocarbons, the heats of combustion expressed in cal./ml. are greater for the linear polyacetylenes. An anomalous result was found in the case of 1,8-cyclotetradecadiyne which has a lower experimental heat of combustion value than its saturated analog, cyclotetradecane, giving a greater negative heat of formation than cyclotetradecane. A possible explanation is that a transannular effect of the two triple bonds may give rise to a lower energy content of the molecule.

[Contribution from the Department of Chemistry, University of California, Davis, Calif.]

Acetic Acid as an Inhibitor in Trifluoroacetic Acid-catalyzed Aromatic Halogenations and in Halogen Addition Reactions

By R. M. Keefer and L. J. Andrews

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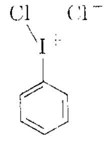
The influence of acetic acid on the trifluoroacetic acid-catalyzed rate of reaction of halogens with alkylbenzenes or substituted alkenes in carbon tetrachloride has been investigated. A wide range of effects, from strong inhibition to mild acceleration, has been observed. The capacity of trifluoroacetic acid to solvate the electronegative portion of the polar activated complexes in the reactions presumably is reduced through interaction with acetic acid to form a mixed dimer. In cases in which only this type of solvation is highly critical to the activation process, acetic acid has the maximum effect. It is assumed that in reactions in which the inhibitory effect of acetic acid is small or non-existent, solvation of the electropositive end of the dipole which develops is also an important feature of the activation process. This interpretation has been satisfactorily applied in explaining the experimental results, which include the observations that in the presence of trifluoroacetic acid the electrophilic reactivity of bromine is less inhibited by acetic acid than is that of chlorine and iodine monochloride and also that the reactions of α, β-unsaturated acids are unusually insensitive to added acetic acid.

Trifluoroacetic acid catalyzes the chlorination of aromatic hydrocarbons in carbon tetrachloride[1] and also promotes the dissociation of iodobenzene dichloride and its substitution products in this solvent.[2] The activated complexes (I and II) for these two types of reaction are presumed to be appreciably polar in character. The activity of the catalyst is attributed to its capacity to function as an electron acceptor in solvating the negatively polarized chlorine atoms of these complexes through hydrogen bond formation. The effectiveness of the catalyst in the aromatic chlorination reaction falls off sharply as acetic acid is added to the medium, probably because of the interaction of the two acids to form a mixed dimer. This substance undoubtedly is less suited for solvation of the negative end of a dipole than is trifluoroacetic acid.



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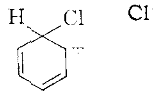

II

It has been found, however, that the rate of trifluoroacetic acid-catalyzed dissociation of the di-

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[1] R. M. Keefer and L. J. Andrews, This Journal, **82**, 4547 (1960).

[2] L. J. Andrews and R. M. Keefer, *ibid.*, **82**, 3057 (1960).

chloride of methyl *p*-iodobenzoate is not much affected by the addition of moderate amounts of acetic acid. Solvation of the positive end of the activated complex dipole, which can better be accomplished by acetic acid than by trifluoroacetic acid, must be more critical to the activation process in this reaction than in aromatic chlorination. That is, the unfavorable effect of added acetic acid on the effective concentration of trifluoroacetic acid is in this case largely offset because of the improved capacity of the medium to stabilize electron-deficient centers.

Obviously there can be wide variations in the effect of acetic acid on the rates of trifluoroacetic acid-catalyzed polar processes in non-polar media. A more extensive investigation of those factors which control the acetic acid sensitivity of the rates of such reactions has now been conducted. In particular a number of reactions in which halogens function as electrophilic reagents in attacking alkylbenzenes and substituted alkenes have been studied to determine how this sensitivity varies with changes in the halogens and the organic reactants. To determine whether or not the insensitivity of the trifluoroacetic acid-catalyzed decomposition of the dichloride of methyl *p*-iodobenzoate to acetic acid is peculiar to this particular dichloride, the kinetics of dissociation of unsubstituted iodobenzene dichloride have been further investigated.

Experimental

Materials.—Acetic and trifluoroacetic acid were purified as in earlier investigations.[1,2] Eastman Organic Chemicals spectro grade carbon tetrachloride was used in most cases without further purification. The sources of the alkylbenzenes, of chlorine and of iodobenzene and its dichloride have been discussed previously.[2,3] Reagent grade bromine and a redistilled commercial sample of iodine monochloride were used. Other materials were Eastman Organic Chemicals. The allyl chloride was fractionated (b.p. 45.0–45.1°) using a 4-foot glass helix packed column. *trans*-Cinnamic and *trans*-crotonic acids were recrystallized from carbon tetrachloride and from ligroin, respectively. Stilbene was recrystallized from ethanol.

The Kinetic Measurements.—The aromatic substitution and halogen addition reactions were studied spectrophotometrically. Known volumes of stock solutions of the organic reactants, of the acids (acetic and trifluoroacetic) and of the halogens in carbon tetrachloride were mixed directly in 1-cm. absorption cells at the temperature of the measurements. The cells were stored in a temperature-controlled housing (±0.1°) of a Beckman spectrophotometer. The halogen concentrations of the reaction mixtures at various times were determined by measuring the optical densities of the solutions at a wave length chosen so as to provide initial readings between 0.3 – 1.0. The reactions of chlorine, bromine and iodine monochloride were usually followed to completion at 380, 520 and 450 mμ, respectively.

In the majority of runs the organic reactant (R) was in large excess of the halogen. In such cases the constants k_0(R) (eq. 1) were calculated using the slopes of plots of the logarithms of the optical densities of the reaction mixtures *versus* time. The measured optical densities were in all

$$-\mathrm{d}(\mathrm{X}_2)/\mathrm{d}t = k_0(\mathrm{R})(\mathrm{X}_2) \qquad (1)$$

cases corrected for small absorption of the reaction mixtures at infinite time.

In runs in which ICl reacted with an alkylbenzene, this final absorption resulted from small amounts of iodine in the reaction products (which had the characteristic color of iodine). It was estimated from the optical density of the reaction products at 520 mμ and the corresponding extinction coefficient for iodine in carbon tetrachloride (934) that approximately 10% of the reacting iodine monochloride was consumed in a process leading to iodine formation. Particularly in reactions with durene, this percentage increased with decreasing trifluoroacetic acid concentration of the medium. As is the case for the uncatalyzed reaction of pentamethylbenzene and iodine monochloride in carbon tetrachloride, the main reaction to form an aryl iodide is accompanied by a side reaction, which is probably[4]

$$\mathrm{ArH} + 2\mathrm{ICl} \longrightarrow \mathrm{ArCl} + \mathrm{I}_2 + \mathrm{HCl} \qquad (2)$$

For a run in which an appreciable fraction of the organic starting material was consumed, the k_0 value (eq. 1) was calculated using the slope of a plot of the logarithms of the concentration ratios of the organic reagent and the halogen *versus* time. The halogen concentrations during the course of a run were calculated from the measured optical densities and the appropriate extinction coefficients.

The runs concerning the rate of dissociation of iodobenzene dichloride in carbon tetrachloride were conducted spectrophotometrically (380 mμ) using the procedures of an earlier investigation.[5] The dissociation rate constants, k_1 (eq. 3), and equilibrium constants, K (eq. 4) were calculated from the experimental data by methods which have also been described

$$-\mathrm{d}(\mathrm{ArICl}_2)/\mathrm{d}t = k_1(\mathrm{ArICl}_2) - k_2(\mathrm{ArI})(\mathrm{Cl}_2) \qquad (3)$$

$$K = (\mathrm{ArI})(\mathrm{Cl}_2)/(\mathrm{ArICl}_2) \qquad (4)$$

The Reaction Products.—The products formed in several of the reactions of the halogens with substituted alkenes and with pentamethylbenzene under conditions approximating those of the rate runs were investigated. Pentamethylbenzene was found to be subject primarily to nuclear rather than side chain attack.

The unsaturates underwent halogen addition rather than allylic substitution or other alternate reactions. The experimental details are given below.

(A) Pentamethylbenzene Bromination.—To 1.00 g. (6.75×10^{-3} mole) of pentamethylbenzene in 40 ml. of carbon tetrachloride were added 4.00 ml. of 4.39 *M* trifluoroacetic acid in carbon tetrachloride and 0.89 g. of bromine (5.55×10^{-3} mole) in 12 ml. of the solvent. The solution was stored in the dark for 12 hours to allow complete consumption of the halogen. It was then washed with water and dilute sodium hydroxide solution and dried over calcium chloride. After the solvent was evaporated, 1.34 g. of a white solid remained. By heating a small sample of this solid with alcoholic silver nitrate and collecting the resultant precipitate of silver bromide, it was estimated that about 0.2% of the reacted bromine had attacked the aromatic side chain rather than the nucleus. A 1.00-g. sample of the white solid was recrystallized from 20 ml. of ethanol. The 6-bromo-1,2,3,4,5-pentamethylbenzene thus obtained (0.70 g.) melted from 160–163° (lit.[6] m.p. 160.5°); yield, based on recrystallized material, 74%.

(B) Pentamethylbenzene Iodination.—The reaction mixture was prepared in exactly the same way as described for the bromination of pentamethylbenzene except that 0.90 g. (5.55×10^{-3} mole) of iodine monochloride was substituted for the bromine. It was allowed to stand in the dark for 12 hours. It was then washed with water and dilute sodium thiosulfate (to remove iodine) and sodium hydroxide solutions. After the solvent was evaporated, 1.44 g. of solid residue remained. A sample of this was analyzed gravimetrically for side chain bound halogen. On the assumption that the silver halide precipitate which was thus collected was pure silver iodide it was estimated that about 1.2% of the iodine monochloride was consumed in iodination of the side chains. By recrystallizing 1.00 g. of the crude reaction product from 15 ml. of ethanol, 0.67 g. of 6-iodo-1,2,3,4,5-pentamethylbenzene (m.p.[7] 134–137°) was obtained; yield, based on recrystallized material, 64%.

(C) Stilbene and Bromine.—To a solution of 0.90 g. (5.0×10^{-3} mole) of stilbene and 1.14 g. (0.01 mole) of trifluoroacetic acid in 24 ml. of carbon tetrachloride was added 6 ml. of 0.029 *M* bromine in carbon tetrachloride.

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[3] R. M. Keefer and L. J. Andrews, THIS JOURNAL, **79**, 4348 (1957).

[4] L. J. Andrews and R. M. Keefer, *ibid.*, **79**, 5169 (1957).

[5] L. J. Andrews and R. M. Keefer, *ibid.*, **82**, 5823 (1960).

[6] E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds, Order I," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 502.

[7] L. J. Andrews and R. M. Keefer, THIS JOURNAL, **79**, 1412 (1957).

The solution was left in the dark for 1 hour to allow complete consumption of the bromine. Some solid precipitated during this time. The mixture was then evaporated to dryness. The 1.06 g. of residual solid was heated with alcoholic silver nitrate. The precipitated silver bromide weighed 0.259 g. (theoretical weight if all of the bromine were converted to stilbene dibromide, 0.272 g.). In other words, little bromine was consumed in attacking the aromatic nuclei of stilbene or in forming a bromotrifluoroacetate, $C_6H_5CHBrCH(OCOCF_3)C_6H_5$.

(D) Allyl Chloride and Bromine.—In a system protected from the atmosphere by a trap containing sodium hydroxide solution were mixed 56 ml. of carbon tetrachloride, 1.00 g. (0.0131 mole) of allyl chloride, 8.00 ml. (0.105 mole) of trifluoroacetic acid and 35 ml. of a 0.0384 *M* solution of bromine in carbon tetrachloride. This mixture was allowed to stand in the dark for several days. The flask contents were then washed with water and dilute sodium hydroxide solution. The aqueous phases were combined with the trap contents, and this mixture was acidified with nitric acid and treated with silver nitrate solution. The silver bromide which precipitated weighed 0.0319 g. (1.70×10^{-4} mole). Thus about 12.7% of the reacted bromine was consumed in other than addition to the carbon-carbon double bond of the allyl chloride (in reactions in which hydrogen bromide was produced).

(E) *trans*-Cinnamic Acid and Chlorine.—To a solution of 0.400 g. (2.70×10^{-3} mole) of cinnamic acid in 27 ml. of carbon tetrachloride were added 9.8 g. (0.086 mole) of trifluoroacetic acid and 16.4 ml. of 0.189 *M* chlorine (2.84×10^{-3} mole) in carbon tetrachloride. The solution was allowed to stand in the dark and was then subjected to evaporation at reduced pressure. The sticky crystalline residue (0.62 g.) was recrystallized from 50 ml. of ligroin. A first crop of white crystals (0.17 g., 29% yield) of m.p. 167–169° and neut. equiv. 223 was obtained (neut. equiv. calcd. for $C_6H_5ClCHClCOOH$, 219). This high melting isomer of cinnamic acid dichloride has recently been found to form when the addition reaction takes place in ethylene chloride in subdued light.[8] This isomer has also been reported to form as the major product when the reaction is carried out with strong illumination.[9]

The mother liquor from the first recrystallization was concentrated to one-half its original volume and then chilled. The resultant crop of sticky crystals was recrystallized from ligroin. The product thus obtained (0.11 g., 18.6% yield) melted over a range of 70–87° and gave a neut. equiv. of 220. This is undoubtedly the low melting cinnamic acid dichloride contaminated with a small amount of its isomer. The low-melting isomer, as formed in the dark in carbon tetrachloride, is reported[10] to melt at 84–86°.

(F) *trans*-Crotonic Acid and Chlorine.—A solution of crotonic acid, chlorine and trifluoroacetic acid in carbon tetrachloride, in which the concentrations of the reactants and catalyst were similar to those described in section E, was allowed to stand in the dark for several days. The solution was then concentrated, first at atmospheric pressure and finally under vacuum. A viscous oil (0.70 g.) which could not be induced to crystallize remained. Attempts to obtain a crystalline product from the reaction of chlorine and crotonic acid in ethylene chloride also have been reported to be unsuccessful.[9]

Results

In Table I a summary of rate constants, k_0, for the trifluoroacetic acid-catalyzed reactions of halogen with various alkylbenzenes and substituted ethylenes in carbon tetrachloride is presented. Rate constants for reactions in which acetic acid was also present in the medium are included. Generally speaking the rates of the catalyzed reaction in carbon tetrachloride which had been dried over freshly ignited calcium sulfate were the same as those for runs with untreated solvent. In most instances the reported constants are based on runs which obeyed the rate law given in eq. 1 throughout the course of the reaction. In some instances, however, the apparent rate constant, k_0, was found to diminish somewhat during the course of the runs. This was noticeable to a small degree in the early phases of reactions of stilbene and bromine at low trifluoroacetic acid concentrations. Under these circumstances there was apparently initially a small rate contribution from a reaction of higher than first order in bromine. Such high order reactions of bromine and substituted olefins in carbon tetrachloride have been observed previously.[11] One run without trifluoroacetic acid was made. From the resultant data it was concluded that a slow uncatalyzed reaction, most probably second order in bromine, does occur.

In the reaction of pentamethylbenzene and bromine at low (< 0.3 *M*) catalyst concentrations a similar downward drift in apparent k_0 values (as evaluated from the slopes of plots of log (Br_2) *vs.* time) during the course of the runs was observed. The drift was generally not large but was most marked in runs at the highest initial bromine concentrations. It was established by comparing k_0 values at various reaction times for runs at different initial bromine concentrations (but at the same pentamethylbenzene concentrations) that the variations in the apparent rate constants resulted from changes in the bromine but not in the hydrogen bromide content of the medium. The reported k_0 values for the runs on this reaction, summarized in Table I, were obtained from the intercepts of plots of k_0 *vs.* bromine concentration.

In the reaction of pentamethylbenzene with iodine monochloride a rather marked change in k_0 values during the course of the runs was observed. Again this drift was most pronounced in runs at the lower catalyst concentration ranges. A comparison of the data for runs at different initial halogen concentrations again led to the conclusion that the drift resulted from some contribution of a reaction of higher order than first with respect to halogen to the over-all rate. It has been demonstrated previously that pentamethylbenzene in the absence of a catalyst reacts with iodine monochloride in carbon tetrachloride by a process which is third order in halogen.[7]

When trifluoroacetic acid is present many of the complexities frequently observed in the kinetics of reaction of halogens and aromatics or unsaturates in carbon tetrachloride are either minimized or completely eliminated. These reactions, without the catalyst, are variously reported to be not only of high order in halogen, but in some cases to be heterogeneous in character or to be sensitive to the water and hydrogen halide content of the reaction mixture.[12,13] Several runs other than those mentioned previously were conducted in connection with the present study to determine the reactivities of the halogens and alkylbenzenes or unsaturates under investigation in the absence of the catalyst or in the presence of acetic rather than trifluoroacetic acid. In the absence of either acid, durene and

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[8] R. E. Buckles and D. F. Knaack, *J. Org. Chem.*, **25**, 20 (1960).

[9] A. Michael and H. D. Smith, *Am. Chem. J.*, **39**, 16 (1908).

[10] C. Liebermann and Finkenbeiner, *Ber.*, **28**, 2235 (1895).

[11] P. B. D. De la Mare, R. A. Scott and P. W. Robertson, *J. Chem. Soc.*, 509 (1945).

[12] P. W. Robertson, N. T. Clare, K. J. McNaught and G. W. Paul, *ibid.*, 335 (1937).

[13] R. M. Keefer, J. H. Blake and L. J. Andrews, THIS JOURNAL, **76**, 3062 (1954).

TABLE I

RATE CONSTANTS (25°) FOR THE HALOGEN ADDITION AND SUBSTITUTION REACTIONS IN CCl_4 IN THE PRESENCE OF CF_3COOH AND CH_3COOH

10^3(R), mole/l.	10^3(X_2), mole/l.	(CF_3-COOH), mole/l.	(CH_3-COOH), mole/l.	10^3k_0, sec.$^{-1}$-mole^{-1} l.
Chlorine and allyl chloride				
132	9.07	0.109	...	54.4
132	10.2, 4.53	.0543	...	26.0^a
132	9.07	.0272	...	9.6
132	10.2	.0543	0.0547	5.5
132	9.07	.109	0.109	13.0
Chlorine and crotonic acid				
465, 233	9.13–4.57	4.31	...	1.13^a
465	7.27	1.73	...	0.028
465	9.13	0.863	...	.0089
465	9.13	1.72	1.72	.048
465	9.13	...	1.72	.0018
Chlorine and cinnamic acid				
58.4, 33.3	9.6–4.4	1.72	...	10.9^a
33.3	9.6	0.867	...	0.39
29.2	3.93	0.433	...	.15
58.4	7.67	1.71	1.73	.99^a
58.4	3.96	...	3.44	.034
Bromine and durene				
423	13.3	2.93	...	14.7
423	13.3	1.95	...	4.2
423–106	13.3–3.32	1.46	...	1.43^a
423	13.3	0.975	...	0.43
423	13.3	.732	...	.17
423	13.0	.366	...	$<$ .034
423	13.0	1.46	0.365	1.03
423	13.0	1.46	0.73	0.60
423	13.0	1.46	1.46	.16
423	13.4	1.46	2.90	.066
Bromine and pentamethylbenzene				
403–108	13.4–3.4	0.293	...	9.2^a
403	13.4–3.3	.146	...	1.27^b
403	13.4–3.3	.073	...	0.25^b
403	12.8	.293	0.073	5.75
403	12.8	.293	.146	3.52
403	13.4	.293	.293	0.97
403	12.8	.732	.733	13.6
Bromine and stilbene				
93.0	12.7	0.437	...	135.7
93.0–23.3	12.7–3.18	.218	...	25.6^a
93.0	12.7–3.18	.109	...	6.6^a
93.0	6.35	.0547	...	1.7
91.3	6.7	.218	0.230	2.19
91.3	6.7	.109	.115	0.76
91.3	6.7	.109	.0575	2.05
91.3	6.7	.0545	.0575	0.28
91.3	6.7	.0545	.0144	0.99
Bromine and allyl chloride				
492–123	13.3–3.16	1.46	...	4.8^a
246	12.7	0.732	...	0.90
246	12.7	.366	...	.20
246	13.4	.728	1.448	.18
246	12.7	.728	0.725	.22
246	12.7	.728	0.362	.47
Iodine monochloride and durene				
423	2.20	2.92	...	13.6
423	7.39–2.22	1.46	...	2.4^a
212	2.20	1.46	...	3.6
106	2.20	1.46	...	5.0
84.7	7.47	1.46	...	4.6
423	2.20	0.732	...	0.58
423	2.20	.366	...	.13
423	2.20	1.46	1.46	.28
423	2.20	1.46	1.10	.44
Iodine monochloride and pentamethylbenzene				
403	4.49–1.12	0.587	...	23.6^c
403	4.49–1.12	.294	...	4.2^c
403	4.49	.147	...	1.09^d
403	4.49	.0734	...	0.27^d
403	4.49	.734	0.734	4.2^d

[a] Average of two or more runs. [b] Values of k_0 increased slightly with increasing concentration of Br_2. The value reported was obtained from the intercept of a plot of k_0 *versus* (Br_2) for three runs at $(Br_2)_i = 13.4, 6.7$ and 3.3×10^{-3} *M*. [c] Values of k_0 increased slightly with increasing concentration of ICl. The value reported was obtained from the intercept of a plot of k_0 *versus* (ICl) for three runs at $(ICl)_i = 4.49, 2.25$ and 1.12×10^{-3} *M*. [d] Extrapolated value for k_0 at $(ICl)_i = 0$ (see note *c*).

iodine monochloride and also allyl chloride and bromine (at concentrations comparable to those in runs reported in Table I) were found to react only very slowly at 25°. Durene and bromine, crotonic acid and chlorine, and cinnamic acid and chlorine reacted only very slowly when an equimolar quantity of acetic acid was substituted for the catalyst acid. The reactions of bromine with pentamethylbenzene and with allyl chloride in the presence of acetic rather than trifluoroacetic acid were subject to initial inhibition and then proceeded autocatalytically; the reaction mixtures, unlike those which contained trifluoroacetic acid, became cloudy when the halogen was partly consumed. Possibly hydrogen bromide is an effective catalyst when acetic acid but not when trifluoroacetic acid is present.

The general order of reactivity of the ethylene derivatives with respect to trifluoroacetic acid-catalyzed reactions with the halogens in the present series of experiments was found to be the same as has been reported for addition reactions in acetic acid[14] (stilbene > allyl chloride > cinnamic acid > crotonic acid). Also, as is normally the case for electrophilic substitution reactions,[3] pentamethylbenzene was found to be more reactive than durene.

Table II presents the results of the study of the influence of acetic acid on the kinetics of the tri-

TABLE II

THE EFFECT OF TRIFLUOROACETIC ACID AND ACETIC ACID ON THE RATE OF DISSOCIATION OF IODOBENZENE DICHLORIDE IN CARBON TETRACHLORIDE AT 25.0°

10^3 ($C_6H_5ICl_2$), mole l.$^{-1}$	(CF_3COOH), mole l.$^{-1}$	(CH_3COOH), mole l.$^{-1}$	10^4k_1, sec.$^{-1}$	10^3K, mole l.$^{-1}$
4.38	2.16	..	4.31^a	12.8^a
4.26	2.15	2.15	2.02	12.5
4.37	2.15	1.08	3.62	13.6
4.37	2.15	0.538	4.61	12.1
4.37	1.08	0.538	0.58	17.8

[a] Illustrative data taken from Table I of ref. 2 which describes in detail the effect of CF_3COOH on the rate of dissociation of $C_6H_5ICl_2$ in the absence of acetic acid.

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(14) P. B. D. De la Mare, *Quart. Revs.*, **3**, 126 (1949).

TABLE III

THE EFFECT OF ACETIC ACID ON THE CATALYTIC ACTION OF TRIFLUOROACETIC ACID (CCl_4, 25.0°)

Organic reactant	Halogen	(CF_3COOH),[a] mole l.$^{-1}$	n[b]	$\frac{(CF_3COOH)_E}{(CF_3COOH)_T}$	$(CF_3COOH)_T$[c] = $(CH_3COOH)_T$, mole l.$^{-1}$
Toluene[d]	Cl_2	0.085–1.5	1.5	0.35	1.36
Durene[d]	Cl_2	.002–0.034	1.5	.30	0.0085
Allyl chloride	Cl_2	.027–0.11	1.26	.31	0.109
Cinnamic acid	Cl_2	.43–1.7	1.45	.95	1.72
Crotonic acid	Cl_2	.86–4.3	1.58	1.4	1.72
Durene	Br_2	.37–2.9	3.0	0.49	1.46
Pentamethylbenzene	Br_2	.037–0.29	*ca.* 2	.45[e]	..
Stilbene	Br_2	.055–0.44	2.0	.32[f]	..
Allyl chloride	Br_2	.37–1.5	2.06	.52	0.73
Durene	ICl	.37–2.9	2.1	.36	1.46
Pentamethylbenzene	ICl	.073–0.73	2.0	.29	0.734
Iodobenzene dichloride dissoc.		.54–4.3	2.2	.75	2.15
Methyl *p*-iodobenzoate[g] dichloride dissoc.		.54–4.3	2.3	1.0	1.05

[a] The concentration range of the catalyst at which the reaction was studied. [b] The minimum reaction order with respect to the catalyst when acetic acid is absent from the reaction mixture. [c] The last column on the right side of the table gives the concentrations of the catalyst and of acetic acid used in runs on which the ratios reported in the preceding column are based. [d] From ref. 1. [e] This same value was obtained from the results of two different runs, in which the values of $(CF_3COOH)_T = (CH_3COOH)_T$ were 0.293 M and 0.723 M. [f] This value is the average of those obtained from two different runs (0.34 and 0.29) in which $(CF_3COOH)_T = (CH_3COOH)_T$ values were 0.109 M and 0.218 M, respectively. [g] From ref. 2.

fluoroacetic acid-catalyzed dissociation of iodobenzene dichloride in carbon tetrachloride. As was the case for the corresponding reaction of the dichloride of methyl *p*-iodobenzoate, the rate effect was very small.

Table III presents a summary of the apparent reaction orders with respect to the catalyst, n (see eq. 5), as well as of the magnitudes of the effects of acetic acid on catalyst activity.

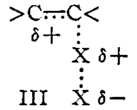
$$k_0 = k_a\,(CF_3COOH)^n \qquad (5)$$

The apparent reaction orders with respect to trifluoroacetic acid which are reported were obtained from the slopes of plots of log k_0 *vs.* log (CF_3COOH). In a few instances the k_0 values increased somewhat with decreases in the concentration of the organic reagent, most noticeably in the reaction of durene and iodine monochloride. This probably occurs because of interaction of the reactants to form molecular complexes.[7] In such cases the evaluation of n was based on the results of runs at a fixed concentration of the organic reactant. In some cases, in particular those of the reaction of bromine with allyl chloride and with pentamethylbenzene, the apparent values of n were found to increase substantially with increasing trifluoroacetic acid content of the medium. In these cases minimum values are reported in Table II. Such increases in the apparent reaction order with respect to this catalyst have been observed previously for the dissociation of iodobenzene dichloride and its *p*-carbomethoxy derivative and for the chlorination of toluene.[1,2,5] The apparent orders, n, which are listed in Table III range from somewhat less than 3/2 to 3. Qualitatively speaking these orders are dependent in magnitude on the catalyst concentration. For example an n value of 3/2 has been found for durene chlorination. That found for toluene chlorination, which has been studied at relatively high trifluoroacetic acid concentrations, is considerably larger.[1] It has been concluded after a detailed analysis of the kinetic data that the latter reaction is actually of mixed order (3/2 and 5/2) with respect to the catalyst. It appears likely that for all of these reactions, the average number of trifluoroacetic acid molecules incorporated in the activated complexes increases with increasing catalyst concentration of the medium. In this regard it should be recalled that the catalyst is very likely largely dimeric in carbon tetrachloride.[1] Thus, in a reaction which is 3/2 order with respect to trifluoroacetic acid, the activated complex must include three acid monomers or one monomer and one dimer.

The rates of most of the trifluoroacetic acid-catalyzed reactions which have been investigated are reduced when acetic acid is added to the reaction mixture. This reduction reaches its maximum in the durene chlorination reaction. With the addition of a large excess of acetic acid, as compared to the catalyst, the rate of this reaction has been lowered to as little as 2% of its value in the absence of the inhibitor.[1] It can be concluded, for practical purposes, that the mixed acetic acid–trifluoroacetic acid dimer is almost completely ineffective as a catalyst for this reaction.

The relative effects of acetic acid on the catalyst activity in the several reactions under investigation are compared in Table III in terms of the ratio $(CF_3COOH)_E/(CF_3COOH)_T$. The term $(CF_3COOH)_E$ represents the effective trifluoroacetic acid concentration in a solution in which its actual concentration is $(CF_3COOH)_T$ and in which acetic acid is present in equimolar amount. The effective trifluoroacetic acid concentration has been determined by referring the observed k_0 value for a reaction in the presence of the equimolar quantities of the two acids to a plot of values of log k_0 *vs.* log (CF_3COOH). In a situation in which both acetic acid and its mixed dimer with trifluoroacetic acid are ineffective as reaction catalysts, as is the case for durene chlorination, the ratio $(CF_3COOH)_E/(CF_3COOH)_T$ should have its minimum value. Actually within the limits of error the figure for this reaction (0.30) is the lowest of any which were determined. In situations in which the experimental ratio is larger than this minimum, it must be concluded that the mixed dimer does have significant catalytic activity.[15] The ratio apparently is not greatly sensitive to changes in medium polarity which must accompany changes in the concentrations of the two acids, as long as $(CF_3COOH)_T = (CH_3COOH)_T$. This fact is illustrated in Table III as it applies to the reactions of bromine with pentamethylbenzene and with stilbene.

The $(CF_3COOH)_E/(CF_3COOH)_T$ values for the reactions of chlorine with durene and allyl chloride and of iodine monochloride with durene and pentamethylbenzene are all close to the minimum value found for toluene chlorination. In these reactions acetic acid or its mixed dimer apparently can make little contribution to stabilization of the polar activated complexes. In these complexes the negative end of the dipole is centered on the departing halide ion, while the positive charge is distributed over several atoms (see structure III).



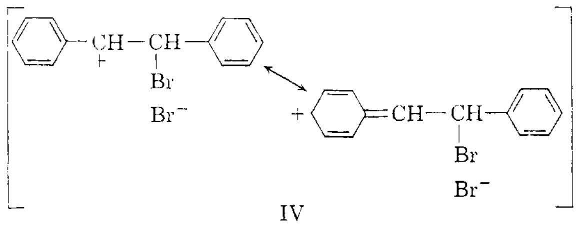
$$\begin{array}{c} >C\overset{\cdots}{-}C< \\ \delta+\ \vdots\quad \\ X\ \delta+ \\ \vdots \\ X\ \delta- \end{array}$$

III

Where the organic reactant is a benzene derivative, the charge can be even further distributed about the aromatic ring. In normal situations, it should be more important for activation in a non-polar medium that a solvating agent for anions (trifluoroacetic acid) rather than one for cations (acetic acid) be available.

The rate of the trifluoroacetic acid-catalyzed dissociation of iodobenzene dichloride is somewhat depressed when acetic acid is added to the medium, but the effect is rather small. Like its *p*-carbomethoxy derivative, this dichloride is probably sufficiently polarized and the center of positive (as well as negative) charge is sufficiently localized in the activation process (see structure II) so that the addition of acetic acid has only a mildly unfavorable effect on the rate of dissociation.

With the exception of the addition of bromine to stilbene, the catalyzed reactions of this halogen are significantly less subject to inhibition by acetic acid than is the chlorination of durene. The values of $(CF_3COOH)_E/(CF_3COOH)_T$ for reactions of bromine with durene, pentamethylbenzene and allyl chloride are of the order of 0.5. Again the need for solvation of the electropositive center of the activated complexes for these reactions must be greater than in toluene chlorination. It seems likely that a generally greater separation of charge must result in the activation process for the attack of bromine than for that of chlorine on a π-electron system. In the reaction of stilbene the positive charge which develops in the activation process is probably dispersed into a phenyl group as shown in formula IV.



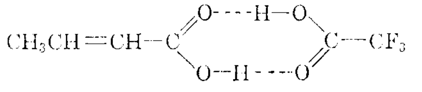
IV

The role of acetic acid in promoting development of the positive charge should in this case be less important than in situations in which resonance stabilization of this kind does not occur.

The $(CF_3COOH)_E/(CF_3COOH)_T$ ratios for the reaction of chlorine with cinnamic and crotonic acids are much larger than those for other halogen addition or substitution reactions which have been investigated. In the case of the crotonic acid reaction the rate is actually enhanced by acetic acid. Either of two explanations may account for the lack of acetic acid inhibition in these two instances.

The first of these is based on the fact that a carbon–carbon double bond which bears a strongly electron-withdrawing (carboxyl) group has an unusually low susceptibility to attack by an electrophilic reagent. Unquestionably more environmental support is required for the release of electrons by an α,β-unsaturated acid to a halogen than for the corresponding reaction of an alkene. That is, stabilization of the electropositively polarized center of the activated complex, as well as of the electronegative center, must be a highly critical feature of the reactions of the unsaturated acids (less so for the reaction of cinnamic acid, in which the phenyl group may contribute to resonance stabilization of the activated complex, than for that of crotonic acid).

The alternate explanation is based on the likely assumption that crotonic and cinnamic acids form mixed dimers (V) with acetic and trifluoroacetic acids.



V

Because of the strongly electron-withdrawing nature of the trifluoromethyl group, interaction of the unsaturated acids with trifluoroacetic acid may be expected to have some unfavorable influence on the availability of the electrons of the double bond. In such a situation the reduction in the effective concentration of trifluoroacetic acid which results when acetic acid is added may have a net effect which is even favorable to the reaction rate.

In the preceding discussion the effect of acetic acid on reaction rates has been interpreted in terms of the degree to which this acid can contribute to solvation of the positive end of the polar activated complexes. An alternate explanation which might be applied in accounting for the variations in the ratios which are listed in Table III has been suggested previously.[1] It is assumed that only the

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[15] Presumably the equilibrium

$$(CF_3COOH)_2 + (CH_3COOH)_2 \rightleftarrows 2CF_3COOH\cdot CH_3COOH$$

is established in solutions containing both acids. It can be shown that the fractions of the pure dimers which are converted to mixed dimer are independent of the total concentrations of the two acids as long as they are present in equimolar quantity. It follows that, barring medium effects, the ratio $(CF_3COOH)_E/(CF_3COOH)_T$ should also be independent of the total concentrations of the two acids as long as they remain equal. This can be shown to be true even if the mixed dimer as well as trifluoroacetic acid dimer has catalytic activity provided the reaction orders with respect to the two dimers are the same. The term $(CF_3COOH)_T$ as used in the discussion is actually $2(CF_3COOH)_2 + (CF_3COOH\cdot CH_3COOH)$.

electronegative portion of the activated complex dipole requires solvation, and again that mixed acetic acid–trifluoroacetic acid dimer is less suited for this purpose than trifluoroacetic acid. The magnitude of the effect of acetic acid on reaction rate is then presumed to be related to the degree to which negative charge develops on activation; that is, the more polar is the activated complex, the more acetic acid will depress the rate of reaction. Since, however, acetic acid in some instances produces little or no rate depression in these polar reactions this second explanation can be accepted only with considerable reservation.

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Fluorodienes. I. Synthesis from Cyclobutenes

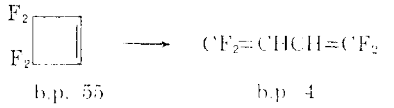
BY J. L. ANDERSON, R. E. PUTNAM AND W. H. SHARKEY[1]

RECEIVED JUNE 8, 1960

A number of fluorodienes have been prepared by pyrolysis of cyclobutenes and cyclobutyl acetates. Reactions of 1,1,4,4-tetrafluorobutadiene with chlorine, bromine, sodium ethoxide, sodium thiophenoxide and peroxytrifluoroacetic acid are described.

Thermal scission of the allylic carbon–carbon bond of cyclobutenes to give 1,3-dienes has been observed in a sufficient number of cases to suggest that it is a general reaction. A number of recently reported examples have been summarized by Vogel.[2] In contrast to the ease of cleavage noted in the hydrocarbon series, hexafluorocyclobutene is resistant to thermal isomerization. Thus, pyrolysis of hexafluorocyclobutene[3] over active carbon at 600–700° has been reported to give a mixture of the cyclobutene and hexafluorobutadiene with a maximum diene concentration of only 12%. We have found that fluorocyclobutenes bearing hydrogens on the ethylenic carbons undergo ring opening upon pyrolysis to give 1,3-dienes in excellent yields.

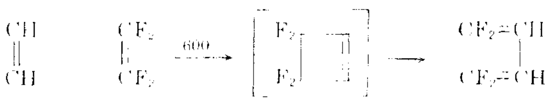
When 3,3,4,4-tetrafluorocyclobutene was heated to 550–750°, it was converted almost quantitatively to 1,1,4,4-tetrafluorobutadiene.[4] The reaction was carried out by addition of the cyclobutene to a hot tube packed with quartz rings as a heat transfer medium and kept at a pressure of 5–25 mm.



The product gases were rapidly quenched in a cold trap.

Identification of the product as 1,1,4,4-tetrafluorobutadiene was accomplished by spectral analysis and by the formation of derivatives. Infrared absorption at 1720 cm.$^{-1}$ confirmed the presence of difluorovinyl groups and absorption at 3120 cm.$^{-1}$ indicated vinyl hydrogens. Nuclear magnetic resonance (n.m.r.) spectra[5] were most unusual in showing a broad, unresolvable band in the range of −575 to −315 c.p.s. for the fluorine resonance. At temperatures of −120 to −80° the spectrum sharpened somewhat but not enough to be interpreted. Reaction of the diene with bromine gave 1,4-dibromo-1,1,4,4-tetrafluorobutene and the n.m.r. proton and fluorine spectra of this derivative were normal. In addition, an infrared spectrum of the dibromide showed the absence of a fluorinated double bond (no absorption at 1720–1750 cm.$^{-1}$). Oxidation of the dibromide produced bromodifluoroacetic acid.[6] In contrast to its reaction with bromine, tetrafluorobutadiene formed a tetrachloride when treated with chlorine under mild conditions.

The cyclobutene used to prepare 1,1,4,4-tetrafluorobutadiene was readily obtained from tetrafluoroethylene and acetylene by reaction of equimolar amounts of these compounds in a shaker tube at 225°. Synthesis[4a] of tetrafluorobutadiene directly from tetrafluoroethylene and acetylene has also been accomplished by passing a mixture of these compounds through a pyrolysis tube maintained at 600° and 1 atm. Undoubtedly the first product is the cyclobutene, which is cleaved to tetrafluorobutadiene at the high reaction temperature. Tetrafluorobutadiene has also been prepared by pyrolysis of 1-acetoxy-2,2,3,3-tetrafluorocyclobutane, which is accessible from tetrafluoroethylene and vinyl acetate.[7] Presumably, loss of acetic acid from the cyclobutane leads to



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(1) To whom inquiries regarding this paper should be addressed.

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(5) Spectra were obtained by means of a high-resolution nuclear magnetic resonance spectrometer and associated electromagnet, both manufactured by Varian Associates, Palo Alto, Calif., operating at 40 Mc. and approximately 10,000 gauss. Spectra were calibrated in terms of displacements in cycles per second (c.p.s.) from the proton resonance of H_2O and the F resonance of CF_3CO_2H. Negative frequency displacements indicate resonances occurring at higher field relative to the reference.

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