a reasonable time and to do this without the use of highly catalytic substances like bromide ion or iodide ion required concentrations so high that trouble with insolubility of some salts, probably chromous sulfate, was encountered. On one rate run which ran for 24 hours with an initial rate of 835 μg./hr., analysis of the solution for divalent chromium at the end of the run showed a 12.5% reduction in concentration while calculations based on the sulfide production would indicate about 7.5% reduction. This would indicate that 40% of the reduction in chromous ion concentration was due to oxidation by hydrogen ions. Consequently any rate constant so derived would be a composite of the two reactions and would not be valid for the reaction under consideration.

The determination of the order of the rate-controlling reaction from consideration of the initial rates also failed. Use of the formula

$$n_A = \frac{\log\left(-\frac{dA_1}{dt}\right) - \log\left(-\frac{dA_2}{dt}\right)}{\log A_1 - \log A_2}$$

where n_A is the order with respect to A, A_1 and A_2 the initial concentrations of A in two runs, and dA_1/dt and dA_2/dt the initial rates in the same two runs, gave values of 2, 4 and 4 for Cr^{+2}, SO_2^{-2} and H^+, respectively. It is felt that the formulas developed for dilute solution kinetics would not be applicable to solutions with ionic strengths on the order of 15–20 in any event.

[CONTRIBUTION FROM THE MALLINCKRODT LABORATORIES, HARVARD UNIVERSITY]

Conductance Studies of Organometallic Chlorides of Group IVB and of Hydrogen Chloride in N,N-Dimethylformamide. Some Observations About the Purification of the Solvent

BY ALVIN B. THOMAS AND EUGENE G. ROCHOW

RECEIVED NOVEMBER 5, 1956

Solutions of organometallic chlorides of the elements of Group IVB in N,N-dimethylformamide have been investigated conductimetrically, and have been found not to dissociate into organometallic cations and chloride ions. Since N,N-dimethylformamide is difficult to purify, appreciable amounts of water may remain in it after purification, so that easily solvolyzed solutes, such as triphenylchlorosilane, produce large amounts of hydrogen chloride in solution. The problem of purifying N,N-dimethylformamide is discussed, and a means of detecting the amount of proton-releasing impurity is described. Data are presented on the conductance of hydrogen chloride in N,N-dimethylformamide.

Introduction

In recent years there has been increasing interest in N,N-dimethylformamide as an electrolytic solvent. Most of this interest has been concerned with conductances of ionophoric[1] compounds such as alkali metal and quaternary ammonium salts[2-5]; however, some attention has been given to conductances of ionogenic[1] compounds such as hydrogen chloride,[6] acyl halides,[7] and organosilicon and organogermanium chlorides.[8,9] This paper presents a study of the conductimetric behavior of organometallic chlorides of the elements of Group IVB and of hydrogen chloride in N,N-dimethylformamide, and includes some observations of general utility concerning the purification of the solvent.

The observation that organochlorosilanes give conducting solutions in N,N-dimethylformamide[8,9] is the first reported instance of possible electrolytic properties for organosilicon compounds. It would be desirable to determine the identity of the ionic species present, especially in view of the observed reaction between organochlorosilanes and N,N-dimethylformamide at high temperatures[10] to form dimethylamine hydrochloride, and also because minute traces of proton-releasing impurities can solvolyze organochlorosilanes to produce hydrogen chloride. The electrolytic behavior of organohalostannanes in water[11] and in various nonaqueous solvents[12,13] also makes the electrolytic properties of such compounds in N,N-dimethylformamide of interest, and measurements have been extended to the entire group.

Experimental

Purification of the Solvent.—N,N-Dimethylformamide (hereafter called DMF) is very difficult to purify. Trace amounts of proton-releasing impurities have a profound effect on the observed conductimetric behavior of any solute which yields a hydrogen halide as a solvolysis product, and every effort must be made to eliminate such impurities or to estimate their concentration so that their effects can be taken into account in the interpretation of the results. Impurities of importance in this respect include water, alcohols and primary and secondary amines.

DMF decomposes slightly at its normal boiling point to give small amounts of dimethylamine and carbon monoxide.

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[1] R. M. Fuoss, *J. Chem. Ed.*, **32**, 527 (1955). Prof. Fuoss makes a valuable distinction between those electrolytes which are discretely ionic in the crystal lattice (ionophores), and those which exist as molecular entities in the original compound to become electrolytes only by virtue of acid–base reaction with appropriate solvents (ionogens).

[2] D. P. Ames and P. G. Sears, *J. Phys. Chem.*, **59**, 16 (1955).

[3] C. M. French and K. H. Glover, *Trans. Faraday Soc.*, **51**, 1418 (1955).

[4] P. G. Sears, D. Wilhoit and L. R. Dawson, *J. Chem. Phys.*, **23**, 1274 (1955).

[5] L. R. Dawson, M. Golben, G. R. Leader and H. K. Zimmermann, *Trans. Kentucky Acad. Sci.*, **13**, 221 (1952).

[6] L. R. Dawson, M. Golben, G. R. Leader and H. K. Zimmermann, *J. Electrochem. Soc.*, **99**, 28 (1952).

[7] H. K. Hall, Jr., THIS JOURNAL, **78**, 2717 (1956).

[8] K. Gingold, E. G. Rochow, D. Seyferth, A. C. Smith, Jr., and R. West, *ibid.*, **74**, 6306 (1952).

[9] K. Gingold, Ph.D. thesis, Harvard University, 1952.

[10] E. G. Rochow and K. Gingold, THIS JOURNAL, **76**, 4852 (1954).

[11] E. G. Rochow and D. Seyferth, *ibid.*, **75**, 2877 (1953).

[12] C. A. Kraus and C. C. Callis, *ibid.*, **45**, 2624 (1923).

[13] C. A. Kraus and W. N. Greer, *ibid.*, **45**, 2946 (1923).

If acidic or basic materials are present this decomposition is catalyzed, and considerable dimethylamine may be produced at lower temperatures. It was found in the present research that considerable dimethylamine was produced at room temperature if DMF was allowed to stand with solid potassium or sodium hydroxide, or with calcium hydride, for a few hours. With regard to water as an impurity, there is evidence for an addition compound DMF·$2H_2O$, which melts at −50° and which may persist in appreciable concentrations at room temperature.[14] We found that when 20% of water is added to dimethylformamide at room temperature, a chemical interaction takes place and the temperature rises about 20°. Such considerations render it very doubtful that distillation alone can remove water from DMF, since any compound existing in solution will re-form in the receiver although it may have been decomposed in the vapor phase. It is difficult to see how conditions of temperature and pressure of the distillation could have much effect on this process. It seems prudent, therefore, to use a chemical method of removing water and other protonic impurities from DMF, and necessarily one which does not cause decomposition. Four methods of purification were used in the present research, and while some are not as satisfactory as others, each will be described to show its relative effectiveness.

Method I.—DuPont Technical Grade DMF was mixed with about 10% by volume of benzene which had been dried over calcium hydride.[9] The benzene was removed by distillation at atmospheric pressure; the temperature never rose above 80°, so there was little decomposition of the DMF, and the bulk of the water present was removed in the benzene–water azeotrope. This initial step was performed in each of the purification methods given below, and the DMF so obtained will be described as "benzene-dry."

Mallinckrodt Analytical Reagent Grade magnesium sulfate was ignited overnight in a muffle furnace at 300–400°, and 25 g. was added to each liter of benzene-dry DMF. The mixture was shaken one day, and then a comparable amount of fresh anhydrous magnesium sulfate was added. The solvent was distilled at 15–20 mm. pressure through a 3-foot vacuum-jacketed column packed with steel helices, and the middle fraction of the distillate retained.

The specific conductances for purified solvents will be given at the end of this section on purification methods.

Method II.—Benzene-dry DMF was shaken repeatedly with powdered barium oxide powder, decanted, and distilled as in method I.

Method III.—Benzene-dry DMF was treated by method I. The distillate was then shaken repeatedly with Merck Chromatographic Grade alumina powder which had been dried by heating in a muffle furnace overnight at 500–600°. Approximately 50 g. of alumina was added for each liter of DMF. The solvent then was distilled from more ignited alumina at a pressure of about 5–10 mm. and the middle fraction was retained.

Method IV.—Benzene-dry DMF was treated by method I and then triphenylchlorosilane was added (about 5–10 g./liter). The mixture was held at 120–140° for 24 hours and then distilled at about 5 mm. pressure.

The effectiveness of the various purification methods is evident from the tabulation below:

	Specific conductance of DMF, mho cm.$^{-1}$ × 10^7	Impurity content (expressed as water), M[a]
Method I	0.9–1.5	0.01
Method II	.4–1.0	.001–0.005
Method III	.3–0.9	.005–0.007
Method IV	.6–1.35	.001 or less

[a] The proton-releasing impurities were determined after purification by the method suggested later in this paper.

The specific conductances obtained for DMF in the present research compare well with those previously reported after using other purification methods, but it must be remembered that specific conductance is no criterion of purity of a solvent with respect to freedom from *covalent* impurities. Specific conductances of 0.3 × 10^{-7} mho cm.$^{-1}$ were the lowest obtained in the present work (as opposed to 0.6 × 10^{-7} mho cm.$^{-1}$ reported in the literature[2,3]), but this merely indicates that efficient distillation removed *ionic* contaminants; it does not mean greater freedom from covalent impurities.

It can be seen that some water remains in DMF no matter how it is purified, and recognition of this possibility is of utmost importance for accurate evaluation of conductance data.

Dimethylamine was estimated by the use of 2,4-dinitrofluorobenzene, which forms a compound with dimethylamine that absorbs in the visible spectrum at 3812 Å. Only methods II and IV above are likely to produce dimethylamine in substantial quantity, and it appears that barium oxide (method II) does not do so at temperatures near room temperature whereas calcium hydride does. Triphenylchlorosilane (method IV) produces hydrogen chloride through reaction with proton-releasing impurities in the solvent, but the resulting complex with DMF, DMF·HCl, is decomposed above 90°, to give dimethylamine hydrochloride and carbon monoxide, and were any dimethylamine present or produced during the heating step it would be taken up by triphenylchlorosilane to give a silylamine and the complex, DMF·HCl, which subsequently would decompose.

Apparatus and Procedure.—A Jones–Josephs a.c. conductance bridge (Leeds & Northrup Co.) was used. A pure sine wave signal at either 400 or 1000 cycles was produced by a General Radio 1214A oscillator; the latter frequency was used for recorded conductances and the former was used as a polarization check. An oscilloscope was used as a detector without pre-amplification of voltage signals.

Temperature was maintained constant to ±0.01° by a thermistor thermoregulator,[15] and the thermostat was filled with a light kerosene (Varsol #2). Unless otherwise noted, all measurements given in this paper are for 25.00 ± 0.01°.

Three conductance cells were used, with constants of 2.2645, 0.1385 and 0.01238. Each of the two cells of lower constant was incorporated into a glass assembly, called a dilution cell (shown in Fig. 1) which allowed preparation and manipulation of solutions without atmospheric contact.

The dilution cells and any other equipment which came in contact with solvents or solutions were treated by the "dry-film" technique.[16,17] Once cells had been given this permanent treatment, drying of them prior to each run was accomplished by rinsing with acetone followed by passing dry nitrogen through them for 15 to 30 minutes. This procedure of drying cells appears to be satisfactory, and is considerably easier and less time-consuming than baking cells *in vacuo*.

The solvent was stored in a Vycor flask fitted with a wash bottle head; middle fractions from solvent distillations were collected directly in this flask. Rubber nipples were used to seal the wash bottle head from the atmosphere except during solvent transfers. Solvent transfers were accomplished by using dry nitrogen pressure to force solvent from the storage flask into the appropriate dilution cell. At the same time a positive pressure of dry nitrogen was maintained inside the dilution cell *via* the sidearm with stopcock. The weight of the solvent admitted was determined by difference in weight of the storage flask before and after transfer.

Solid solute or hydrogen chloride–dimethylformamide solution was admitted to the dilution cells through the uppermost ground-glass joint while a positive pressure of nitrogen was maintained inside the cell. All weighings of solutes were performed to the nearest 0.1 mg. and errors as great as 3–5% may exist in the final data since frequently only a few milligrams were weighed for a given addition to the cell. Increasing concentration of solute was obtained by continuing these additions to a batch of solvent in the dilution cell.

Preparation and Purification of Solutes.—All solutes were analyzed for chloride content, and the results are reported as percentage purity with respect to the pure compounds. Samples for analysis usually weighed about 0.1 g. and were dissolved in solutions of acetone and water to which had been added two pellets of sodium hydroxide. The amount of acetone present was in the range of 80–95% by volume and served to ensure homogeneity of the solutions during

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(14) F. Blankenship and B. Clampitt, *Proc. Oklahoma Acad. Sci.*, **31**, 106 (1950).

(15) R. L. Burwell, Jr., A. H. Peterson and G. B. Rathmann, *Rev. Sci. Instr.*, **19**, 608 (1948).

(16) E. G. Rochow "Introduction to the Chemistry of the Silicones," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1951, p. 131 ff.

(17) J. A. Hawkins and M. K. Wilson, *J. Chem. Phys.*, **21**, 360 (1953).

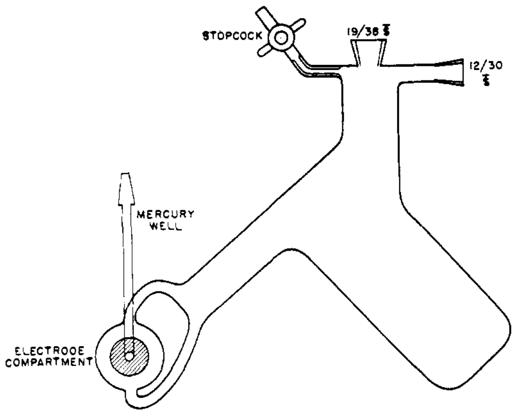

Fig. 1.—Dilution cell.

titration. A Leeds & Northrup Type K potentiometer was used to detect end-points, and a dilute aqueous solution of silver nitrate (1.000 g./l.) was used as titrant.

Hydrogen chloride was prepared by allowing concentrated hydrochloric acid to drip into concentrated sulfuric acid. The issuant gas was dried by passing it through phosphorus pentoxide towers, and it was then immediately absorbed into conductance-grade dimethylformamide.

Eastman Purified Grade triphenylchloromethane was dissolved in diethyl ether and the solution was saturated with dry hydrogen chloride at 0°. Crystals were obtained by cooling in a Dry Ice–acetone bath, and these were repeatedly recrystallized from 30–60° petroleum ether using Dry Ice–acetone baths; m.p. 112–113°; purity 99.5 ± 0.1%.

Dow-Corning Purified Grade triphenylchlorosilane was recrystallized twice from ethanol-free chloroform, and twice from 30–60° petroleum ether by cooling in a Dry Ice–acetone bath; m.p. 97°; purity 96.5 ± 0.3%. The impurities present in this compound are likely to be tetraphenylsilane and small amounts of hexaphenyldisiloxane, with traces of triphenylsilanol,[18] none of which interfere with the present work. An early report of a melting point of 110–111° for this compound[19] has not been substantiated, and several workers report melting points of 97–99° after extensive purification treatments.[20,21]

Triphenylchlorogermane was prepared from tetraphenylgermane[22] by the action of bromine in ethylene dibromide solution followed by hydrolysis to the oxide and conversion to the chlorogermane.[23] The product was repeatedly recrystallized from 30–60° petroleum ether using a Dry Ice–acetone bath; m.p. 117–118°; purity 100.7 ± 0.5%.

Triphenylchlorostannane was donated by the Metal and Thermit Corporation and was purified by repeated recrystallization from 30–60° petroleum ether by Dr. A. L. Allred of these Laboratories; m.p. 103–104°; purity 99.9 ± 0.1%.

Triphenylfluorostannane was prepared from triphenylchlorostannane by the method of Krause and Becker[24]; m.p. 340–57° (decomposed and sublimed). The material was not analyzed.

Trimethylchlorostannane was recrystallized from dimethyldichlorostannane residues available in these Laboratories. Repeated recrystallizations from 30–60° petroleum ether using a Dry Ice–acetone bath yielded a low melting solid which was further purified by sublimation; m.p. 36.5°; purity 105 ± 0.5% (impurity probably dimethyldichlorostannane).

Dimethyldichlorostannane was recrystallized from methylcyclohexane and from 30–60° petroleum ether. The original material was synthesized by Dr. D. Seyferth of these laboratories using the method of Smith and Rochow,[25] m.p. 108°; purity 99.8 ± 0.1%.

Triphenylchloroplumbane was prepared from tetraphenylplumbane[26] by the method of Gilman and Robinson[27]; m.p. 206–207°; purity 101.5 ± 0.1%.

Results

In the tables below concentration, c, is in moles/liter; specific conductance, k, is in mho cm.$^{-1}$, and molar conductance, Λ, is in mho cm.^{2} mole^{-1}.

A. Hydrogen Chloride.—The data in Table I and the following data were fitted to the Ostwald dilution law by the method of least-squares; the most concentrated solution in Table I was omitted from the calculation since the law fails at high concentrations. These physical constants were obtained: $\Lambda_0 = 79.3$; $K_i = 2.83 \times 10^{-4}$. The data in Table I are plotted conventionally in Fig. 2, and the plot according to the Ostwald dilution law is shown in Fig. 3.

TABLE I

0.0893 *M* HCl IN DMF (METHOD III) ADDED TO DMF (METHOD III)

Temperature 20.00 ± 0.01°

$c \times 10^4$	$k \times 10^7$	Λ	$c \times 10^4$	$k \times 10^7$	Λ
0.558	39.4	70.6	6.45	246.7	38.25
0.584	40.1	68.6	7.01	257.2	36.65
1.265	74.95	59.3	9.50	310.2	32.65
1.40	82.4	58.9	14.6	410.2	28.1
2.17	112.9	52.0	15.06	415.2	27.6
2.62	130.3	49.8	21.0	509.2	24.2
3.99	176.2	44.25	31.8	653.2	20.5
4.58	192.5	42.1	54.0	898.2	16.6

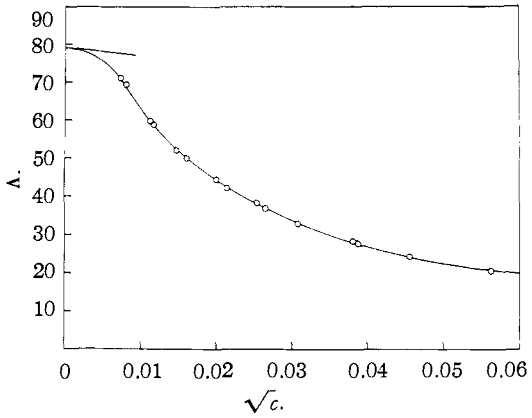

Fig. 2.—Phoreogram of HCl in DMF.

B. Triphenylchloromethane and Triphenylchlorosilane.

(The two most concentrated solutions were omitted from the least-squares calculation).

If the data in Tables II and III are combined and fitted by least-squares (again omitting the two most concentrated solutions in Table III) the following constants are obtained: $\Lambda_0 = 75.5$, $K_i = 3.02 \times 10^{-4}$.

The conductimetric behavior of triphenylchloromethane and triphenylchlorosilane in DMF prepared by method III closely parallels that of hy-

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[18] K. Gingold, Ph.D. thesis, Harvard University, 1952, p. 40.

[19] F. S. Kipping and H. Marsden, *J. Chem. Soc.*, **93**, 198 (1908).

[20] N. S. Nametkin, A. V. Topchev and F. F. Machus, *Doklady Akad. Nauk S.S.S.R.*, **83**, 705 (1952); *cf. C. A.*, **47**, 2723 (1953).

[21] Priv. Communication, Prof. N. N. Lichtin, Boston Univ. Chem. Dept.

[22] D. L. Tabern, W. R. Orndorff and L. M. Dennis, THIS JOURNAL, **47**, 2039 (1925).

[23] W. R. Orndorff, D. L. Tabern and L. M. Dennis, *ibid.*, **49**, 2512 (1927).

[24] E. Krause and R. Becker, *Ber.*, **53**, 173 (1920).

[25] A. C. Smith, Jr., and E. G. Rochow, THIS JOURNAL, **75**, 4103 (1953).

[26] H. Gilman and J. D. Robinson, *ibid.*, **49**, 2315 (1927).

[27] H. Gilman and J. D. Robinson, *ibid.*, **51**, 3112 (1929).

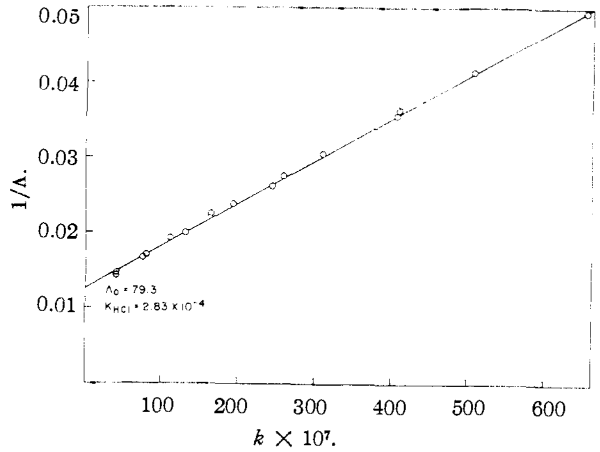

Fig. 3.—Oswald plot of HCl in DMF.

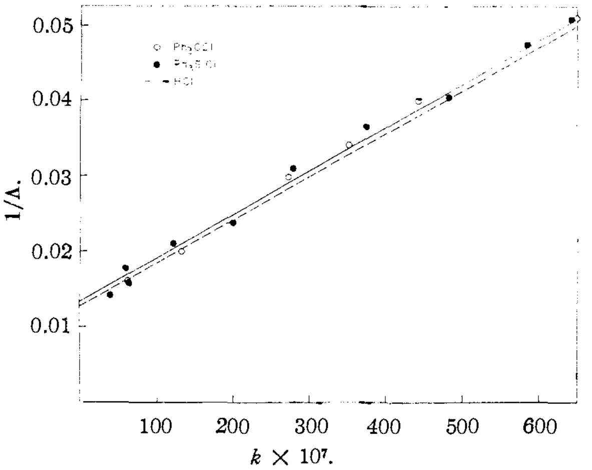

Fig. 4.—Oswald plots of Ph_3SiCl and Ph_3CCl in DMF (method III).

drogen chloride in this solvent; this is evident from the plot of the data of Tables II and III according to the Ostwald Dilution Law shown in Fig. 4.

TABLE II

SOLID TRIPHENYLCHLOROMETHANE ADDED TO DMF (METHOD III)

Temperature 19.9 ± 0.1°

$\times 10^4$	$k \times 10^7$	Λ
1.010	63.5	62.1
2.66	132.5	49.9
8.12	272.3	33.5
12.06	353.3	29.3
17.51	442.3	25.2
32.5	649.3	19.95

$\Lambda_0 = 70.4$; $K_i = 3.68 \times 10^{-4}$

TABLE III

TRIPHENYLCHLOROSILANE ADDED TO DMF (METHOD III)

Temperature 19.9 ± 0.1°

$c \times 10^4$	$k \times 10^7$	Λ
0.541	39.7	73.25
1.030	58.0	56.3
1.078	67.9	63.0
2.57	121.7	47.4
4.75	200.5	42.2
8.70	281.3	32.3
13.59	372.3	27.4
19.45	479.3	24.6
23.55	533.3	22.6
27.6	584.3	21.1
32.65	644.3	19.7
37.5	704.3	18.8
44.9	784.3	17.4

$\Lambda_0 = 77.8$; $K_i = 2.78 \times 10^{-4}$

There is thus a strong suggestion that hydrogen chloride is the electrolyte in all cases. That this is indeed so is shown by the following facts:

(1) Solutions of triphenylchlorosilane in DMF prepared by method III were prepared without exposure to the atmosphere. The DMF was removed from these solutions by vacuum distillation at room temperature and collected in a receiver kept at −78°. The distillate of DMF contained large amounts of protons and active chloride ions. The only conceivable volatile compound in this system which could contain protons and active chloride is hydrogen chloride.

(2) Solutions of dry congo red in DMF prepared by method III were made up and carefully protected from the atmosphere. These solutions were bright red in color, but upon addition of solid triphenylchlorosilane a dark, blue-violet color appeared immediately. This color was identical with that of hydrogen chloride in solutions of congo red in DMF. Addition of dry triethylamine restored the bright red color to all solutions. These color phenomena occurred with triphenylchloromethane solutions also.

(3) The following data were obtained with a Beckman *p*H meter at 25° using solutions of triphenylchlorosilane and of hydrogen chloride in DMF prepared by method III.

Ph_3SiCl, *M*	*p*H Reading	HCl, *M*	*p*H Reading
0.00525	2.3	0.0054	2.2
.00150	2.7	.00154	2.7

The *p*H readings above are the averages of several determinations made by quickly immersing the electrodes in the appropriate solutions. Before each immersion the electrodes were washed with water, then acetone, and briefly dried.

The above facts leave no doubt that hydrogen chloride is present in solutions of triphenylchloromethane and triphenylchlorosilane in DMF, and that the conductances given in Tables II and III relate to the behavior of stoichiometrically equivalent quantities of hydrogen chloride.

The data in Table IV (below) show unambiguously that for triphenylchlorosilane this hydrogen chloride arises from impurities in the solvent and that once these impurities are consumed no further ions are produced.

TABLE IV

TRIPHENYLCHLOROSILANE ADDED TO DMF (METHOD IV)

$c \times 10^4$	$k \times 10^7$	Λ
2.95	152.1	51.6
10.34	337	32.6
13.41	382	28.5
19.1	500	26.2
31.0	565	..
47.2	572	..
71.8	575	..
104.5	577	..

The minute changes in specific conductance that are observed at higher concentrations most likely arise from traces of moisture on the glass walls of the dilution cell which react with the solution when it may have been rinsed on to previously unexposed portions of the glass. It should be mentioned that addition of small amounts of water to solutions of triphenylchloromethane or triphenylchlorosilane under conditions such as pertain in Tables II and III had little effect on the conductance of the solutions. However, the addition of water to solutions of triphenylchlorosilane at higher concentrations under the conditions that pertain in Table IV produced great increases in conductance.

That water is the principal impurity in dimethylformamide purified by the methods given in this paper is apparent from the observation that when dilute solutions of triphenylchlorosilane in purified DMF are allowed to stand overnight, crystals of pure hexaphenyldisiloxane are obtained. The conductance values given in Tables III and IV were constant upon mixing the solute with the solvent and did not change over 24-hour periods; those values given in Table II for triphenylchloromethane, however, required as long as 24 hours to reach constancy. The work with congo red, which is cited above, also showed this time-dependency in that color changes were instantaneous with solutions of triphenylchlorosilane, but corresponding color changes required about one-half hour with solutions of triphenylchloromethane. These observations concerning rates of reaction are consistent with the knowledge that the rate of hydrolysis of triphenylchloromethane is independent of the basicity of the medium while it is to be expected that the rate for triphenylchlorosilane would be profoundly increased in a basic solvent.[28]

C. Organometallic Halides of Germanium, Tin and Lead.

TABLE V

TRIPHENYLCHLOROGERMANE ADDED TO DMF (METHOD IV)

$c \times 10^4$	$k \times 10^7$	Λ
3.045	18.45	6.06
9.10	25.25	2.78
12.47	28.45	2.28
19.92	32.75	1.642
25.6	35.45	1.385
29.7	37.25	1.258

TABLE VI

TRIPHENYLCHLOROSTANNANE ADDED TO DMF (METHOD IV)

$c \times 10^4$	$k \times 10^7$	Λ
2.86	4.49	1.57
7.39	6.35	0.860
12.82	8.31	.648
21.8	11.63	.535
31.5	15.33	.487

TABLE VII

TRIMETHYLCHLOROSTANNANE ADDED TO DMF (METHOD IV)

$c \times 10^4$	$k \times 10^7$	Λ
5.04	9.90	1.963
8.48	13.32	1.572
21.7	25.15	1.159
29.2	31.25	1.071
41.5	40.55	1.001

TABLE VIII

TRIPHENYLFLUOROSTANNANE ADDED TO DMF (METHOD IV)

$c \times 10^4$	$k \times 10^7$	Λ
0.969	0.47	0.486
3.28	1.09	.333
5.62	1.67	.298
8.98	2.93	.327
16.4	4.57	.279

TABLE IX

DIMETHYLDICHLOROSTANNANE ADDED TO DMF (METHOD IV)

$c \times 10^4$	$k \times 10^7$	Λ
2.84	10.83	3.82
8.80	19.25	2.17
20.2	30.95	1.532
30.3	40.85	1.349
46.0	53.95	1.172

TABLE X

TRIPHENYLCHLOROPLUMBANE ADDED TO DMF (METHOD IV)

$c \times 10^4$	$k \times 10^7$	Λ
2.38	1.02	0.429
6.28	1.76	.280
10.35	2.24	.216
16.34	3.22	.191
(24.7)	(6.14)	(.248)

Discussion

It has been shown that solutions of triphenylchloromethane or triphenylchlorosilane in dimethylformamide produce hydrogen chloride from residual water in the solvent. For triphenylchlorosilane it has been shown that the hydrogen chloride does not arise to any extent from a reaction between the solute and dimethylformamide under the conditions of measurement, and that also no "siliconium" ions are produced from the solute in conductimetrically detectable quantities.

These considerations lead to the proposal that triphenylchlorosilane can be used as a convenient material for determining the amount of proton-releasing impurities which may be present in dimethylformamide and in other non-reactive basic solvents, *e.g.*, pyridine. The fair degree of stability which triphenylchlorosilane exhibits toward atmospheric moisture allows the material to be handled without much precaution.

It cannot be said that the methods of purification described in this paper are necessarily better than others; it would appear, however, that the use of barium oxide or triphenylchlorosilane as desiccant shows promise. Although barium oxide does not appear to cause any decomposition of dimethylformamide, this reagent has the disadvantage shared by all basic desiccants in that it does not necessarily remove covalent impurities of basic nature that may be present. It is possible that the reported use of phosphorus pentoxide as a desiccant gives dimethylformamide essentially free of impurities, but this method, like others reported in the literature, does not appear to have been scrutinized for its effectiveness for removal of traces of covalent impurities. The use of molecular sieves is a further possible purification method and may offer freedom from decomposition effects.

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(28) C. G. Swain, R. M. Esteve and R. H. Jones, THIS JOURNAL, **71**, 965 (1949).

Examination of the data given for organometallic halides of germanium, tin and lead leads to the conclusion that none of these compounds is an electrolyte in dimethylformamide. The conductances that are observed can be attributed to solvolysis of the solute to small and varying extents by water present as an impurity. There were slight variations of conductance with time which further support this view, *i.e.*, increases of about 1% per hour were observed for triphenylchlorogermane, and increases of about 5% over several hours were observed for the organotin halides.

This conclusion of non-ionogenic behavior is reached arbitrarily by weighing the data against the behavior of known electrolytes in solvents of lower dielectric constant. There is a practical limit to the applicability of the conductance method as a means of detecting ions from weak electrolytes, and it follows that there is a limit to the significance of designating certain solutes as electrolytes or non-electrolytes. One convenient criterion of electrolytic behavior is the application of the Ostwald dilution law, which should give linear plots at low concentrations with symmetrical electrolytes, and while this law is not accurate enough to be used to evaluate physical constants of electrolytes with high precision it is capable of serving as a guide in discerning the presence of symmetrical electrolytes such as might be expected to form from the solutes under consideration here. Since the Ostwald dilution law is not obeyed by the present solutes, and since both specific and molar conductances for these solutes are of very low magnitude, we are left with the conclusion that these solutes are not electrolytic. It might be contended that the Ostwald law would have been valid at lower concentrations, but this is a *reductio ad absurdum* since the weaker the electrolyte the higher the concentrations to which the Ostwald law is applicable; indeed, measurements could hardly have been extended to lower concentrations since the specific conductance of the solvent was already being approached at the lower concentrations given in the tables.

It can be seen from the tables that the conductances observed for the organometallic halides of Group IVB increase in the order of ease and extent of hydrolysis, *i.e.*, triphenylchlorosilane is most easily and most extensively hydrolyzed, next triphenylchlorogermane, then the methylchlorostannanes, and least the triphenylhalostannanes and triphenylchloroplumbane. This order of conductances is the opposite of what might be expected if bond polarities and examples of ionic behavior in other systems of solvents were considered. The known presence of water in the dimethylformamide used for this research forces the conclusion that the hydrolysis is responsible for the conductances observed, and it can be assumed that if very dry dimethylformamide were used, the observed conductances would be negligibly low.

One minor point should be mentioned in connection with the conductance of triphenylchloroplumbane, and that is that the conductances for the two most concentrated solutions *decreased* about 15% upon standing for a few hours. Such a phenomenon may be explained in terms of the formation of an organolead anion such as $Ph_3PbCl_2^-$, resulting from combination of triphenylchloroplumbane with chloride ions; these latter possibly are formed by slight hydrolysis of triphenylchloroplumbane.

An example of the validity of the Ostwald dilution law for electrolytes in dimethylformamide can be seen in Fig. 3 for hydrogen chloride. The data are not accurate enough to be treated by modern theory, but physical constants of some accuracy can be obtained from the Ostwald plot. These constants differ from those obtained in previous work[6] at 20.00° where the molar conductance at infinite dilution was found to be 70 (*vs.* 79.3 here) and the ionic dissociation constant was 5.24×10^{-4} (this latter calculated by the present authors). The difference between the early values and those of this research may be rationalized to some extent by considering the possible effects of water on the electrolytic properties of hydrogen chloride in dimethylformamide. The dimethylformamide used in the earlier work was purified by one reduced-pressure distillation apparently without any chemical drying technique; it is reasonable to conclude that such dimethylformamide contained considerably more water than that herein reported.

In the earlier paper[6] it was concluded that the conductance of the proton in dimethylformamide does not proceed *via* the Grotthus–Hückel mechanism as it does in water. This is evident from the consideration that the molar conductance at infinite dilution of ammonium chloride in dimethylformamide is 90.6; that is, hydrogen ions are not moving in an abnormal rapid manner since ammonium ions have higher mobility. The present work does not invalidate this conclusion even though the conductance of hydrogen chloride at infinite dilution was found to be greater than that in the earlier report. Indeed, the mobility of the proton would appear to be approaching that of other cations in dimethylformamide (*i.e.*, the molar conductance at infinite dilution for triphenylmethylammonium chloride at 25° is 86.9),[4] and it may be that in very dry dimethylformamide the mobility of the proton is entirely consistent with the size of the dimethylformamidonium ion, $DMF{\cdot}H^+$ which should be roughly of the same primary ionic size as ammonium and triphenylmethylammonium ions. It is possible that the presence of water acts to increase the degree of dissociation of hydrogen chloride in dimethylformamide and to solvate the dimethylformamidonium ion in a secondary but preferential manner. This would increase the ionic size, thereby decreasing its mobility, although primary solvation of the proton itself by water to give large aggregates cannot totally be excluded as a possibility. The basicity of dimethylformamide and the existence of complexes such as $DMF{\cdot}HCl$ makes the idea of a dimethylformamidonium ion, $DMF{\cdot}H^+$, plausible as a primary solvodynamic entity.

The authors wish to express their gratitude to the Office of Naval Research for funds for the purchase of equipment and reagents.

CAMBRIDGE, MASSACHUSETTS