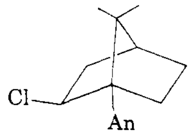


X

Experimental

Preparations.—All the compounds used in the kinetic experiments have been previously reported and their preparations described.[1]

Solvents.—Commercial dioxane was purified by the method of Hess and Frahm.[9] It was found necessary to continue the initial heating with hydrochloric acid for nearly a week. The material used boiled at 100.7–100.9°, had a constant refractive index of 1.4204 at 25° throughout the distillation, and showed no detectable absorption at 384 mμ.

Anhydrous formic acid was prepared in various ways. Distillation of reagent grade 88% formic acid (Merck and Company) with phthalic anhydride after a 6-hour reflux period gave about 75% yield of apparently anhydrous material. A drying of 88% formic acid with freshly prepared anhydrous copper sulfate for several days gave an acid 94% pure by titration. Distillation yielded a fraction boiling at 99.0–99.2° (uncor.) which by titration showed a purity of 100.1%. Titration of formic acid (Eastman Kodak Co.) showed a purity of 99.6% and that from the Victor Chemical Co. gave figures of 98.25 and 98.34%. Freezing points of formic acid samples were determined with thermometers calibrated by the Bureau of Standards. Some samples were also titrated: 1.5 g. of formic acid was diluted with 50 g. of water, and then 5 g. of this solution was titrated to a phenolphthalein end-point with 0.1 N sodium hydroxide. Eastman 98^{+}% formic acid was used for most of the non-kinetic experiments. Samples from three bottles of this acid had freezing points of 7.57°, 7.47° and 7.87°. These corresponded to formic acid concentrations of 99.56, 99.49 and 99.75% assuming that water was the sole impurity and using 8.25° as the freezing point of formic acid and 2.77 degrees per mole per 1000 g. as the cryoscopic constant. Two independent titrations of the sample with a freezing point of 7.87° gave values of 99.59 and 99.53% formic acid. Samples of Eastman acid were distilled through vacuum-jacketed columns packed with small rings. A small amount of the distillate was discarded, and then about two-thirds of the material was collected within a range of 0.2° at about 101°. A sample distilled through a 51-cm. column had a freezing point of 8.17°, corresponding to 99.95% formic acid; two independent titrations gave values of 99.97 and 99.97% formic acid. Two other samples distilled through a 101-cm. column had freezing points of 8.19° and 8.26°, corresponding to 99.96 and 100.01% formic acid. Other concentrations of formic acid were made by dilutions by weight.

Kinetics Procedure.—The standard solutions of formic acid were made up gravimetrically. One ml. of water was pipetted into a 50-ml. volumetric flask and weighed. Formic acid was then added to the mark, and the flask was again weighed. This gave 98.4% formic acid. The other acid solutions were made up similarly. A concentrated stock solution of the reactant solute was prepared containing 10 mg. in 10 ml. of dioxane, and approximately 100 mg. of this solution was weighed into a 10-ml. volumetric flask. This flask was then filled to the mark with the desired standard acid, shaken vigorously for 30 seconds, and placed in the quartz spectrophotometer cells. The determination of the spectrum was started immediately. Runs with the isomeric 2-*p*-anisylcamphenilols, using the Cary spectrophotometer, were carried out at the temperature of a thermostated room (about 26°). All other runs were made with a Beckman DU spectrophotometer using a thermostated cell holder which has been described.[10] These runs were made at either of two thermostat settings, 25.06 ± 0.03° or 25.00 ± 0.03°.

Continuous spectra were taken with a Cary recording spectrophotometer in 100.0% formic acid from 325 to 450 mμ on all the materials related to *p*-anisylcamphenilol: *p*-anisylapocyclene, *p*-anisylapocamphene, epi-*p*-anisylcamphenilol, the formates isolated after 4 minutes and after 4 hours from reactions of *p*-anisylcamphenilol and formic acid, and the alcohol mixtures obtained from the formates isolated after 9 minutes and after 4 hours from this reaction. The spectra were taken when the absorptions of the solutions were about at their maxima, and several spectra were taken in succession for those solutions whose absorptions were rapidly changing. Identical spectra were observed in all these cases.

For the determination of conductivity, a solution of *p*-anisylcamphenilol was made in dioxane. The alcohol is not too readily soluble in this solvent, and hence more dioxane was needed than might have been desirable. Three grams of the dioxane solution which had been allowed to come to temperature in a thermostat at 25.0° was added to 30.43 g. of 96.8% formic acid that had been similarly thermostated. The solution was shaken vigorously and then poured into a conductivity cell (Central Scientific Co. no. 7005) having a cell constant of 0.307. The conductivity bridge used was a Central Scientific Co. type 70000 employing an "electric eye" null indicator. During the conductivity run, the cell was thermostated at 25.0°.

Acknowledgments.—We thank the National Science Foundation and the Mallinckrodt Chemical Works for support of this research and the National Science Foundation and the Ethyl Corporation for fellowships at different times to H. G. Richey, Jr.

---

[9] K. Hess and H. Frahm, *Ber.*, **71B**, 2627 (1938).

[10] Designed by F. H. Westheimer and J. Kumamoto; see P. D. Bartlett and R. E. Davis, THIS JOURNAL, **80**, 2514 (1958).

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY, EAST LANSING, MICH.]

A Stable Dipositive Carbonium Ion[1,2]

BY HAROLD HART AND RICHARD W. FISH[3]

RECEIVED MARCH 19, 1960

Evidence is presented for the existence of dipositive carbonium ion II, produced by the ionization of trichloromethylpentamethylbenzene (I) in 100% sulfuric acid according to equation 1. The significance and generality of the results are discussed.

Carbonium ion theory has been invaluable in interpreting many organic reactions, and numerous types of carbonium ions have been discovered or suggested. Some are stable and unequivocally established through the isolation of crystalline salts; others are reaction intermediates for which the evidence is inferrential, but sometimes overwhelming.[4] With the exception of ions produced in a mass spectrometer or by other high energy means,[5]

---

[1] This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund.

[2] For a preliminary account, see THIS JOURNAL, **80**, 5894 (1958).

[3] Petroleum Research Fund Fellow, 1958–1960.

[4] For an excellent brief review, see D. Bethell and V. Gold, *Quart. Revs.*, **12**, 173 (1958).

[5] See F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957, pp. 183–185.

carbonium ions thus far studied by organic chemists bear a single positive charge. But multicharged cations are well known in inorganic chemistry. Perhaps this possibility has been ignored in the past by the organic chemist because carbonium ions with unit charge are already rather high energy, reactive species; isolation of stable ones requires a highly polar, yet not nucleophilic solvent. In this paper we report the evidence for the first example of a stable dipositive carbonium ion produced formally by loss of two anions from a single carbon atom.

Trichloromethylpentamethylbenzene (I) was readily prepared by the Friedel–Crafts reaction of pentamethylbenzene with carbon tetrachloride.[6–8] It was obtained as colorless crystals, m.p. 95.5–96.0°.[9] Analytical data and quantitative methanolysis to methyl pentamethylbenzoate unequivocally establish the structure of I.

Because of its facile solvolysis[7] and because of the structural relationship to highly hindered polymethylbenzoic acids and the unusual behavior of the latter in 100% sulfuric acid,[10a,b] a sample of I was added to concentrated acid. Whereas neither benzotrichloride nor pentamethylbenzene were separately very soluble in cold concentrated sulfuric acid,[11] compound I dissolved readily to form an intense deep-red solution. Concentrated solutions evolved hydrogen chloride. When poured on ice or into cold methanol, these solutions gave pentamethylbenzoic acid or its methyl ester, respectively, in essentially quantitative yield. Since the precursor of these products was obviously not the pentamethylbenzoyl cation, which is colorless,[12] efforts were directed toward determining the nature of these red sulfuric acid solutions.

Freezing Point Depressions.—The number of particles[13] produced when I is dissolved in 100% sulfuric acid was determined by the freezing point method. The results are given in Table I, which also includes typical data on several compounds of known ν-value. Measurements were made on chlorosulfonic acid, benzoic acid, *o*-phenylenediamine and pentamethylbenzoic acid, with ν = 1, 2, 3 and 4, respectively, and which produce 0, 1, 2 and 2 bisulfate ions (γ-values). Self-dissociation of sulfuric acid sometimes leads to erroneous results in i-determinations[14]; for those solutes with $\gamma = 1$ or 2, measurements were made both with maximum freezing point acid (10.36–10.41°) and on the water side. i-Values calculated without correction for self dissociation agreed well with literature values, and were not significantly different when determined in 100% sulfuric acid or in slightly aqueous acid.

Hydrogen chloride was known to be among the particles produced from I. It was necessary, therefore, to make freezing point measurements at such concentrations of I that the solubility of hydrogen chloride in sulfuric acid not be exceeded at the temperature of the measurements. Precise measurements of this solubility have been made.[14] In 100% sulfuric acid at 25°, hydrogen chloride is soluble to the extent of about 0.11 molal[14a] and the solubility increases with decreasing temperature[14b] as expected. The maximum molality of I used in the freezing point determinations was 0.0231; depressions were nevertheless large and accurately measurable because of the high ν-value.

From the data in Table I it is clear that I produces 5 particles when it dissolves in 100% sulfuric acid, and this value of ν is rapidly established and is not altered appreciably in 24 hours.[15]

Stoichiometry.—Since hydrogen chloride was obviously (odor, litmus) one product of the reaction of I with sulfuric acid, the stoichiometry with respect to this substance was investigated. The amount of hydrogen chloride produced was determined quantitatively by passing a stream of nitrogen through solutions of I in 100% sulfuric acid at 10–15°; hydrogen chloride was trapped in a 2% sodium hydroxide solution, the latter acidified and titrated for chloride (Fajans' method). The results are given in Table II.

Each mole of I, dissolved in 100% sulfuric acid, produced *precisely two moles* of hydrogen chloride. This quantity of hydrogen chloride was rapidly[16] flushed from the solution, and prolonged sweeping gave negligible additional hydrogen chloride.

The nitrogen used in these experiments was predried and saturated with SO_3 by passage through two scrubbers containing 100% sulfuric acid; in this way SO_3 swept from the solution containing I was continuously replaced, enabling freezing point (Table I) and conductance (Table III) measurements to be made on the hydrogen chloride-free solutions. Consistent with the hydrogen chloride

---

[6] We are indebted to Dr. R. J. Rolih, Standard Oil Co. (Indiana), Whiting, Ind., for samples of I and for its method of synthesis, which is presented in slightly modified form in the Experimental Part of this paper.

[7] Our first interest in trichloromethylpentamethylbenzene (1) was with its solvolysis. Substitution of highly branched alkyl groups on a carbon with a leaving group may accelerate solvolysis, due either to steric effects (B-strain) or to neighboring alkyl participation or both. (For a brief, critical survey, see E. L. Eliel in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 71–73.) It seemed that solvolysis of benzyl, benzal or benzohalides substituted with large groups in both *ortho* positions might be free of this duplicity of interpretation. (The 2000-fold increased rate of solvolysis of α-mesitylethyl chloride over α-phenethyl chloride[8] may be in part due to this effect.) Results of solvolysis studies will be reported separately, but preliminary kinetics show that I solvolyzes many times more rapidly then benzotrichloride ($t_{1/2}$ approximately 30 minutes at 30° in 90% aqueous acetone).

[8] G. Baddeley and J. Chadwick, *J. Chem. Soc.*, 368 (1951).

[9] For an interesting decomposition reaction of I which occurs just above its melting point, see H. Hart and R. W. Fish, THIS JOURNAL, **82**, 749 (1960).

[10] (a) H. P. Treffers and L. P. Hammett, *ibid.*, **59**, 1708 (1937); (b) M. S. Newman, *ibid.*, **63**, 2431 (1941).

[11] But when separate colorless suspensions of these were mixed, both solutes dissolved rapidly, and the solution became deep red: the phenomenon is being studied.

[12] M. S. Newman and N. C. Deno, THIS JOURNAL, **73**, 3651 (1951); concentrated solutions were observed by us to be pale yellow.

[13] We will use the terminology of R. J. Gillespie, *Rev. Pure Appl. Chem.*, **9**, 1 (1959); ν is the number of moles of particles (molecules or ions) produced in solution by one mole of solute, i is the observed multiple of the molal freezing point depression and γ is the number of moles of HSO_4^- ions (or $H_3SO_4^+$ ions) produced by one mole of any solute.

[14] (a) V. Cupr, *Rec. trav. chim.*, **44**, 478 (1925); (b) **47**, 55 (1928).

[15] The slight rise in ν which is sometimes noted when these solutions stand for extended periods may be due either to absorption of traces of moisture, or to the reaction $HCl + 2H_2SO_4 \rightleftarrows H_3O^+ + HSO_4^- + ClSO_3H$.

[16] The time obviously depends upon the rate of nitrogen flow; in experiments with other trihalomethylpolyalkylbenzenes to be reported later, times as short as 10–15 minutes were sufficient.

TABLE I

FREEZING POINT DATA

Compound	Wt., g.	H_2SO_4, g.	T_1, °C.	ΔT, °C.	Time, hr.[a]	i[b]	ν	γ
$ClSO_3H$	0.2818	33.6	10.390	0.420	x	0.95^e	1	0
	.2339	33.6	9.970^d	.351	x	0.96^e		
$C_6H_5CO_2H$	.1984	34.3	10.403	.600	x	2.07^c	2	1
	.3700	34.3	10.403	1.121	x	2.08^c		
	.4709	106.53	9.838^c	0.430	x	1.91		
				.383	12	1.73		
o-$C_6H_4(NH_2)_2$	.3792	95.60	10.363	.620	x	2.76	3	2
				.661	24	2.94		
	.4751	114.97	10.060^c	.682	x	2.91		
				.689	12	2.95		
PMBA[f]	.1946	117.56	10.361	.194	x	3.68	4	2
				.206	18	3.91		
	.2021	101.91	10.100^e	.239	x	3.79		
				.253	16	4.01		
I	$.1541^g$	32.77	10.407	.524	x	4.84^c	5	2
				.524	4	4.84^c		
	$.1648^h$	34.41	10.397	.585	x	5.30^c		
	$.5012^i$	81.72	10.356	.731	x	5.17		
				.761	24	5.30		
	$.4137^i$	88.60	10.003^e	.548	x	5.09		
				.572	12	5.32		
	$.2040^j$	45.85	10.407	.302	0.5	2.95^e	3	2
	$.3577^j$	45.85	10.407	.480	12	2.68^c		

[a] x signifies that the determination was made immediately, the time to reach equilibrium being 10 to 30 minutes. [b] i is calculated from the equation $\Delta T/6.12\ m_s$, when m_s is the molality of the solute. [c] Apparatus with magnetic stirrer; all others in apparatus with mechanical stirring (see Experimental). [d] Solute was added to the solution from the previous experiment. [e] 98% sulfuric acid was purposely added to 100% sulfuric acid, to bring it to the water side. [f] Pentamethylbenzoic acid. [g] The sum of two smaller additions which, separately, gave i = 4.68, 4.98. [h] The sum of three smaller additions which, separately, gave i = 4.81, 5.16, 4.95. [i] Solute added in CCl_4 solution; see C. M. Welch and H. A. Smith, THIS JOURNAL, 72, 4748 (1950). [j] Determinations made after the solutions were swept with anhydrous nitrogen for the time shown, to remove the hydrogen chloride (*vide infra*).

TABLE II

STOICHIOMETRY WITH RESPECT TO HYDROGEN CHLORIDE

Wt. of I,[a] g.	t, min.[b]	$AgNO_3$, ml.	Moles Cl^-/mole I
0.2040	30	14.29^c	2.006
.3577	60^e	25.12^c	2.010
.2501	60	18.81^d	2.051
.2320	60	17.07^d	2.008

[a] In 25 ml. of 100% sulfuric acid. [b] Time nitrogen swept through the solution; the rates of flow varied. [c] 0.1078 N. [d] 0.1027 N. [e] 12 more hours of sweeping at the same rate gave no additional detectable Cl^-.

stoichiometry, the swept solutions had $\nu = 3$. The spectrum (*vide infra*) was unchanged.

The hydrogen chloride-free solution when poured on ice gave pentamethylbenzoic acid in 93.3–96.3% yield. Chloride determinations on the filtrate from these hydrolyses gave 1.05 moles/mole of I.

It was clear at this point that two of the five particles produced when I is dissolved in 100% sulfuric acid are hydrogen chloride. One might infer that these would be accompanied by the formation of two bisulfate ions,[17] requiring that the fifth particle: (a) produce pentamethylbenzoic acid on hydrolysis, (b) contain one chlorine atom, (c) be intensely red and (d) to preserve neutrality, *bear two positive charges*. Experiments were undertaken to verify the production of two bisulfate ions.

Conductance Measurements.—Some years ago, Hammett and Lowenheim[18] showed that the transference numbers of barium ion and strontium ion in solutions of the corresponding bisulfates in sulfuric acid were exceedingly small, and that greater than 99% of the current was carried by the bisulfate ion. This was explained in terms of the Grothuss chain mechanism[19] in which protons are transferred from sulfuric acid molecules to bisulfate ions. Gillespie and Wasif[20] extended these measurements and pointed out the very useful fact that since the conductance of any basic solute in sulfuric acid is due almost exclusively to bisulfate ions one can determine from molar conductivities the number of bisulfate ions (γ) produced by the ionization of one mole of solute. This tool was applied to the present problem.

Using the procedure described in detail in the Experimental part, the molar conductances of potassium bisulfate, o-phenylenediamine and trichloromethylpentamethylbenzene (I) in 100% sulfuric acid were determined at several concentrations. The results, rounded off with regard to concentration, are given in Table III, and the data for the first two compounds are compared with those of Gillespie and Wasif.[20] (See Table V in the Experimental part for the actual data.) There can be no doubt that the results are consistent only with the

---

[17] The methyl groups were unaffected, as they were recovered upon hydrolysis as pentamethylbenzoic acid. The only other source of hydrogen for the hydrogen chloride was the solvent, and sulfate ions are basic to 100% sulfuric acid.

[18] L. P. Hammett and F. A. Lowenheim, THIS JOURNAL, 56, 2620 (1934).

[19] C. J. T. de Grothuss, *Ann. chim.* (*Paris*), 58, 54 (1806).

[20] R. J. Gillespie and S. Wasif, *J. Chem. Soc.*, 204, 209, 221 (1953).

formation of *two* moles of bisulfate ion per mole of I dissolved in sulfuric acid (see Table I for γ-values). Conductance measurements on the hydrogen chloride-free solutions (*vide supra*) also verified the production of two bisulfates.

Interpretation.—The data which require explanation are that trichloromethylpentamethylbenzene (I), when dissolved in 100% sulfuric acid, produces five species; two are hydrogen chloride, two are bisulfate ion, and the fifth is red and furnishes pentamethylbenzoic acid and chloride ion quantitatively when hydrolyzed. Equation 1, which involves the loss of two chloride ions from a single carbon resulting in the dipositive carbonium ion (II),[21] constitutes the most satisfactory explanation.

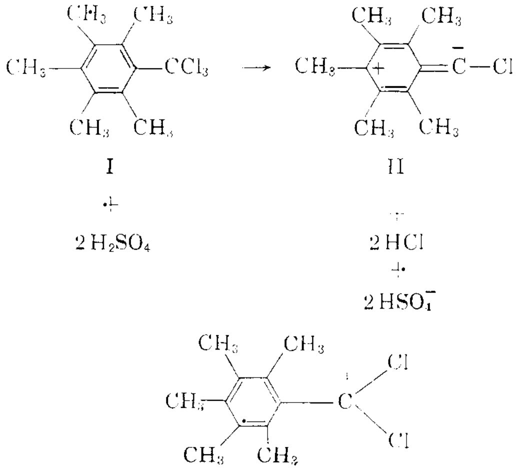
Structure II is but one contribution to the resonance hybrid; the methyls and chlorine undoubtedly also help to distribute the two positive charges so as to minimize the energy of the particle. The driving force for formation of II must arise in part from steric repulsion between the trichloromethyl group and adjacent methyls.[22] Ionization of one chloride from the trichloromethyl group does not help the situation markedly, for in order to spread the positive charge to the ring in the resulting pentamethylphenyldichlorocarbonium ion VI, the remaining two chlorines would be obliged to lie coplanar with the aromatic ring. The resulting interaction with the *ortho* methyls is sterically unfavorable. A second ionization results in the presumably linear $=\overset{+}{C}-Cl$ or $=C=\overset{+}{Cl}$ group which eliminates the steric repulsion; the situation is analogous to the behavior of pentamethylbenzoic acid in sulfuric acid[11] (see especially the n.m.r. spectrum below).

TABLE III

MOLAR CONDUCTIVITIES[a] IN 100% SULFURIC ACID AT 25°

M	$KHSO_4$	$o\text{-}C_6H_4(NH_2)_2$	I[c]
0.05	......	314(306)[b]	307
.10	157(156)	227(236)	212
.20	121(116)	164(187)	156

[a] Rounded off with regard to molarity. Actual data, measured at at least four frequencies, are given in Table V. [b] Values in parentheses from Gillespie and Wasif, ref. 21, p. 229. [c] Several runs were made at each concentration; one run each at approximately 0.05 and 0.10 M gave no different values from those recorded, after hydrogen chloride was flushed from the solutions (see Table V for details).



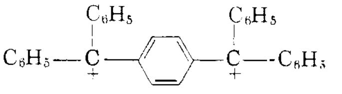
(1)

Steric strain may be only one factor in dication formation. It appears also that electron-releasing groups substituted on the benzene ring may be required to stabilize the positive charges in ions of the type described in this paper. Perchlorotoluene is reported by Ballester[23] to hydrolyze quantitatively but slowly (48 hours) in hot concentrated sulfuric acid to pentachlorobenzoic acid. Pentachloro-*o*-xylene, a fairly strained but unfavorably substituted trichloromethyl compound, was found by us not to be soluble in 100% sulfuric acid. It is obvious that the structural requirements necessary

---

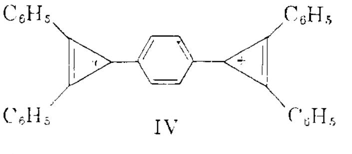
[21] Because it now seems likely that one can prepare many multiply charged carbonium ions and indeed obtain their crystalline salts (unpublished results) the need for a systematic way of naming such ions has become apparent. Bethell and Gold (ref. 4) considered the problem for unipositive carbonium ions, and used either the "carbinol" or or the "cation" conventions. Thus CH_3^+ is carbonium ion or "methyl cation"; $(C_2H_5)_3C^+$ would be the "triethylcarbonium ion"; $C_6H_5CH_2^+$ would be "phenylcarbonium ion" or "benzyl cation." For nomenclature purposes, the parent structure from which the ion is derived is used as the frame of reference, and no effort is made to describe the various contributors to the resonance hybrid.

This system can be extended to describe multiply charged carbonium ions (for simplicity, we consider only dipositive ions, but the system can be generalized). We propose, first, two major categories of dipositive ions, to be termed "*ordinary*" and "*extraordinary*." *Ordinary* dipositive ions are produced by single ionizations at two separate sites in a molecule. A typical example would be III, derived from the



III

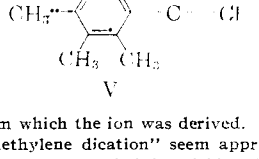
corresponding glycol or dihalide. (One can visualize many such ions, and we are currently investigating their spectra, *pK*'s and chemistry.) It is proposed that the prefix *di* (or *tri*, etc.) be placed before the words "carbonium ion" or "cation" to describe such species; III would then be tetraphenyl-*p*-phenylenedicarbonium ion. Just as $C_6H_5^+$ is the phenyl cation, $C_6H_4^{++}$ would be *o*-, *m*- or *p*-phenylene dication, and IV



IV

would be tetraphenyl *p*-phenylenecyclopropenyl dication.

Extraordinary dipositive carbonium ions are defined as those which have been produced in a formal sense by two ionizations at a single carbon atom. Ion II is of this type, and can be named as a derivative of CH_2^{++}, the name being based on the formal structure V, related to the



V

parent molecule from which the ion was derived. The names "dicarbonium ion" or "methylene dication" seem appropriate for CH_2^{++}. Ion II then becomes pentamethylphenylchlorodicarbonium ion or pentamethylphenylchloromethylene dication.

[22] For another chemical consequence of this steric strain, see ref. 10. Whether both methyl groups are necessary or whether one may be sufficient will be discussed in a separate paper, but some evidence is in hand that one methyl is sufficient.

[23] M. Ballester and C. Molinet in an abstract of the D.Sc. thesis of the latter, 1958, p. 18; we are indebted to Professor Ballester for reprints of his papers.

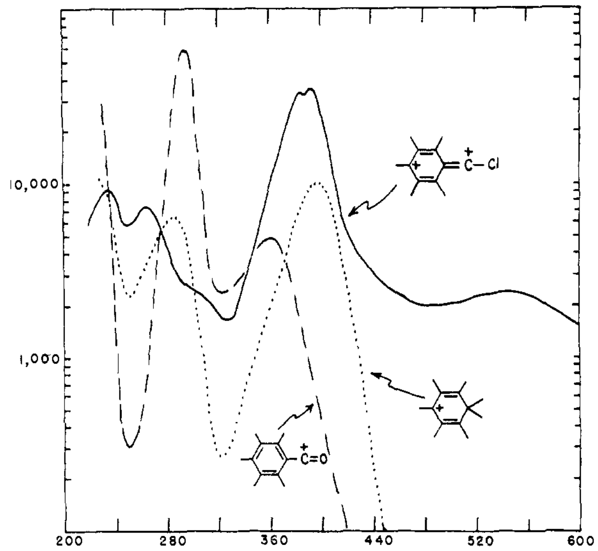
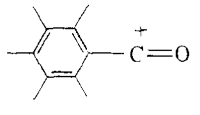


Fig. 1.—Visible and ultraviolet absorption spectra of three carbonium ions: II, —, and VII, — —, in 100% sulfuric acid; VIII, ..., in concentrated hydrochloric acid, data from ref. 26.

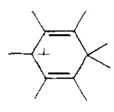
to the formation and stability of "extraordinary" dications will have to be investigated.[24]

The evidence for the existence of II thus far presented is circumstantial. It seemed desirable to make some direct observations on the dication itself, and we report here on its visible, ultraviolet and nuclear magnetic resonance spectra.

Spectra of II.—Compound II is deep red. Its visible and ultraviolet absorption spectrum is compared in Fig. 1 with those of the pentamethylbenzoyl cation (VII) (determined by us, but previously reported by Newman and Deno[12]) and the 1,1,2,3,4,5,6-heptamethylbenzeneonium ion (VIII) of Doering.[25,26] Compound II shows five maxima



VII



VIII

at 235 mμ (log ε 3.96), 265 mμ (log ε 3.87), 385 mμ[27] (log ε 4.51), 393 mμ (log ε 4.54) and 545 mμ (log ε 3.38).

Although there is some similarity in general shape, the positions of the maxima in the spectrum of VII are very different from those of II and whereas one can write plausible mechanisms for the formation of the acyl cation, it does not seem to be a product of the reaction of I with sulfuric acid. The gross features of the spectra of II and VIII also show some similarity, which is not surprising in view of certain structural features which the two ions have in common. The long wave length absorption of II is presumably associated with transitions made possible by the second positive charge and unavailable to VII or VIII. The spectrum of II was unchanged by flushing out the dissolved hydrogen chloride with nitrogen.

The n.m.r. spectrum of II is consistent with its structure. In Fig. 2, its spectrum in 100% sulfuric

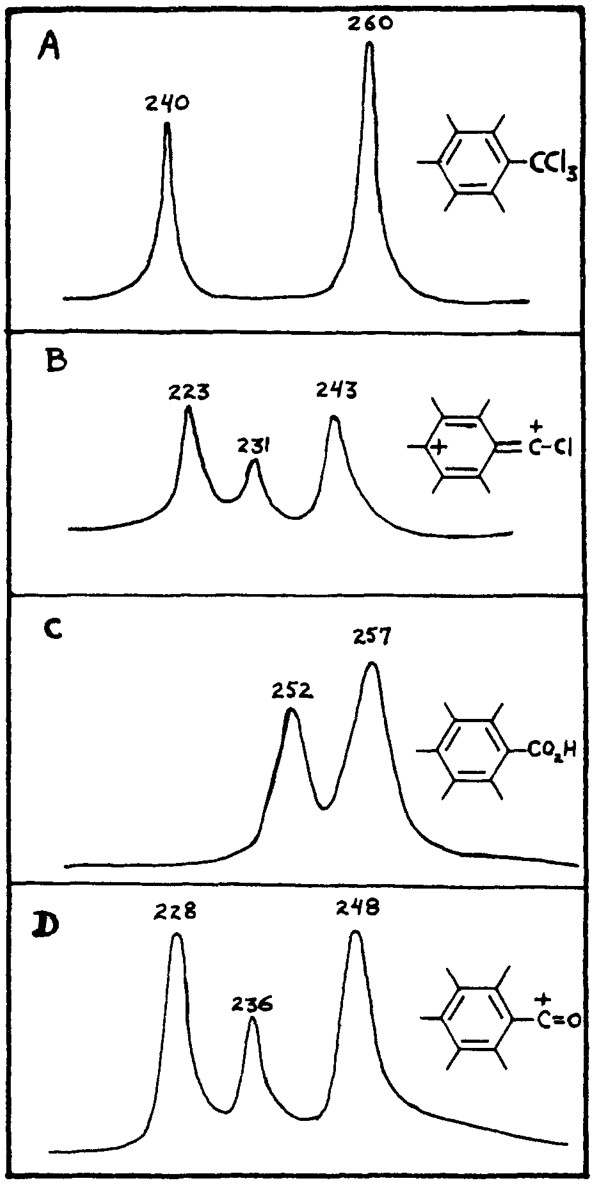


Fig. 2.—Nuclear magnetic resonance spectra, 60 mc.; numbers refer to c.p.s. from benzene; concentrations are about 2 *M* except for C, which is more dilute: A, I in CCl_4; B, I in 100% H_2SO_4; C, pentamethylbenzoic acid in chloroform; D, pentamethylbenzoic acid in 100% sulfuric acid.

acid is compared with that of the parent trichloromethylpentamethylbenzene (I) in carbon tetrachloride; also shown are the spectra of pentamethyl benzoic acid (IX) and the pentamethylbenzoyl

---

(24) One can visualize other driving forces for dication formation as, for example, the formation of an aromatic system. Thus an eight-membered ring with three double bonds and two positive charges (the carbonium homolog of the tropylium cation) or a four-membered ring with one double bond and two positive charges may have some aromaticity. We have some evidence for aromaticity, rather than steric strain, as a driving force in dication formation, and are actively pursuing this hypothesis (unpublished results with T. Sulzberg).

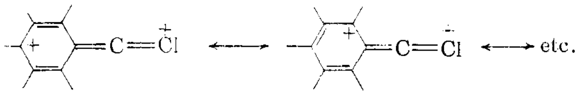
(25) W. von E. Doering, M. Saunders, H. G. Boyton, H. W. Earhart, E. F. Wadley, W. R. Edwards and G. Laber, *Tetrahedron*, **4**, 178 (1958). The curve in Fig. 1 is replotted from Fig. 2 of their paper.

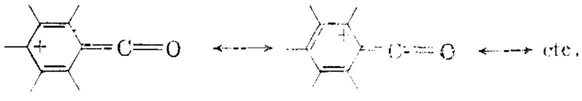
(26) Due to an arithmetical error, the extinction coefficients in our original communication[2] are low by a factor of about two.

(27) Reported in ref. 2 as an inflection.

cation VII.[28] The parent molecules and their derived ions have remarkably similar spectra. Both I and IX show two bands with relative areas 2:3; the first band presumably corresponds to the six protons on the two methyl groups *ortho* to the electron-withdrawing CCl_3 or COOH group. The protons on the *m*- and *p*-methyls appear at higher field and are not resolved. The separation between peaks is appreciably greater in I (20 c.p.s.) than in IX (5 c.p.s.).

The spectra of the two ions (II and VII) are virtually identical with three distinct bands having relative areas 2:1:2. These presumably correspond to the *o*-, *p*- and *m*-methyls, respectively, the *o*-protons occurring at lowest field (this assignment is tentative). The spectrum of VII may be shifted about 5 c.p.s. toward higher field than that of II, but this difference is possibly within the experimental error; the separations ($o - p = 8$ c.p.s. and $o - m = 20$ c.p.s.) are identical for both ions. It is gratifying that both ions have nearly identical spectra, because of the similarity of important contributing structures as IIa with VIIa, IIb with VIIb, etc.


IIa IIb

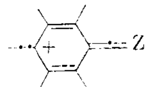

VIIa VIIb

The virtual identity of the magnetic environment of the methyl protons in both species is expected.

It is interesting to compare these results with the assignment given by Doering, *et al.*,[25] to the bands in the n.m.r. spectrum of VIII. This is done in Table IV (the chemical shifts of VIII were converted to 60 mc. by multiplication of the reported[22] values by 3/2). In each case the *m*-methyls appear at highest field, but in II and VII the *o*-methyls are at lower field than the *p*-methyl, whereas the reverse is true for VIII. This is consistent with the presence of strongly electron-withdrawing groups (Z in Table IV) adjacent to the *o*-methyls in II and VII, but of insulating and indeed electron-releasing gem-dimethyl as Z in VIII. Thus similarities (to VII) and differences (from VIII) in the n.m.r. spectrum of II when compared with ions of known structure provide confirmatory evidence for its structure.

TABLE IV

CHEMICAL SHIFTS OF SOME CARBONIUM IONS[a]



Ion	Z	*ortho*	*para*	*meta*
II[b]	$=C=\overset{+}{Cl}$ $(=\overset{+}{C}-Cl)$	223	231	243
VII[b]	$=C=O$	228	236	248
VIII[c]	$\begin{matrix}/CH_3\\ \backslash CH_3\end{matrix}$	218	206	234

[a] Shifts in c.p.s. relative to benzene, 60 mc. [b] In 100% sulfuric acid. [c] In concentrated hydrochloric acid; data taken from ref. 25.

Miscellaneous Experiments and Further Scope of these Investigations.—As reported earlier[2] the dipositive ion II can be prepared from I in nitromethane by adding a large excess of aluminum chloride (the excess is needed because much of the aluminum chloride is complexed with nitromethane). Several other procedures have now been developed. Compound I is not very soluble in trifluoracetic acid, but when boron trifluoride is passed through the suspension, the trichloromethyl compound dissolves rapidly giving a deep red solution of II. Evaporation of the solvent furnishes a red crystalline material insoluble in hexane, slightly soluble in chloroform and stable for long periods in trifluoracetic acid containing a little of the anhydride. Its spectra (visible, n.m.r.) are similar to those of II, except for solvent effects. Compound II may also be prepared by treating I in nitromethane with silver tetrafluorate ($AgBF_4$). Isolation of crystalline salts of II, which will be described in detail in a future publication, offers the opportunity to study the chemistry of dipositive ions without the obvious encumbrances associated with 100% sulfuric acid. Such studies are in progress, including reactions with nucleophiles, with olefins, etc.

Limited quantities of water can be tolerated in sulfuric acid and still give ion II from I, although slow hydrolysis occurs. The pink color is formed even in 85% sulfuric acid. Quantitative studies will be reported later of the *pK*'s of both ordinary and extraordinary multipositive carbonium ions.

Experimental[29]

Trichloromethylpentamethylbenzene (I).[6]—To a stirred suspension of 80.0 g. (0.6 mole) of anhydrous aluminum chloride in 100 ml. of carbon tetrachloride there was added slowly (2 hours) a solution of 45.0 g. (0.3 mole) of pentamethylbenzene[30] in 100 ml. of carbon tetrachloride. The slurry became deep purple and hydrogen chloride evolved immediately. The stirred reaction mixture was maintained at 37–42° by occasional heating. After all the pentamethylbenzene was added, stirring was continued for 2 more hours, after which hydrogen chloride evolution had ceased. The purple aluminum chloride complex was poured *slowly* into a stirred mixture of 300 g. of ice, 200 ml. of water and 50 ml. of concentrated hydrochloric acid. The brown organic layer was washed with three 50-ml. portions of warm (40°) water and dried over calcium chloride. The solvent was removed, either by distillation under reduced pressure or on a Rinco rotary evaporator, leaving a light brown residue of crude product in nearly quantitative yield. Several recrystallizations from *n*-pentane gave 55.5 g. (91%) of cream-colored platelets, m.p. 92–94°. Early work on physical properties of sulfuric acid solutions was done on this material, but it was not quite analytically pure (C about 1% high, Cl about 1% low, H in agreement with theory). Later, analytically pure white crystals of I, m.p. 95.5–96.0°, were obtained by repeated Norite treatment of a dilute solution of I in pentane, followed by concentration and crystallization.

Anal. Calcd. for $C_{12}H_{15}Cl_3$: C, 54.26; H, 5.69; Cl, 40.05. Found: C, 54.33; H, 5.72; Cl, 39.97.

---

(28) All peaks are in c.p.s. relative to benzene as an external standard, determined at 60 mc.

(29) Analysis by Spang Microanalytical Laboratory, P. O. Box 1111, Ann Arbor, Mich.

(30) We are grateful to Dr. R. J. Rolih and Dr. Ellis K. Fields, Standard Oil Co. (Indiana), for a generous supply of pentamethylbenzene.

Methanolysis of I.—Compound I (1.007 g.) was added to 0.707 g. of sodium methoxide in 15 ml. of absolute methanol. After the initial exothermic reaction, the mixture was refluxed for 3 hours. Methanol was removed (reduced pressure), water added and residual methanol removed by distillation. Cooling gave 0.711 g. of crystals. A second crop, obtained by further evaporation and extraction with ether, amounted to 0.048 g. The total yield of methyl pentamethylbenzoate before recrystallization was 0.759 g. (97.1%), m.p. (crude) 64–65.5°.

Reactions of Solutions of I in 100% Sulfuric Acid. With Water.—Compound I (5 g.) was dissolved in 25 ml. of cold 100% sulfuric acid. The intensely red solution was slowly poured onto crushed ice giving a flocculent white precipitate of pentamethylbenzoic acid, m.p. 208–210° [10b] from ethanol, in nearly quantitative yield. **With Methanol.**—In a similar experiment the solution of I in sulfuric acid was poured carefully into 50 ml. of absolute methanol kept at 0°. Work-up by the esterification procedure described by Newman[10b] gave a nearly quantitative yield of methyl pentamethylbenzoate, m.p. 67–67.5° from methanol.

Freezing Point Determinations. Apparatus.—The apparatus was similar to that described by Gillespie, Hughes and Ingold[31] except that a thermistor, calibrated from −5 to 20° against a U. S. Bureau of Standards platinum resistance thermometer (No. 1016073), was used in place of a Beckmann thermometer. The thermistor resistance was measured with a Leeds and Northrup Wheatstone bridge and galvanometer. Measurements were precise to 0.002° but accurate perhaps only to 0.010°. The cryoscopic apparatus was surrounded by a Styrofoam-insulated air jacket provided with an upward sloping side arm through which a piece of Dry Ice could be inserted to touch the cell wall and induce crystallization. Early measurements were made with magnetic stirring. A magnet, sealed in glass, was placed in the body of the apparatus, the whole of which, including cooling bath, was mounted above a magnetic stirrer. Although reliable results were obtained with known solutes, we were perturbed by the stirrer stopping after freezing commenced, and have now switched to a mercury-sealed motor-driven stirrer of special design to permit scraping of the vessel walls without touching the sensitive thermistor. In making a freezing point determination, all recommended precautions[32] concerning use of 100% sulfuric acid were observed. We are deeply indebted to Professor James L. Dye for assistance with the freezing point and conductance measurements. **Sulfuric Acid.**—Reagent grade acid was brought to maximum freezing point either by distilling in sulfur trioxide (all glass apparatus) or, simpler and equally satisfactory, by dilution with J. T. Baker reagent grade fuming sulfuric acid. The maximum was usually in the range 10.36 to 10.41°, compared with the generally accepted[13] value of 10.371° reported by Kinzler and Giauque.[33] The cryoscopic constant 6.12° kg./g.-mole, based on Rubin and Giauque's heat of fusion data[34] was used to calculate i, according to $i = \Delta T/6.12\ m_s$, where ΔT is the observed freezing point lowering and m_s is the molality of the solute. The data are summarized in Table I.

Quantitative Determination of Hydrogen Chloride.—A stream of nitrogen, dried by bubbling through two traps of 100% sulfuric acid, was passed through a solution of trichloromethylpentamethylbenzene in 100% sulfuric acid (all sulfuric acid solutions were maintained at 10–15° in the same cold bath) and then through a trap containing 2% sodium hydroxide. After various time intervals, the aqueous alkali trap was changed, acidified to *p*H 8 and chloride determined by the Fajans method, using dichlorofluorescein indicator and dextrin as the protective colloid. Control experiments on the Fajans method in the presence of varying amounts of sulfate (some SO_3 would be carried over from the 100% sulfuric acid) gave excellent results. The results are summarized in Table II.

In one experiment using 0.2136 g. of I, hydrogen chloride was removed as above for 60 minutes. The remaining solution was poured on crushed ice and there was isolated 0.1441 g. (93.3%) of pentamethylbenzoic acid. In a duplicate experiment, 0.2412 g. of I gave 0.1682 g. (96.3%) of pentamethylbenzoic acid. Titration of the aqueous layer (this was rather inaccurate, the end-point being difficult to see in the large volume of water) gave 1.050 moles of Cl^-/mole of I.

Conductance Measurements—The apparatus is described in detail by Thompson and Rogers.[35] Measurements were made at 25.000 ± 0.003° at frequencies of 400, 600, 1000, 2000 and 4000 c.p.s. The cell was a 30-ml. Leeds–Northrup–Jones type B conductance cell (constant 29.9) with bright platinum electrodes. The cell was rinsed several times with each solution whose conductance was to be measured, and thermostated for 30–45 minutes before measurements were begun. All transfers were carried out under a blanket of dry nitrogen. After each series of measurements, the cell was rinsed 12 times with distilled water, 12 times with conductivity water, then dried for several hours at 110° and allowed to cool in a dry nitrogen atmosphere.

Minimum conductance sulfuric acid, prepared by mixing 98% and fuming acid until a maximum resistance was obtained, had a specific conductance of 0.01046 ± 0.00003 ohm^{-1} $cm.^{-1}$ for about 10 determinations taken over a period of a year. Considering that we did not take the extreme (and necessary, for definitive work) precautions of Gillespie, Oubridge and Solomons,[36] our value agrees tolerably well with theirs (0.010432 ohm^{-1} $cm.^{-1}$) and was sufficiently precise to determine the molar conductances of various solutes. The experimental data are given in Table V (rounded average values, obtained from nearly linear plots of log λ *vs.* log c, were given in Table III). Variation with frequency was less than 0.1%; therefore only a single value for each molarity is given in Table V.

TABLE V

CONDUCTANCE DATA IN 100% SULFURIC ACID, 25.000°

Solute	M	λ
$KHSO_4$	0.1006	156.7
	.1987	121.6
o-$C_6H_4(NH_2)_2$	.05502	301.2
	.05306	307.0
	.1052	207.8
	.1128	215.1
	.2046	166.5
	.2044	161.7
I	.0513	304.3
	.0538	292.8, 297.3[a]
	.1001	210.5[b]
	.1005	213.4
	.2008	155.3

[a] The second value was obtained after flushing the solution free of hydrogen chloride with a dry N_2 stream; the first value was obtained before removing the hydrogen chloride. [b] Measured on a hydrogen chloride-free solution.

Spectra.—Ultraviolet and visible spectra were determined in 1-cm. ground glass stoppered quartz cells using a Beckman DK2 or DU spectrophotometer. N.m.r. spectra were determined on a Varian Associates instrument at 40 and 60 Mc. Only the 60 mc. spectra are reported, but the 40 mc. spectra were similar to them, with 2/3 the chemical shifts.

---

(31) R. J. Gillespie, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.* 2473 (1950).

(32) M. S. Newman, H. G. Kuivila and A. B. Garrett, THIS JOURNAL, **67**, 704 (1945).

(33) J. E. Kinzler and W. F. Giauque, *ibid.*, **74**, 5271 (1952).

(34) T. R. Rubin and W. F. Giauque, *ibid.*, **74**, 800 (1952).

(35) H. B. Thompson and M. T. Rogers, *Rev. Sci. Instruments*, **27**, 1079 (1956).

(36) R. J. Gillespie, J. V. Oubridge and C. Solomons, *J. Chem. Soc.*, 1804 (1957).