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Acetonitrile–Nitromethane Mixtures as Media for Aromatic Chlorination and Chlorine Addition Reactions

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RECEIVED APRIL 24, 1962

The rates of reaction of chlorine with toluene, 2-chloronaphthalene, 2,3-dichloropropene, crotonic acid, acrylonitrile and iodobenzene (to form iodobenzene dichloride) have been determined using various mixtures of acetonitrile and nitromethane as solvent. The two aromatic chlorination reactions increase appreciably in rate with increases in the nitromethane content of the medium. The rates of the other reactions are relatively insensitive to the solvent change. These reactions also have been investigated using carbon tetrachloride as solvent and trifluoroacetic acid as catalyst. The addition of acetic acid slows the catalyzed aromatic chlorinations markedly. The rates of the other catalyzed reactions are less subject to inhibition by acetic acid. The function of the polar solvent or the polar catalyst in solvating the activated complexes in these reactions is discussed in terms of the results of the rate studies.

Trifluoroacetic acid catalyzes a variety of reactions of chlorine and other halogens in carbon tetrachloride, including aromatic substitutions, additions to double bonds and the reaction to form iodobenzene dichloride.[1] These reactions are presumed to proceed *via* polar activated complexes of the type SX^+X^-, where S is the organic reactant and X_2 is the halogen. The catalytic effect of trifluoroacetic acid is modified in different ways, depending on the particular type of organic reactant which is used, when acetic acid is added to the medium.[1-3] It seems likely that the capacity of the catalyst to solvate the negative end of the activated complexes (an electrophilic solvation process) must be reduced by interaction with acetic acid to form the mixed dimer, $CF_3COOH \cdot CH_3COOH$. On the other hand, the medium should be better constituted to provide for solvation of the positive end of a polar particle (nucleophilic solvation) when acetic acid is present.

In the case of a reaction which is subject to marked rate depression by acetic acid, *e.g.*, the chlorination of toluene or durene, the polar additives (the carboxylic acids) are believed to serve primarily to provide for electrophilic solvation in the activation process. Under these circumstances the organic reactant itself must at the same time provide for the development of positive charge, with relatively limited assistance from the medium, by dispersing that charge over several atoms or over the whole aromatic nucleus if the reactant is benzenoid in character. In situations in which the addition of acetic acid causes only mild rate depression (*e.g.*, in the reactions of iodobenzene and chlorine and of allyl chloride and bromine) or in which it produces some rate acceleration (the addition of chlorine to crotonic acid), the need for nucleophilic solvation of the activated complexes is considered to be greater than in the aromatic chlorination reaction.

To assess the plausibility of the interpretation of the different effects of added acetic acid on the rates of the catalyzed reactions, several of the reactions involving chlorine have been subjected to further rate study without a catalyst and with various mixtures of acetonitrile and nitromethane as solvent. Since these two liquids have essentially the same dielectric constant,[4] the free energies of activation and consequently the rates[5] of the various polar reactions of chlorine should not be subject to a dielectric effect as the composition of the mixed solvent is changed. Acetonitrile is a considerably stronger donor in molecular complex formation with iodine monochloride than is nitromethane.[6] It is, therefore, reasoned that acetonitrile will function more effectively than nitromethane as a nucleophilic solvating agent and that, of the two solvents, the latter will be the better electrophilic solvating agent.[7] If the capacity of the medium to solvate the activated complex, rather than the reactants, is the rate-controlling factor, then the reactions of chlorine should fall into like behavior groups (in their responses to a change in solvent from acetonitrile to nitromethane) which are similar to those established on the basis of the influence of acetic acid on the trifluoroacetic acid-catalyzed reactions in carbon tetrachloride.

Experimental

Materials.—The sources and methods of purification of the solvents and most of the reagents have been indicated in earlier publications.[1,8] Samples of acrylonitrile (Eastman Organic Chemicals) and 2,3-dichloropropene (Columbia Organic Chemicals, Co.) were redistilled before use. Eastman Organic Chemicals white label 2-chloronaphthalene was used without further purification.

The Rate Runs.—The rates of the substitution and addition reactions of chlorine in nitromethane, acetonitrile or their mixtures were determined spectrophotometrically using 1-cm. glass stoppered silica absorption cells as reaction vessels. The chlorine concentrations of the reaction mixtures during the course of the runs were calculated from the optical densities of the rate samples, measured at some fixed wave length (375–400 mμ) against the solvent as a blank. The extinction coefficients of the halogen in the various solvent mixtures were established by separate measurement of solutions, the chlorine concentrations of which were determined iodometrically. Further details of the experimental procedures are to be found in the description of the methods used in earlier work on toluene chlorination.[8] The rate studies of the reaction of iodobenzene and chlorine were also conducted spectrophotometrically (390 mμ) in much the same way as was an earlier investigation

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(1) R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **83**, 376 (1961).

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

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(4) A. A. Maryott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids," Natl. Bur. Standards Circ. 514 (1951).

(5) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 137–142.

(6) W. B. Person, R. E. Humphrey, W. A. Deskin and A. I. Popov, *J. Am. Chem. Soc.*, **80**, 2049 (1958).

(7) Nitro compounds in general show a specific capacity for interaction with basic substances. See for example, (a) L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954); (b) N. S. Bayliss and C. J. Brackenridge, *J. Am. Chem. Soc.*, **77**, 3959 (1955).

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

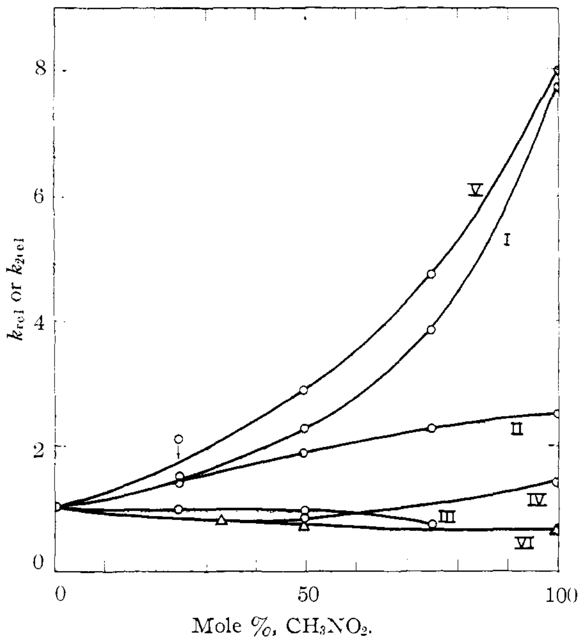

Fig. 1.—Values of k_{rel} or k_{2rel} for reactions of chlorine in acetonitrile–nitromethane mixtures. The several curves apply to the reactions of: I, toluene; II, crotonic acid; III, 2,3-dichloropropene; IV, acrylonitrile; V, 2-chloronaphthalene; VI, iodobenzene.

of the formation of iodobenzene dichloride in nitromethane.[9] In most cases the reactions were followed to completion or, in the runs with iodobenzene, to the establishment of equilibrium. Because they were very slow, the runs on mixtures of chlorine and acrylonitrile were carried no further than to 35% of completion. The reaction of 2,3-dichloropropene in pure nitromethane was autocatalytic in character, and reliable rate constants for the uncatalyzed reaction in this medium could not be obtained. Attempts to study the reactions of chlorine with cinnamic acid in acetonitrile and with trichloroethylene in nitromethane at 25° were unsuccessful. The former reaction was too fast and the latter too slow for convenient rate study.

The rate constants k for the reactions in acetonitrile–nitromethane solutions which are reported later are defined by eq. 1. Since in the majority of runs the organic reactant

$$-d[Cl_2]/dt = k[S][Cl_2] \qquad (1)$$

was in large excess of the halogen, k[S] values were in most cases calculated from the slopes of plots of the logarithms of the optical densities of the reaction mixtures *versus* time. The methods used to evaluate k_2 from rate data for the formation of iodobenzene dichloride have been discussed previously.[9]

$$-d[C_6H_5ICl_2]/dt = k_1[C_6H_5ICl_2] - k_2[C_6H_5I][Cl_2] \qquad (2)$$

The rates of certain of the reactions in carbon tetrachloride in the presence of trifluoroacetic and acetic acids were determined spectrophotometrically by the same procedure as has been used before.[1] A wave length of 350 mμ was used in establishing the chlorine concentrations of the reaction mixtures during the course of the runs. Rate constants k_0, which are later reported for the trifluoroacetic acid-catalyzed reactions, are defined in eq. 3. An attempt

$$-d[Cl_2]/dt = k_0[S][Cl_2] \qquad (3)$$

was made to investigate the effect of changes in trifluoroacetic acid concentration on the rate of reaction of chlorine with acrylonitrile in carbon tetrachloride. At the relatively high catalyst concentration range (1–4 *M*) at which this reaction was suitably fast for rate work, the rate actually increased as the catalyst concentration dropped. Apparently an interaction takes place between the organic reactant and the catalyst, which is unfavorable to the reaction of the halogen and which is relatively extensive at these high catalyst concentration levels.

Results

The rate constants k (eq. 1) for the reaction of chlorine with aromatic and unsaturated substances in acetonitrile–nitromethane mixtures are listed in Table I along with constants k_2 (eq. 2) for the formation of iodobenzene dichloride in mixtures of the same two solvents. For each reaction investigated a plot is presented in Fig. 1 of k_{rel} (the

TABLE I

RATE CONSTANTS FOR REACTIONS OF CHLORINE IN CH_3CN-CH_3NO_2 MIXTURES (25.4 ± 0.1°)

[S], mole/l.	$10^2[Cl_2]$, moles/l.	Solvent, mole % CH_3NO_2	10^3k, l. mole^{-1} sec.$^{-1}$
	S = Toluene		
0.362	3.89	100	13.8[a]
.362	2.61	74.5	6.94
.362	2.39	49.5	4.15
.362	2.55	24.6	2.65
.362	2.94	0	1.80[b]
	S = Crotonic acid		
0.111	2.16	100	64.3
.111	1.65	74.5	57.8
.111	1.77	49.5	48.2
.111	1.53	24.6	36.6
.111	2.65	0	25.6
	S = 2,3-Dichloropropene		
0.730	1.22	74.5	0.97
.730	1.53	49.5	1.19
.730	1.20	24.6	1.26
.730	2.30	0	1.28
	S = Acrylonitrile		
4.01	7.03	100	0.00362
2.01	3.17	100	.00368
4.03	7.3	49.5	.00213
2.01	7.3	49.5	.00151
4.01	7.03	0	.00259
	S = 2-Chloronaphthalene		
0.100	1.52	100	123.0
.100	2.70	74.5	73.4
.200	2.41	49.5	44.3
.200	1.91	24.6	32.9
.200	2.00	0	15.6
.100	2.00	0	15.4
.200	3.52	0	17.0

THE REACTION OF C_6H_5I WITH Cl_2[c,d]

$[C_6H_5I]_i$, mole/l.	$10^3[Cl_2]_i$, moles/l.	Solvent, mole % CH_3NO_2	10^3k_2, l. mole^{-1} sec.$^{-1}$
0.0143–0.0329	0.801–1.60	100	76.5[e]
0.0207	1.62	49.5	92.0
0.0325–0.0356	0.743–1.13	32.9	94.3[f]
0.0170–0.0339	1.43 –2.67	0	114[g]

[a] Values ranging from 9.6–12.4 at 25.0° have been reported previously.[8] [b] Values ranging from 1.16–1.64 at 25.0° have been reported previously.[8] [c] See eq. 2 for the definition of k_2. [d] The authors are indebted to Dr. John L. Cotter who determined the k_2 values which are reported. [e] Average constant for 4 runs in which initial reactant concentrations varied as shown. [f] Average constant for 3 runs in which initial reactant concentrations varied as shown. [g] Average constant for 2 runs in which initial reactant concentrations varied as shown.

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TABLE II

RATE CONSTANTS FOR REACTIONS OF CHLORINE IN CARBON TETRACHLORIDE IN THE PRESENCE OF CF_3COOH AND CH_3COOH (25.4 ± 0.1°)

[S], mole/l.	$10^3[Cl_2]$, moles/l.	$[CF_3COOH]$,[a] moles/l.	$[CH_3COOH]$,[a] mole/l.	10^3k_0, l. mole^{-1} sec.$^{-1}$
S = 2-Chloronaphthalene				
0.457	6.67	1.72	...	12.0
.457	6.67	0.689	...	2.02
.457	9.40	.689	...	2.14
.457	9.40	.689	0.689	0.226
.229	9.40	.689	...	1.52
.457	6.67	.344	...	0.544
.457	6.67	.172	...	0.182
S = 2,3-Dichloropropane				
0.144	6.18	1.724	...	2.06
.144	6.18	0.862	...	0.56
.144	6.18	.862	...	.50
.144	6.18	.862	0.863	.13
.144	6.18	.431	...	.18

[a] Calculated on the assumption that the acid is entirely in monomeric form.

ratio of the rate constant for a particular solvent mixture to that for reaction in 100% acetonitrile) *versus* solvent composition. It is noteworthy that no maxima appear in the curves shown in Fig. 1. That is, in no case does any mixture of the two solvents provide for a faster reaction than in one or the other of the pure solvents. Such behavior should be observed if the two solvents were highly specific in their capacities to function as solvating agents (one as a nucleophile and the other as an electrophile) and if both types of solvation were of comparable importance insofar as stabilization of the activated complexes is concerned. Actually the reactions appear to fall into two general types, (a) those in which k_{rel} increases appreciably as the solvent is changed from acetonitrile to nitromethane and (b) those in which k_{rel} (or k_{2rel}) is comparatively insensitive to the change in composition of the medium. In the first category are the reactions of the aromatic substances, toluene and 2-chloronaphthalene, while the reactions of the substituted alkenes and the formation of iodobenzene dichloride fall into the second group.

Following the reasoning which is outlined in the Introduction, it is now suggested that in the chlorination of 2-chloronaphthalene, as well as of toluene, the primary role played by the polar medium is that of an electrophilic solvating agent for the activated complexes. The reactions of crotonic acid, 2,3-dichloropropene, acrylonitrile and iodobenzene with chlorine then fall into a class in which the need for nucleophilic solvation of the activated complexes is greater than in the aromatic substitution processes.

The influence of acetic acid on the capacity of trifluoroacetic acid to catalyze these several reactions in carbon tetrachloride had not in every case been investigated previously. Table II reports the results of a study of the effects of changes in trifluoroacetic acid (and acetic acid) concentrations on the rate constants for reaction of chlorine with 2-chloronaphthalene and 2,3-dichloropropene in carbon tetrachloride. An attempt to make a similar study of acrylonitrile was, for reasons discussed in the Experimental section, unsuccessful. It seems likely that if a rate study on this compound at relatively low catalyst concentration levels could have been made conveniently, an effect of acetic acid on catalyst activity similar to that found for crotonic acid should have been observed.

Following the procedure employed previously,[1] the effects of acetic acid on the catalytic activity of trifluoroacetic acid in the several reactions in question have been summarized in terms of the ratios $[CF_3COOH]_E/[CF_3COOH]_T$, where $[CF_3COOH]_E$ represents the effective concentration of the catalyst in a solution in which its actual concentration is $[CF_3COOH]_T$ and acetic acid is present in equimolar amount. The effective trifluoroacetic acid concentration has been determined, as has been done before, by referring the observed k_0 value for a reaction in the presence of equimolar quantities of the two acids to a plot of log k_0 *vs.* log $[CF_3COOH]$. The ratios (for reactions involving chlorine in carbon tetrachloride solvent at 25°) increase in the order 2-chloronaphthalene (0.32), toluene[1] (0.35), 2,3-dichloropropene (0.48), iodobenzene[1] (0.75) and crotonic acid[1] (1.4). The two aromatic chlorination processes have nearly the minimum value (0.30) which has so far been observed for a reaction involving chlorine (the chlorination of durene[1]). This supports the observation based on the use of acetonitrile–nitromethane solvent mixtures that 2-chloronaphthalene falls into the same behavior group, with respect to the influence of changes in medium on rates of reaction with halogens, as does toluene. It is presumed that the chlorination reactions of aromatic substances will in general fall into this same group.

The processes which show little rate variation as the medium changes from acetonitrile to nitromethane (the reactions of 2,3-dichloropropene, iodobenzene and crotonic acid) all have $[CF_3COOH]_E/[CF_3COOH]_T$ ratios for reaction in carbon tetrachloride which are significantly greater than the minimum observed ratio of 0.30. It is assumed that the ratio for acrylonitrile is similar to that for crotonic acid. Thus in the results of kinetic work both on the uncatalyzed reactions in acetonitrile–nitromethane mixtures and on the catalyzed reactions in carbon tetrachloride there is evidence that the requirements for nucleophilic solvation of the activated complex in reactions of chlorine with substituted alkenes and iodobenzene (to form iodobenzene dichloride) are greater than for the aromatic chlorination process. In this sense the substituted alkenes and iodobenzene fall into a like behavior group as regards their reactions in the two types of media. Actually there is more variation in the magnitude of the responses of their reactivities to added acetic acid in the catalyzed reaction than to their responses to changes in medium when the polar solvent mixtures are used. A very close correlation in these behavior characteristics for the two different sets of reaction conditions is not necessarily to be expected since the rate picture is influenced by the capacities of the various media to solvate the reactants (as well as the activated complexes), and this factor has been discounted in this interpretation. It is generally accepted, however, that for qualitative purposes the change in the rate picture for a polar process as the solvent is changed is dominated by the capacity of the medium to contribute to the stabilization of the activated complex.[10] It would be of considerable interest to test the responses of other polar reactions of chlorine to the influence of medium changes as has been done in this investigation. Unfortunately, the number of such reactions, so far discovered, which are readily subject to kinetic study with carbon tetrachloride as the solvent and trifluoroacetic acid as catalyst and also with acetonitrile–nitromethane mixtures as the solvent are limited in number.

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

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Microwave Absorption and Molecular Structure in Liquids. XLVIII. The Dielectric Relaxation of Diphenyl Sulfide, Triphenylamine and Diphenylmethane[1,2]

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RECEIVED FEBRUARY 5, 1962

The dielectric constants and losses at wave lengths of 1.20, 3.30, 10 and 25 cm. have been measured for diphenyl sulfide in benzene solution at 20° and in Nujol solution at 20, 40 and 60°; measurements being made in the latter case at 50 cm. also. Measurements have been made at wave lengths of 1.25 and 3.22 cm. on triphenylamine in benzene solution at 40° and on diphenylmethane, as the pure liquid, at 40 and 60°. Measurements of dielectric constant alone were made at a wave length of 575 m. and refractive indices were determined for the sodium D-line. Dielectric relaxation times and distribution parameters have been calculated from these data. The data obtained for diphenyl sulfide in benzene solution have been analyzed in terms of two relaxation times, the value of the relaxation time corresponding to the high frequency dispersion region being consistent with an intramolecular mechanism. The relaxation time of diphenyl sulfide in Nujol solution at 20° was observed to be about one tenth as large as would be expected if the molecule were completely rigid. Dipole orientation by intramolecular motion has been found to occur in the molecule of triphenylamine. The contribution to the dipole orientational mechanism of diphenylmethane by internal motion has been found to be somewhat smaller than previously believed. Dipole moment values of 0.22 and 0.43 *D* have been determined for diphenylmethane and triphenylamine, respectively.

The abnormally low dielectric relaxation time found for diphenyl ether[4-7] has been attributed to intramolecular rotation of the phenyl rings with accompanying shift of pi electronic charge.[8] Similarly low relaxation times found for diphenylmethane[7] and diphenylamine[9-11] have suggested a similar relaxation mechanism for these molecules. To obtain further evidence as to possible mechanism, diphenylmethane, which had been impossible to measure accurately because of the smallness of its moment, was redetermined, and diphenyl sulfide and triphenylamine were measured to see if an intramolecular relaxation mechanism could be detected.

Experimental Methods

Apparatus.—The apparatus and the various methods of measurement have been described in previous papers.[12-14]

Purification of Materials.—Diphenyl sulfide, obtained from the Eastman Kodak Company, was fractionally distilled under reduced pressure and stored over Drierite. It gave a refractive index n^{18}D 1.63411. Triphenylamine, obtained from the Aldrich Chemical Company, was recrystallized three times from a mixture of benzene and absolute ethanol. The resulting material, after recrystallization three times from ethyl ether, gave a melting point of 127.3–127.9°. Diphenylmethane, obtained from Matheson, Coleman and Bell, Inc., was fractionally distilled under reduced pressure and stored over Drierite. It gave a refractive index n^{40}D 1.56831. Benzene, obtained from the Allied Chemical Corporation, was of the reagent grade, thiophene-free quality. It was used as received. Nujol, purchased from a local drug store, was treated as previously described.[15]

Experimental Results

The experimental results obtained from the solution studies were treated in the manner described in earlier papers.[16,17] The slopes of the straight lines thus obtained, a' corresponding to ϵ', and a'' corresponding to ϵ'', were plotted in Cole–Cole arcs[18] in the usual fashion[16] to obtain the critical wave lengths, λ_m, the corresponding relaxation times, τ_0, the distribution parameters, α, and the arc intercepts at infinite frequency, a_∞. The values of these quantities are given in Tables I and III. The dipole moment calculated for triphenylamine from the 3.22 cm. dielectric constant and loss data by a method described previously[19] is also included in Table III. The data obtained for di-

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[1] This research was supported by the U. S. Army Research Office—Durham. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

[2] This paper represents part of the work submitted by E. N. DiCarlo to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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