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The Trifluoroacetic Acid Catalyzed Chlorination of Aromatic Hydrocarbons in Carbon Tetrachloride. Inhibition by Acetic Acid

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

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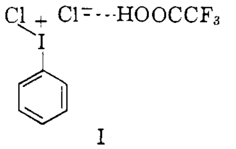
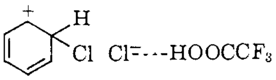
Trifluoroacetic acid, which has previously been shown to be a very effective catalyst for the dissociation of iodobenzene dichlorides in carbon tetrachloride, also promotes the chlorination of aromatic hydrocarbons in this solvent. At relatively low catalyst concentrations durene chlorination occurs by a process which is 3/2 order in trifluoroacetic acid. Toluene chlorination, which requires a higher catalyst concentration, is mixed order (3/2 and 5/2) with respect to trifluoroacetic acid. Apparently a minimum of three catalyst monomers (or one monomer and one dimer) are incorporated in the activated complexes for the aromatic chlorinations. The catalyst activity of trifluoroacetic acid in durene and toluene chlorination is grossly diminished when acetic acid is also in the reaction mixtures. However acetic acid does not markedly inhibit the action of the catalyst in inducing the dissociation of iodobenzene dichlorides or their formation from the components. Presumably in carbon tetrachloride the two acids interact to form a mixed dimer which is ineffective as a chlorination catalyst but which compares favorably in catalyst strength with trifluoroacetic acid in the iodobenzene dichloride reaction. Explanations for the differences in the effect of acetic acid on the rates of the two reactions have been suggested. The equilibrium constant for formation of the mixed dimer has been estimated using the rate constants for trifluoroacetic acid catalyzed chlorination of toluene both in the presence and absence of acetic acid.

In solution the dissociation of an iodobenzene dichloride (to the component iodobenzene and chlorine) and the non-radical chlorination of an aromatic hydrocarbon both occur readily in polar media but take place in non-polar media only in the presence of an extraneous polar catalyst. The two reactions are sufficiently similar, as regards the effects of solvents on rates, so that it has been concluded that parallel electronic polarizations occur in their activation processes.[1] Both reactions proceed with exceptional speed in trifluoroacetic acid,[1,2] and it is presumed that the unusual effectiveness of this solvent lies in its capacity to solvate the negatively polarized atoms of the activated complexes through hydrogen bonding, as shown crudely in formulas I and II.

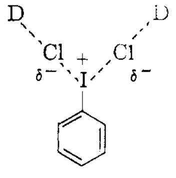


I



II

In a recent study of the kinetics of the trifluoroacetic acid catalyzed dissociation of methyl *p*-iodobenzoate dichloride in carbon tetrachloride it was shown that at 25° in the presence of about 1 *M* trifluoroacetic acid the order with respect to the catalyst is slightly greater than two.[3] At this same concentration acetic acid had no catalytic activity for the reaction in carbon tetrachloride. Also in a solution which was 1 *M* with respect to both acids the dichloride dissociated at about the same rate as when only trifluoroacetic acid was present. Since acetic acid is more basic than trifluoroacetic acid, it was concluded that solvation of the cationic center of the activated complex (the iodine atom—see formula I) is not critical insofar as the energetics of the activation process are concerned. Otherwise the mixture of acids, one to solvate chlorine and the other to solvate iodine, should be a far more effective catalyst for dichloride dissociation than the individual acids. It was also argued that since acetic acid does not alter the catalytic activity of trifluoroacetic acid appreciably the two substances probably do not cross dimerize extensively in dilute solution in a non-polar medium. On the basis of these observations and the fact that carboxylic acids are largely dimeric in carbon tetrachloride[4] it has been concluded that in the trifluoroacetic acid catalyzed reaction of the dichloride two acid dimers, D, must be included in the solvation sphere of the activated complex in association with the two chlorine atoms (formula III). It is implied in this argument that the two chlorine atoms remain electronically equivalent in the activation process.



III

The kinetics of the trifluoroacetic acid catalyzed chlorination of toluene and of durene in carbon tetrachloride have now been investigated, and particular attention has been given to the rate effect of adding acetic acid to the reaction mixtures. In sharp contrast to its behavior in the trifluoroacetic acid catalyzed dissociation of an iodobenzene dichloride, acetic acid markedly inhibits these chlorination rates. The unexpected differences in the rate response of the two types of reaction to added acetic acid can best be explained on the assumption that acetic and trifluoroacetic acids actually do form a mixed dimer in carbon tetrachloride.

Experimental

Materials.—Acetic, trichloroacetic and trifluoroacetic acids and toluene were purified as described previously.[1-3] A commercial sample of durene was recrystallized from

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(1) L. J. Andrews and R. M. Keefer, THIS JOURNAL, **81**, 1063 (1959).

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

(3) L. J. Andrews and R. M. Keefer, *ibid.*, **82**, 3059 (1960).

(4) (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).

ethanol, m.p. 80.5–82°. Eastman Organic Chemicals spectro grade carbon tetrachloride was used without further purification; some samples were exposed to ignited (300°) Drierite for a week before use to reduce the trace water content. Methyl *p*-iodobenzoate dichloride was prepared for rate work as described earlier.[5]

The Chlorination Rate Studies.—The rates of chlorination of toluene and durene in carbon tetrachloride in the presence of various organic acids were followed spectrophotometrically. Rate samples were prepared by mixing known volumes of stock solutions of the reactants and catalysts in 1-cm. absorption cells. The cells were stored in a temperature controlled (±0.1°) housing of a Beckman spectrophotometer, and the consumption of chlorine in the reaction mixtures was followed by measuring the changes in their optical densities at 350 mμ with time against a carbon tetrachloride blank. Most runs were followed to completion. The recorded optical densities were corrected for the small absorption of the product mixtures at infinite time. In all cases the aromatic hydrocarbon concentration was in substantial excess of the chlorine concentration of the mixture. Rate constants, k (eq. 1), for individual runs were evaluated from the lines obtained by plotting the logarithms of the corrected optical densities *versus* time.

$$-\mathrm{d}(\mathrm{Cl_2})/\mathrm{d}t = k(\mathrm{Cl_2}) \qquad (1)$$

For those runs with durene at very low trifluoroacetic acid concentrations (8×10^{-3} M or less) the slopes of the lines diminished toward the end of the run. In such cases the reported rate constants are based on the initial slopes of the lines. Possibly the hydrogen chloride produced inhibited the reaction by interacting with the catalyst. In runs with toluene the catalyst concentration was so much larger than that of chlorine that a hydrogen chloride effect of this kind is not to be expected and was not observed. Other details of the method are given in an earlier publication.[1]

The Rate of Equilibration of Methyl *p*-Iodobenzoate Dichloride with its Components.—A few rate runs were made, in addition to those reported previously,[3] to determine the effects of added acetic acid and trichloroacetic acid on the rate of dissociation of this dichloride and of its formation (from methyl *p*-iodobenzoate and chlorine) in carbon tetrachloride in the presence of trifluoroacetic acid. Experimental details are given elsewhere.[3]

The Products of the Trifluoroacetic Acid Catalyzed Chlorination of Toluene and Durene.—The products of chlorination of toluene and durene, as formed at reactant and catalyst concentrations approximating those used in rate runs, were examined to determine the extent to which side chain as opposed to nuclear halogenation occurred.

A carbon tetrachloride solution (50 ml.) which was initially 0.60 M in toluene, 0.34 M in trifluoroacetic acid and 0.010 M in chlorine was stored in the dark overnight in a glass stoppered erlenmeyer flask. The solution was then washed with dilute alkali and water and dried over calcium chloride. Solvent was removed by slow distillation (distillate boiling range, 76–82°) until the volume was reduced to 10 ml. Through the courtesy of Mr. J. D. Davis an analysis of the concentrate was made by G.L.C. using a Loe Engineering Co. fractometer equipped with an 18-ft. column of diethylene glycol succinate impregnated on firebrick (column temperature, 142°). Under these conditions the retention times, referred to the air peak, of known materials were: carbon tetrachloride, 3 min.; toluene, 8 min.; *o*-chlorotoluene, 25 min.; *m*- and *p*-chlorotoluenes, 27 min.; benzyl chloride, *ca.* 80 min. A 10-μl. sample of the concentrate produced peaks at all of these times except 80 min., and the *o*- and *m,p*-chlorotoluene peaks overlapped to some extent. From the area ratios of the toluene and combined chlorotoluene peaks, it was estimated that the ratio of chlorotoluene to toluene in the product was 1/63.5 (theoretical, 1/59).

To 1.34 g. (0.0100 mole) of durene in 75 ml. of carbon tetrachloride was added 0.14 ml. (0.0018 mole) of trifluoroacetic acid and 25 ml. of a solution of 0.0403 M chlorine in carbon tetrachloride. The solution was stored overnight in the dark in a glass stoppered erlenmeyer flask. It was then washed with dilute alkali and water and dried over calcium chloride. The solvent was evaporated, and the 1.03 g. of solid residue was dissolved in warm ethanol. Excess alcoholic silver nitrate was added to the solution, and the mixture was heated to precipitate silver chloride. From the weight of precipitated silver halide (21.5 mg.) it was estimated that 14.9% of the reacting chlorine had attacked the durene side chain.

The Infrared Spectra of Carbon Tetrachloride Solutions of Acetic and Trifluoroacetic Acids.—The infrared spectra of equimolar mixtures of acetic and trifluoroacetic acid in carbon tetrachloride solutions were compared with those of solutions of the individual acids (at the same concentrations as in the mixtures) in carbon tetrachloride. Two sets of solutions of different acid concentrations (0.0085 and 0.051 M) were used. The spectra were measured on a Beckman IR4 spectrophotometer using a 1-mm. rock-salt prism and a 1-mm. reference cell containing the solvent. The spectra of the acid mixtures did not in all respects appear to be the summation of the spectra of the individual acids. Perhaps the most striking deviation was observed in the region of the O–H out-of-plane bending vibration of a carboxylic acid dimer.[6] In the 0.051 M acetic acid solution the characteristic absorption peak appeared at about 940 cm.$^{-1}$. For the corresponding trifluoroacetic acid solution this peak was found at about 900 cm.$^{-1}$. In the mixture (0.051 M with respect to each acid) the peak was very broad, ranging from about 940–990 cm.$^{-1}$. Apparently some interaction between the two acids occurs in carbon tetrachloride solution.

Results

The Reaction Order with Respect to Trifluoroacetic Acid.

—The apparent reaction order, with respect to the acid, of the trifluoroacetic acid catalyzed dissociation of iodobenzene dichloride in carbon tetrachloride was observed to increase somewhat with increasing catalyst concentration.[3] It has therefore seemed of interest to vary the acid concentration widely in studying the influence of this catalyst on the rate of aromatic chlorination. By investigating the kinetics of chlorination both of durene and of substantially less reactive toluene a catalyst concentration range of 2×10^{-3} to 1.5 M has been spanned.

As described in the Experimental section these hydrocarbons undergo substitution primarily in the aromatic nucleus rather than at the side chain under the conditions of the rate experiments. At fixed catalyst concentrations the experimental values of $k/(\mathrm{ArH})_i$ are essentially independent of $(\mathrm{ArH})_i$. Actually $k/(\mathrm{ArH})_i$ values for the runs with durene show a slight downward drift with increasing hydrocarbon concentration, while the reverse behavior is noted in the case of the toluene rate constants.

To determine the order of the durene reaction with respect to the catalyst a plot of values of log $[k/(\mathrm{ArH})_i]$ *vs.* the logarithms of the corresponding trifluoroacetic acid concentrations has been made. The slope of the straight line which best accommodates the points is 1.5. The rate law (2) for durene chlorination holds over a trifluoroacetic acid concentration range of 2×10^{-3}–34×10^{-3} M, as is indicated by the approximate constancy of values of $k/(\mathrm{ArH})(\mathrm{TFA})^{3/2}$ with changes in the catalyst strength (see Table I). The term (TFA) represents the total catalyst concentration calculated as if the acid were entirely monomeric.

$$-\mathrm{d}(\mathrm{Cl_2})/\mathrm{d}t = k'(\mathrm{ArH})(\mathrm{Cl_2})(\mathrm{TFA})^{3/2} \qquad (2)$$

In most of the runs summarized in Table I the carbon tetrachloride which was used had been dried by prolonged exposure to Drierite, a procedure which is known to be effective for reducing

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[5] R. M. Keefer and L. J. Andrews, THIS JOURNAL, **81**, 5329 (1959).

[6] D. Hadži and N. Sheppard, *Proc. Roy. Soc.* (*London*), **A216**, 247 (1953).

trace water content of this solvent.[7] In a few cases duplicate runs were made in which water-saturated carbon tetrachloride was substituted for the dried solvent. With one exception no marked effect of water on reaction rate was observed. The rate constant for a run with low catalyst concentration (4.3×10^{-3} M) is significantly less with wet than with the dry solvent. Possibly there is some interaction between water and trifluoroacetic acid which reduces catalyst effectiveness and which is reflected in these reaction rates only when the catalyst concentration is dropped to a level approximating the solubility of water in carbon tetrachloride.

TABLE I

RATE CONSTANTS FOR DURENE CHLORINATION (CCl_4, 25.0°)

$10^3(\mathrm{ArH})_i$, moles/l.	$10^3(\mathrm{Cl_2})_i$, moles/l.	$10^3(\mathrm{TFA})$,[a] moles/l.	$\frac{k}{(\mathrm{ArH})(\mathrm{TFA})^{3/2}}$ sec.$^{-1}$ l.$^{5/2}$ mole$^{-5/2}$
340	4.40	8.53	14.4
340	4.43	4.27	12.5
169	8.3	8.47	16.3
169	6.3	8.47	17.6
169	4.15	8.47	16.7
169	2.07	8.47	16.3
169	6.3	4.23	16.1
170	4.43	2.13	14.4
84.7	4.23	34.2	19.6[b]
85.0	4.43	34.1	17.8
84.7	3.96	16.9	18.2
84.7	4.23	17.1	19.3[b]
84.7	8.3	8.47	17.3
84.7	4.23	8.55	18.7[b]
85.0	4.43	8.53	19.2
84.7	4.23	4.28	9.8[b]
84.7	3.97	4.21	16.6
42.3	4.57	8.53	19.9
21.2	2.28	17.1	16.1

[a] The trifluoroacetic acid concentrations were calculated on the assumption that the acid is monomeric. [b] The solvent was water saturated before use.

The order of the toluene reaction with respect to trifluoroacetic acid has been estimated graphically by the procedure used in analyzing the durene chlorination data. The apparent reaction order of the catalyst increases from about 1.7 to 2.2 as the acid concentration varies from 0.085–1.46 M. Since the durene chlorination, which was investigated at much lower catalyst concentrations, is unequivocally 3/2 order in trifluoroacetic acid, the possibility has been considered that a two-term rate law of the form of eq. 3 (in which $x > 3/2$)

$$-\mathrm{d}(\mathrm{Cl_2})/\mathrm{d}t = k'(\mathrm{ArH})(\mathrm{Cl_2})(\mathrm{TFA})^{3/2} + k''(\mathrm{ArH})(\mathrm{Cl_2})(\mathrm{TFA})^{x} \quad (3)$$

may satisfactorily account for the variation in $k/(\mathrm{ArH})_i$ values for toluene[8] with (TFA). To test this point values of $k/(\mathrm{ArH})(\mathrm{TFA})^{3/2}$ have been plotted against the corresponding values both of $(\mathrm{TFA})^{1/2}$ and of (TFA). As is required by eq. 4 (see eq. 1 and 3)

$$k/(\mathrm{ArH})_i(\mathrm{TFA})^{3/2} = k' + k''(\mathrm{TFA}) \quad (4)$$

a linear plot is obtained when (TFA), but not when $(\mathrm{TFA})^{1/2}$, values are used; that is, $x = 5/2$. The various rate runs on toluene are summarized in Table II, and the plot of the results according to eq. 4 is given in Fig. 1. Two lines are shown in this plot. These correspond to two sets of runs which were carried out at two different toluene concentrations. As was noted earlier the experimental values of $k/(\mathrm{ArH})_i$ at fixed catalyst concentration increase somewhat with increasing toluene concentration. It now appears that these increases result entirely from the influence of toluene concentration changes on k'' (see eq. 4). If anything the k'-values, which are measured by the intercepts of the lines in Fig. 1, diminish slightly with increasing aromatic hydrocarbon concentration, as is also the case for k'-values of durene. From the line corresponding to a toluene concentration of 0.693 M, values of k' and k'' of 0.00090 sec.$^{-1}$ l.$^{5/2}$ mole$^{-5/2}$ and 0.00203 sec.$^{-1}$ l.$^{7/2}$ mole$^{-7/2}$, respectively, have been estimated. The k'-value for durene is therefore of the order of 20,000 times as large as that for toluene.

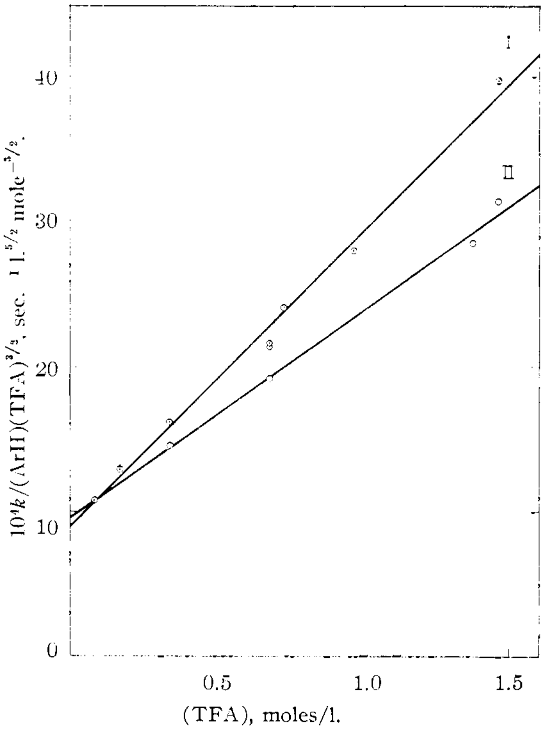

Fig. 1.—The change in $k/(\mathrm{ArH})_i$ values for toluene chlorination with changes in trifluoroacetic acid concentration. The runs on which lines I and II are based were conducted at toluene concentrations of 0.693–0.695 and 0.347 M, respectively.

Since, as observed earlier, trifluoroacetic acid is very likely largely dimeric[4] in carbon tetrachloride solution, it follows that the concentration of trifluoroacetic acid monomer in the solution is essentially proportional to the square root of the total acid concentration. Because of the applicability of rate law 2 to durene chlorination it must be concluded either that three molecules of tri-

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

[8] Acid-catalyzed reactions in non-polar media are frequently observed to show mixed order dependence on the catalyst concentration; see for example (a) R. P. Bell, O. M. Lidwell and J. Wright, *J. Chem. Soc.*, 186 (1938); (b) R. P. Bell and J. A. Sherred, *ibid.*, 1202 (1940).

fluoroacetic acid monomer or one molecule each of catalyst monomer and dimer are included in the activated complex for the reaction as conducted in this investigation.[9] It appears that at the relatively high trifluoroacetic acid concentrations of the toluene runs activation may also occur by a process in which two additional catalyst monomers or a catalyst dimer may participate.

TABLE II

RATE CONSTANTS FOR TOLUENE CHLORINATION (CCl_4, 25.0°)[a]

$(ArH)_i$, mole/l.	$10^3(Cl_2)_i$, moles/l.	(TFA),[b] moles/l.	$\frac{10^4 k}{(ArH)(TFA)^{3/2}}$, sec.$^{-1}$ l.$^{5/2}$ mole$^{-5/2}$
0.695	5.30	1.457	39.7
.695	5.30	0.970	28.0
.695	5.30	.728	24.1
.693	4.70	.682	21.6
.693	5.03	.680	21.4
.693	5.03	.340	16.2
.693	5.03	.170	12.9
.693	5.03	.085	10.8
.439	5.97	1.22	30.3
.347	4.97	1.46	31.2
.347	10.5	1.46	31.4
.347	4.70	1.36	28.3
.347	4.70	0.682	19.2
.347	4.70	.341	14.6
.173	4.70	.682	17.2

[a] The rate constants were essentially the same when water-saturated and Drierite dried carbon tetrachloride were used as the solvent. [b] The trifluoroacetic acid concentrations were calculated on the assumption that the acid is monomeric.

The inadequacy of eq. 2 for the interpretation of rate runs at high catalyst concentrations also may less formally be ascribed to a medium effect. That is, the rate constant k' may be subject to enhancement as the trifluoroacetic acid concentration becomes appreciable simply because the polar process is favored environmentally by the increase in the dielectric constant of the medium which accompanies the addition of the catalyst.

The apparent order of the trifluoroacetic acid catalyzed dissociation of methyl *p*-iodobenzoate dichloride in carbon tetrachloride with respect to catalyst also increases (from 2.27 at 0.53 M acid to over 3 at 4.3 M acid[3]). Presumably this value should reach its maximum only when no carbon tetrachloride remains in the medium; that is, when the solvent is pure trifluoroacetic acid. It is interesting in this regard that the reaction of *t*-butyl chloride with phenol (which is both a reactant and a catalyst), at high concentrations of the latter is sixth order with respect to phenol.[10] Unfortunately the dichloride is sufficiently unreactive so that the minimum number of catalyst molecules in the activated complex cannot be ascertained by making kinetic studies at low catalyst concentrations. On the basis of what has been found for aromatic chlorination, it seems possible that this minimum figure may be less than that (two dimers) assigned previously.[3]

The Effect of Acetic Acid on the Catalytic Properties of Trifluoroacetic Acid.—The inhibiting effect of acetic acid on the trifluoroacetic acid catalyzed chlorination of durene and of toluene in carbon tetrachloride is clearly apparent in the summary of rate runs presented in Tables III and IV. In the several runs on durene the concentrations of hydrocarbon and catalyst were held essentially constant, while that of acetic acid was progres-

TABLE III

THE EFFECT OF ACETIC ACID ON THE TRIFLUOROACETIC ACID CATALYZED REACTION OF CHLORINE WITH DURENE (CCl_4, 25.0°)

10^3(TFA),[a] moles/l.	$10^3(Cl_2)$, moles/l.	10^3(HOAc),[a] moles/l.	$10^4 k$, sec.$^{-1}$
Durene = 0.0847 M			
8.47	8.3	....	11.4
8.53	4.13	1.07	9.4
8.53	4.13	2.13	7.6
8.53	4.13	4.26	4.6
8.53	4.13	8.51	2.0
8.77	4.73	9.27	2.3
8.77	4.73	23.2	0.76
8.77	4.73	46.3	.41
8.77	4.73	92.7	.26
8.77	4.73	185	.22
..	4.43	120	Very slow

[a] The acid concentrations were calculated on the assumption that each acid is monomeric.

TABLE IV

THE EFFECT OF ADDED SUBSTANCES ON THE TRIFLUOROACETIC ACID CATALYZED REACTION OF CHLORINE WITH TOLUENE (CCl_4, 25.0°)

		—Added substance—		$10^4 k$/(toluene), —sec.$^{-1}$ mole^{-1} l.—	
(TFA),[a] moles/l.	$10^3(Cl_2)$, moles/l.	Formula[a]	Concn., moles/l.	Added substance	No added substance
Toluene = 0.690 M					
1.36	5.30	HOAc	1.71	5.1	58.1[b]
0.680	5.30	HOAc	0.855	1.14	12.0
.340	5.30	HOAc	0.428	0.29	3.2
.680	5.30	HOAc	1.71	0.48	12.0
Toluene = 0.41 to 0.44 M					
1.36	13.2	HOAc	1.37	6.1	50[b]
1.36	4.66	HOAc	1.37	5.7	50[b]
..	5.11	HOAc	1.24	<0.05	
1.22	5.97	TClA[c]	1.22	55.1	40.5
..	5.97	TClA[c]	1.22	3.1	
1.22	4.30	BuEt[c]	1.00	2.9	40.5
..	4.30	BuEt[c]	1.00	0.22	
(TClA)[c] 1.22	5.11	HOAc	1.24	2.3	3.1

[a] The concentrations of catalysts and added substance were calculated on the assumption that the substances are monomeric. [b] These values were estimated from Fig. 1, since actual runs at these particular reactant and catalyst concentrations were not made. [c] The terms TClA and BuEt represent trichloroacetic acid and *n*-butyl ether, respectively.

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[9] It is reported, on the basis of cryoscopic studies, that in nonpolar media trichloroacetic acid exists mainly as the dimer even at concentrations as low as 0.01 M; (a) R. P. Bell, E. C. Baughan and M. W. Vaughan-Jackson, *J. Chem. Soc.*, 1969 (1934); ref. 4b. It is presumed that the properties of trifluoro- and trichloroacetic acids are similar. More recently a value of 19 × 10^{-4} has been reported [4a] for the dissociation constant of trichloroacetic acid dimer in carbon tetrachloride at 25°. If trifluoroacetic acid dimer were equally unstable, it seems unlikely that, as is the case, the durene chlorination rate should still be 3/2 order dependent on the total catalyst concentration as it drops below 0.01 M (see Table I).

[10] H. Hart, F. A. Cassis and J. J. Bordeaux, THIS JOURNAL, **76**, 1639 (1954).

sively increased until it was in over twenty-fold excess of trifluoroacetic acid. As shown in Table III the rate constants k for the various runs continue to drop as the acetic acid concentration exceeds that of trifluoroacetic acid and do not become insensitive to further increases in inhibitor concentration until the acetic acid is in large excess of the catalyst. At this point the rate constant k is of the order of 2% of that when no acetic acid is present. In the absence of trifluoroacetic acid, durene chlorination does not occur even in a solution relatively concentrated with respect to acetic acid.

The rate effect of acetic acid can be ascribed to the reduction in concentration of trifluoroacetic acid monomer and dimer through formation of a mixed dimer (eq. 5), which presumably has very low catalytic activity. Apparently the equilibrium constant K_d is of such magnitude that a significant fraction of trifluoroacetic acid must remain in the free form, as contrasted to the mixed dimer, when the concentrations of the catalyst and the inhibitor are equal.

$$(CF_3COOH)_2 + (CH_3COOH)_2 \overset{K_d}{\rightleftarrows} 2CF_3COOH{\cdot}CH_3COOH \quad (5)$$

In studying the effect of acetic acid on the rate of the toluene reaction, a series of runs was made in which the concentrations of the reactants and of the catalyst as well as of the inhibitor were varied. As was the case with durene the rate constants k for runs at fixed toluene and catalyst concentrations were found to drop with increases in the inhibitor content of the medium even after the acetic acid concentration exceeded that of the catalyst (see Table IV). The rate constants [k/(toluene)] for the first six runs in Table IV were used to calculate equilibrium constants (eq. 5) for formation of mixed dimer, $CF_3COOH{\cdot}CH_3COOH$. In making this calculation it was assumed that the mixed dimer was completely inactive as a catalyst. The concentration of trifluoroacetic acid dimer in the medium in a particular run was estimated from the rate of the reaction (actually k/(toluene)) using eq. 4 and the known values of k' and k''. The mixed dimer concentration was then calculated using this value and the concentration of trifluoroacetic acid (as it was originally introduced in the reaction mixture). The equilibrium concentration of free acetic acid dimer was calculated from the concentration of acetic acid, as originally added, and that of the mixed dimer. The equilibrium constants, $K_d = [CF_3COOH{\cdot}CH_3COOH]^2/[(CF_3COOH)_2][(CH_3COOH)_2]$, thus obtained are 10.3, 13.2, 16.1, 9.3, 12.4 and 13.2, respectively, for the first six runs of Table IV. The agreement in the several values is surprisingly good considering that it was assumed in making the calculations that values of k/(toluene) were unaffected by changes in medium polarity which accompany the variation in total acid content of the reaction mixtures. Also these K_d values are further subject to error because in evaluating them it was assumed not only that the mixed dimer was not a chlorination catalyst but also that the degree of dissociation of acid dimers to monomers was negligibly small. The data of Table III may also be used to calculate K_d values for mixed dimer formation; the constants which have been obtained in this way range from 10 to 30 for runs in which the acetic acid concentration exceeds or equals that of the trifluoroacetic acid. In the case of the runs at lower acetic acid concentrations the rate constant is reduced somewhat more than should result if an amount of the catalyst equivalent to the added inhibitor were converted to mixed dimer. Actually the reproducibility in rate constants for the durene reaction was not as good as for toluene chlorination. Rather small errors in experimental k values may be expected to lead to rather large errors in calculated values of K_d.

A few runs with toluene were made in which trichloroacetic acid was substituted for acetic acid as a potential inhibitor. Actually the rate constant, k/(toluene), for a run in which the two trihaloacetic acids were present at approximately equal concentrations (1.2 M) is somewhat larger than the sum of the constants for the two runs in which one or the other, but not both, of the acids is present at 1.2 M concentration (see Table IV). Actually in contrast to acetic acid, trichloroacetic acid has a significant catalytic effect, although it is considerably less powerful than trifluoroacetic acid. Very likely the trichloro-trifluoroacetic acid dimer, which is undoubtedly present in the reaction mixture to some degree compares favorably with trifluoroacetic acid dimer as a catalyst. The effect of adding trichloroacetic acid on the rate of the trifluoroacetic acid catalyzed reaction may result at least in part from the accompanying increase in medium polarity. The difference in the nature of the influence of added acetic and trichloroacetic acids on the halogenation rates certainly must be traced to the difference in acidity of the two compounds.

The rate of the trichloroacetic acid catalyzed reaction of toluene and chlorine is also subject to some inhibition by acetic acid (see the last entry in Table IV), although the effect is much less pronounced than in the case of the trifluoroacetic acid catalyzed reaction. That is, the stronger the acid catalyst the more marked is the change in rate produced by the addition of acetic acid.[11]

One run on the trifluoroacetic acid catalyzed chlorination of toluene was conducted with *n*-butyl ether in the reaction mixture. Again the additive proved to be a strong inhibitor. Like acetic acid the ether must interact with trifluoroacetic acid and lower its catalytic activity by reducing its acid strength. The rate effect of the ether must be very similar in origin to that of dioxane on the reaction of *t*-butyl chloride with phenol.[10]

A few rate runs were made to check the influence of acetic acid on the trifluoroacetic acid catalyzed dissociation of methyl *p*-iodobenzoate dichloride. As was observed earlier,[3] the effect is very small. As shown in Table V, the dissociation rate constant k_1 (see eq. 6) for a run in which the catalyst

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[11] The ionization constants of trifluoroacetic and trichloroacetic acids in water at 25° are reported, respectively, as 0.59 and 0.23; (a) A. L. Henne and C. J. Fox, This Journal, **73**, 2323 (1951); (b) H. v. Halban and J. Brüll, *Helv. Chim. Acta*, **27**, 1719 (1944).

$$\mathrm{ArICl_2} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{ArI} + \mathrm{Cl_2} \quad K = k_1/k_2 \qquad (6)$$

concentration was 1.08 M is only slightly greater than that for a similar run in which acetic acid was also present at a concentration of 2.11 M. The possibility has been considered that the rate inhibition by acetic acid, which is observed in aromatic chlorination but not in the dichloride dissociation reaction, may result because of interaction of the inhibitor with chlorine rather than with trifluoroacetic acid. That this is not the case was proved by showing that acetic acid had essentially no influence on the rate of the trifluoroacetic acid catalyzed formation of the dichloride from chlorine in the presence of a substantial excess of methyl p-iodobenzoate. It should be noted that this particular dichloride undergoes essentially complete dissociation in carbon tetrachloride at the concentration levels of the present experiments unless the free iodo compound is present in relatively large quantity.

TABLE V

THE EFFECT OF CARBOXYLIC ACIDS ON THE TRIFLUOROACETIC ACID CATALYZED DISSOCIATION OF METHYL p-IODOBENZOATE DICHLORIDE (CCl_4, 25.0°)

(TFA),[a] moles/l.	10^3 (Dichloride)$_i$, moles/l.		—Added acid[a]— Acid	Concn., moles/l.	$10^4 k_1$, sec.$^{-1}$
1.22	2.69		....	...	0.23
..	2.69		TClA	1.22	.08
1.22	2.69		TClA	1.22	.76
1.08	2.65		....	...	.17
1.08	2.60		HOAc	2.11	.12
..	2.70		HOAc	2.11	No reacn.
	$10^3(Cl_2)_i$, moles/l.	$10^3(ArI)_i$, moles/l.			$10^4 k_2$, sec.$^{-1}$ mole^{-1} l.
1.08	9.1	64.0	....	...	0.61
1.08	9.1	64.0	HOAc	1.055	0.58

[a] The concentrations of all acids were calculated on the assumption that the acids are monomeric.

It is interesting to observe (refer to the first three runs of Table V) that when trichloroacetic acid is added, the rate of the trifluoroacetic acid catalyzed dichloride dissociation is subject to substantial enhancement. Actually the rate constant for a run in which both acids were present at the same concentration is over twice as large as the sum of the rate constants for runs in which the individual acids were used as catalysts. It appears that the mixed dimer of the two strong acids is a somewhat more effective catalyst than trifluoroacetic acid dimer. However, at least a part of the rate enhancement which occurs when trichloroacetic acid is added to the reaction mixture which contains trifluoroacetic acid may stem from the change in medium polarity.

As noted in the introduction, the results of the kinetic studies on aromatic chlorination do not support the previous conclusion, based on the work on methyl p-iodobenzoate dichloride, that acetic and trifluoroacetic acids do not form a mixed dimer in carbon tetrachloride. It must now be concluded that the mixed dimer does form and that as a catalyst for dissociation of the dichloride in carbon tetrachloride it is, on a mole for mole basis, about one-half as effective as trifluoroacetic acid dimer. In discussing the reasons why this mixed dimer is so ineffective in promoting aromatic chlorination, it should be recalled that in many instances a pair of substances of different acidity (or basicity) may function with great effectiveness as cocatalysts for polar reactions in non-polar media. The combined function of phenol and p-chlorophenol in promoting the isomerization of 5α,6β-dibromochloestone in benzene solution is a case in point.[12] Another is the action of phenol–methanol mixtures in inducing the conversion of triphenylmethyl chloride to an ether in benzene.[13] It is generally conceded that the rate advantage of using a mixture of acids of different strengths results because one, the more acidic, is better constituted to solvate the electronegative region of the activated complex while the other is structurally more appropriate for the solvation of the positive center of the dipole.[14]

Since acetic acid has a grossly unfavorable effect on the catalytic action of trifluoroacetic acid in aromatic chlorination, it seems likely that in this particular reaction solvation of the electronegative end of the activated complex dipole is energetically much more critical, insofar as the reaction rate is concerned, than is solvation of the electropositive region. The positive charge can be considered to be widely distributed about the benzene ring. That is, when trifluoroacetic acid is the only acid in the medium, the catalyst molecules (a minimum of three monomers or of one dimer and one monomer) which are required for activated complex solvation must be clustered about the Cl^- portion of the dipole (see structure II). It is possible that solvation of the positively polarized region of the activated complex may occur more extensively in the iodobenzene dichloride dissociation reaction than in aromatic chlorination since acetic acid has relatively little inhibiting effect on the catalytic activity of trifluoroacetic acid in the former reaction. However, it must be inferred that solvation of the negative, as opposed to the positive, end of the activated complex dipole is also the more critical feature of the activation process in the dichloride reaction. This conclusion seems reasonable since unlike trifluoroacetic acid, acetic acid by itself is ineffective as a catalyst for the reaction in carbon tetrachloride.

Structure III, which has been suggested earlier[3] for the activated complex for the dichloride reaction, is still acceptable. Although the catalyst molecules, two dimers or four monomers (a smaller number may participate at lower catalyst concentrations—see above), are probably most intimately associated with the chlorine atoms through hydrogen bonding, they may also offer some stabilization to the iodine atom by coördinations which involve their oxygen atoms. The mixed acetic acid-trifluoroacetic acid dimer is apparently, because of its effectiveness in contributing to iodine

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[12] H. Kwart and L. B. Weisfeld, THIS JOURNAL, **78**, 635 (1956).

[13] C. G. Swain, *ibid.*, **70**, 1119 (1948).

[14] P. D. Bartlett, "Organic Chemistry," Vol. III, Edited by H. Gilman, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 30.

atom solvation, not much less active as a catalyst than trifluoroacetic acid.

An alternate explanation, which cannot be discounted, can be offered for the difference in rate response of the aromatic chlorination and dichloride dissociation reactions to the replacement of trifluoroacetic acid catalyst by its mixed dimer with acetic acid. Again it is assumed that the primary solvation sites in the activated complexes are the negative ends of the dipoles and that the mixed dimer is less suited for this purpose than is trifluoroacetic acid. The magnitude of the effect of change in the acid may then be related to the degree to which polarization (in one case of an I–Cl bond and in the other of a Cl–Cl bond) occurs in the activation process. That is, the extent to which the changes in solvating power of the catalyst (as it is converted to mixed dimer) is reflected in reaction rate will depend on the extent to which development of negative charge takes place when activation occurs. If this argument is correct, the activated complex for aromatic chlorination in carbon tetrachloride must be substantially more polar than that for dichloride dissociation.

Whether the magnitude of the acetic acid effect is related to the degree to which polarization accompanies activation or to the degree to which solvation of an electropositive center controls the energetics of activation, it seems reasonable that trichloroacetic acid should be less inhibitory than acetic acid (see Table IV and V). The stronger acid, which itself has some catalytic activity, should not reduce the anion solvating power of trifluoroacetic acid through mixed dimer formation as much as should acetic acid. It has been observed previously that combinations of acids may be less effective as catalysts for reactions in non-polar media than one would predict on the basis of their individual activities, in particular when the reactivities of the two compounds are far apart.[15]

Acknowledgment.—The authors are indebted to the National Science Foundation for a grant in support of this research.

(15) J. N. Brönsted and R. P. Bell, THIS JOURNAL, **53**, 2478 (1931).

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF FLORIDA]

Fluorocarbon Nitrogen Compounds. VII.[1] The Indirect Fluorination of Some Fluorocarbon Nitrogen Derivatives[2]

BY JOHN A. YOUNG, WILLIAM S. DURRELL AND RICHARD D. DRESDNER

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The indirect fluorination of some fluorocarbon nitrogen compounds has been investigated and reactions of the following functional groups have been determined under mild conditions: $-N{=}C<$, $N{\equiv}C-$, c—$(-N{=}C<)_3$, $>N-H$, $>NCOF$, $-N{=}C{=}O$, $-NHCOF$, $-CONH_2$ and $-CONHCO-$. Fluorocarbon N-F compounds can be synthesized in certain cases by the action of silver difluoride on carbon–nitrogen unsaturation, by replacement of amine hydrogen or by cleavage of an acyl group from nitrogen. Rearrangement and coupling of the free radical intermediates are competitive with N-F bond formation, coupling becoming more important with progressively milder conditions. Volatile fluorocarbon isocyanates can be conveniently prepared from the corresponding amides by reaction with AgF_2, and fluorocarbon azoalkanes, $R_FCF_2N{=}NCF_2R_F$, from nitriles by use of the same reagent. Similarity of the isocyanate synthesis to the Hofman and Curtius reactions is discussed.

Although the fluorination of many nitrogen compounds by various methods has been rather extensively studied,[3] little has been done with fluorocarbon nitrogen derivatives, which, by virtue of their lack of hydrogen external to the functional group, might be expected to exhibit cleaner, less complex behavior toward fluorinating agents. This paper describes the reaction of three types of functional groups—carbon–nitrogen unsaturation, amine or amide hydrogen and carbonyl—when fluorocarbon compounds containing these groups, alone or in combination, are treated with silver difluoride under mild conditions.

It has previously been shown[4,5] that fluorination of carbon–nitrogen unsaturation in fluorocarbon derivatives proceeds *via* a nitrogen-containing free radical. Extension to functional groups other than unsaturation, as described in the present work, shows that this generalization holds true. In every case the products may be adequately explained by postulating initial formation of an intermediate carrying an unpaired electron on nitrogen, this intermediate then reacting by coupling, rearrangement or saturation with fluorine.

The primary intermediate may be formed in any of several ways, depending on the structure of the reactant. If carbon–nitrogen unsaturation is present, fluorine attacks the carbon atom.

$$CF_3N{=}CF_2 \longrightarrow (CF_3)_2N\cdot \qquad (1)$$

$$R_FC{\equiv}N \longrightarrow R_FCF{=}N\cdot \qquad (2)$$

If an N-acyl bond is present, the acyl group may be eliminated as an acid fluoride.

$$(CF_3)_2NCOF \longrightarrow (CF_3)_2N\cdot + COF_2 \qquad (3)$$

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(1) For the preceding paper in this series, see J. A. Young, S. N. Tsoukalas and R. D. Dresdner, THIS JOURNAL, **82**, 396 (1960).

(2) Presented in part at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959. This work was supported by the Office of Naval Research and by the Office of Ordnance Research; reproduction in whole or in part is permitted for any purposes of the U. S. Government.

(3) (a) O. Ruff and H. Giese, *Ber.*, **69**, 598 (1936); (b) O. Ruff and W. Willenburg, *ibid.*, **73**, 724 (1940); (c) W. Huckel, *C. A.*, **44**, 4359 (1950); (d) G. E. Coates, J. Harris and T. Sutcliffe, *J. Chem. Soc.*, 2762 (1951); (e) F. Nerdel, *Naturwiss.*, **39**, 209 (1952); (f) J. Cuculo and L. A. Bigelow, THIS JOURNAL, **74**, 710 (1952); (g) F. P. Avonda and L. A. Bigelow, *ibid.*, **78**, 2978 (1956).

(4) J. A. Young, W. S. Durrell and R. D. Dresdner, *ibid.*, **81**, 1587 (1959).

(5) J. H. Attaway and L. A. Bigelow, *ibid.*, **81**, 3599 (1959).