

TABLE XV
 SELECTED POTENTIAL ENERGY DISTRIBUTION DATA FOR THE DIMETHYLCARBONIUM ION

Mode	Frequency	K_{CC}	K_{CH}	H_{CC}	H_{CH}	H_{CH}	H_{HH}	H_{γ}	t	F_{CC}	F_{CH}	F_{HH}	ρ	C_{HH}	F_{CH}
(CH ₃) ₂ C+H															
a ₁	ν_4	1443	0	0.01	0	0	0.04	0.87	0	0	0.04	0.04	0	0	0
	ν_5	1362	0.05	.01	0	0	.28	.46	0	0	0.01	.18	0.03	-0.03	0
	ν_6	1127	.16	.01	0.08	0.02	.26	.06	0	0	.01	.34	0	-0.01	0
	ν_7	892	.39	.02	0	0	.15	.02	0	0	.05	.30	0	0	0.02
b ₁	ν_{15}	1443	0	.01	0	0	.04	.87	0	0	0	.03	0.04	0	0
	ν_{16}	1388	0.05	.02	0	0.33	.09	.12	0	0	0	.17	.01	0	0.01
	ν_{17}	1348	.16	0	0	.12	.22	.34	0	0	0	.09	.02	-0.02	.01
	ν_{18}	1156	.46	0.01	0	.07	.02	.02	0	0	0	.19	0	- .02	.02
	ν_{19}	964	.06	.01	0	0	.40	.07	0	0	0	.44	0	- .02	.02
(CD ₃) ₂ C+D															
a ₁	ν_6	1110	0.33	0.01	0.02	0.01	0.19	0.26	0	0	0.03	0.08	0.02	-0.02	0
	ν_4	1037	0	.01	.01	0	.01	.91	0	0	0	.01	.05	0	0
	ν_5	958	0.06	.02	.08	0.02	.25	.17	0	0	0.01	.35	.01	- .01	0
	ν_7	734	.22	.01	.01	0	.25	.04	0	0	0.05	.40	0	- .01	0.02
b ₁	ν_{18}	1251	.61	0	0	0.13	.04	.03	0	0	0	.15	0	0	.04
	ν_{17}	1051	.01	0.02	0	.12	.14	.46	0	0	0	.10	0.03	-0.02	0
	ν_{16}	1032	0	.02	0	.01	.09	.77	0	0	0	.07	.04	- .01	0
	ν_{15}	884	0.08	.01	0	.26	.05	.11	0	0	0	.15	.01	- .01	0.03
	ν_{19}	735	0.02	.01	0	.02	.43	.04	0	0	0	.47	0	- .01	0.03

The force constants used were based on the previous set (Table XI), but additional constants were required because of the presence of the unique H atom on the central carbon atom. Table XIII presents the assumed constants while Table XIV gives the calculated frequencies. A selected portion of the potential energy distribution data is reproduced in Table XV, where the modes most likely to arise in the region of experimental accessibility are collected.

Looking first for modes involving considerable K_{CC} contributions, we find ν_{18} in the b₁-species which, in the D-compound, has a 61% contribution. This mode is the antisymmetric CCC stretching mode and, although the calculated values are lower than the observed bands by about 100 cm.⁻¹ in both H and D compounds, we assign these strong bands to ν_{16} ; see Table IX. The agreement between observed and cal-

culated values could readily be improved by assuming a higher K_{CC} value. This implies a greater delocalization of the charge in this ion than in the trimethylcarbonium ion where the same K_{CC} value was found to be adequate.

The other outstanding band which remains to be assigned is that near 930 cm.⁻¹ in the D-compound, and this is probably to be associated with the band near 1500 cm.⁻¹ in the H-compound. If we argue by analogy with the trimethylcarbonium ion, we would require that these be CD₃ and CH₃ deformation modes, probably ν_{16} . However, another assignment seems to be more attractive and that is to ν_{16} which is approximately described as the in-plane bending mode of the CH bond involving the unique H. The calculated values are both low but could be increased by assuming a larger H_{CH} constant. Of course, ν_6 and ν_{16} may both be contributing to the 930 cm.⁻¹ band.

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The Hydrolysis of Dicarbonium Ions. Kinetics and Mechanism^{1,2}

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The hydrolysis of dicarbonium ions of the type I in concentrated aqueous sulfuric acid proceeds in a stepwise fashion, *via* an oxocarbenium (acylium) ion as a discrete intermediate. The nucleophile in 90–99.75% sulfuric acid is most likely the water molecule. Factors which influence the hydrolysis rates of different dicarbonium ions are discussed.

Certain substituted benzotrichlorides ionize in 100% sulfuric acid with the loss of two chloride ions, resulting in long-lived dicarbonium ions (I)³; the evidence for the structures of these ions will not be reviewed here, but it might be mentioned that crystalline salts of these dications can be prepared.⁴ Hydrolysis of I gave the corresponding benzoic acid quantitatively.

(1) Paper VI on Dicarbenium Ions; for the previous paper in this series, see H. Hart, T. Sulzberg, and R. R. Rafos, *J. Am. Chem. Soc.*, **85**, 1800 (1963).

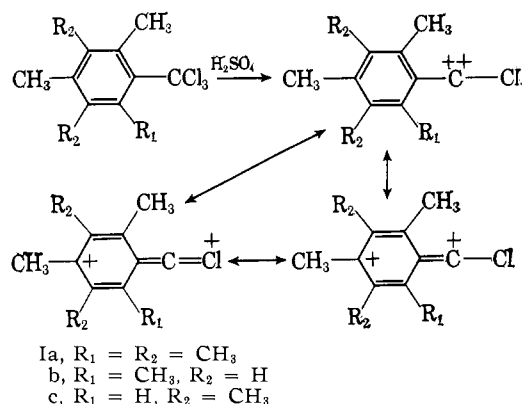
(2) We are indebted to the National Science Foundation for financial support and to the Dow Chemical Co. for a summer fellowship to N. R. R.

(3) H. Hart and R. W. Fish, *J. Am. Chem. Soc.*, **82**, 5419 (1960); **83**, 4460 (1961).

To examine factors which influence the stability of these ions, it would be desirable to measure their pK' 's of formation, by studying the ionization in sulfuric acid of varying strength. Unfortunately, hydrolysis of these ions in less than 100% acid prevents such experiments.⁵ It seemed that the rates of these hydrolyses might reflect the relative energies of dicarbonium ions, because one would expect the reaction of a doubly charged carbonium ion with a nucleophile to be highly

(4) H. Hart and J. S. Fleming, *Tetrahedron Letters*, 983 (1962).

(5) Although such experiments were thwarted in the present instance, they are possible for oxocarbenium (acylium) ions: H. Hart, C. Y. Wu, and J. T. Fleming, manuscript in preparation.



exothermic. The transition state, therefore, ought to resemble reactants,⁶ and substituent effects on the rate of the hydrolysis reaction might well parallel substituent effects on the stability of the dications.

This paper presents a kinetic study of the hydrolysis of three dicarbonium ions (Ia, b, c) and delineates some of the mechanistic details of the reaction. Solutions of the dicarbonium ions were prepared by dissolving weighed amounts of the corresponding benzotrichlorides in 100% sulfuric acid. These solutions were then mixed with appropriate volumes of more dilute (say 80–90%) sulfuric acid to bring the mixture to the desired acid–water composition, and the rate of disappearance of absorption bands due to the dicarbonium ions was followed spectrophotometrically. The acids produced are transparent in the region where the dicarbonium ions absorb intensely. All reactions were followed at $25.0 \pm 0.08^\circ$.

Results and Discussion

The reactions were pseudo first order; plots of $\ln A$ (absorbance) *vs.* time gave excellent straight lines and rate constants were calculated from their slopes in the usual way. The rate constants are summarized in Table I; each value of k is the average of two or more experiments.⁷

TABLE I

RATE DATA FOR THE HYDROLYSIS OF DICARBONIUM IONS IN AQUEOUS SULFURIC ACID AT $25.0 \pm 0.08^\circ$

Ion	H ₂ SO ₄ , ^a %	$k_1 \times 10^5$, sec. ⁻¹ ⁷	$a_w \times 10^{10}$	k_1/a_w
Ia	90.0	122 ± 1	24.0	5.1
	92.0	59.2 ± 1.9	11.2	5.2
	94.0	38.7 ± 0.1	5.02	7.7
	96.0	17.0 ± .3	2.08	8.2
	97.6 ^b	10.2 ± .1	0.72	14.2
	97.6 ^c	9.3 ± .1		
	99.0	3.02 ± 0.06	0.14	21.6
	99.25	2.03 ± .02		
	99.50	1.25 ± .01		
	99.75	0.53 ± .02		
Ib	97.6 ^d	538 ± 10		
Ic	97.6	1090 ± 10		

^a Rates were followed at 545 $m\mu$. ^b Initial concentration of dication was $9.06 \times 10^{-4} M$. ^c Followed at 393 $m\mu$; initial concentration of dication was $9.94 \times 10^{-5} M$. ^d Followed at 485 $m\mu$. ^e Values obtained by interpolation from a graph of the data given in ref. 8, Table IX.

By following the hydrolysis of Ia at two wave lengths (545 and 393 $m\mu$) it was possible to vary the initial ion

(6) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

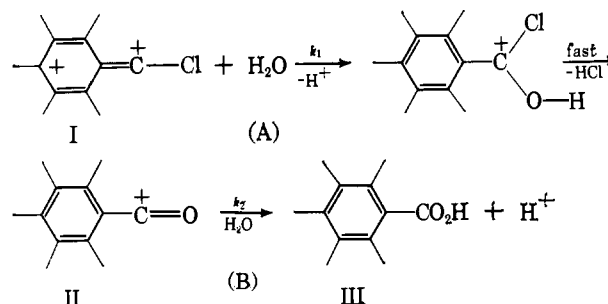
(7) As will be demonstrated below, these rate constants represent conversion of the dicarbonium ion to the corresponding oxocarbonium ion, rather than the complete hydrolysis to the acid.

concentration conveniently by a factor of ten. Reasonable agreement permits one to conclude safely that the reaction is first order in dicarbonium ion.

A decision about the nucleophile in 90–100% sulfuric acid has not been established unequivocally, but one would expect it to be the neutral water molecule, and a reasonably good case can be made for this experimentally. Of the major species present (H_3O^+ , HSO_4^- , H_2O), H_3O^+ , though present in much greater concentration than H_2O , is unlikely to react with a highly charged species of like sign, and bisulfate ion is bulkier and does not form a covalent bond with the dication even in 100% sulfuric acid.

The activity of water in aqueous sulfuric acid has been the subject of numerous measurements, the latest and most reliable of which are probably those of Giauque, *et al.*⁸ Even these are only approximate in regions of high acidity and extend only to 99% acid (*i.e.*, do not include part of the region of kinetic interest here). One can appreciate the considerable experimental difficulties associated with accurate activity measurements in this region. Furthermore, the activity of water changes rapidly in this region, decreasing by nearly 10^2 from 90 to 99% acid, and an estimated 10^3 from 99 to 100% acid.⁸ The ratio (k_1/a_w) of the observed pseudo-first-order rate constants for dicarbonium ion hydrolysis to the activity of water, which should be constant if water is the nucleophile, varies by a factor of 4 from 90–99% acid (Table I). Since k_1 and a_w each vary by about 10^2 over this range of acid composition, we consider that the variation of their ratio by only a factor of 4 is good evidence that it is the water molecule which reacts with the dicarbonium ion. Small errors in either a_w or in the composition of the acid used to measure the hydrolysis rates could easily account for the deviation of the k_1/a_w from precise constancy.

A reasonable mechanism for hydrolysis is attack of water on the carbonium carbon atom of I, followed by rapid loss of hydrogen chloride to form the oxocarbonium (acylium) ion II, which then reacts with a second water molecule to furnish the final product III. It seemed likely that since I and II have similar geometries



but II has less charge than I, the last step ought to be slower than the first ($k_2 < k_1$) and the oxocarbonium ion ought to be a discrete and detectable intermediate in the hydrolysis. This was, in fact, the case.

Pentamethylbenzoyl ion (II), obtained by dissolving the benzoic acid in 100% sulfuric acid, was hydrolyzed in 90 and 92% sulfuric acid, the rate being followed by disappearance of the intense band at 294 $m\mu$. Plots of $\ln(A_t - A_\infty)$ *vs.* time were linear and the pseudo-first-order rate constants (k_2 , Table II) were only about

(8) W. F. Giauque, E. W. Hornung, J. E. Kunzler, and T. R. Rubin, *J. Am. Chem. Soc.*, **82**, 62 (1960).

TABLE II

PSEUDO-FIRST-ORDER RATE CONSTANTS FOR THE SEQUENCE
 $Ia \xrightarrow{k_1} II \xrightarrow{k_2} III$ AT 25.0° IN AQUEOUS SULFURIC ACID

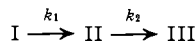
H ₂ SO ₄ , %	$k_1 \times 10^{12}$	$k_2 \times 10^4$ ^b	$k_1 \times 10^{12}$ ^c	$k_2 \times 10^4$ ^c
90.0	12.2 ± 0.1	1.13 ± 0.01	11.0	1.0
92.0	5.9 ± 0.2	0.41 ± 0.01	6.8	0.60

^a By disappearance of the 545 mμ band from solutions of Ia.

^b By disappearance of the 294 mμ band from solutions of II.

^c By fitting the curve for the appearance and disappearance of the 294 mμ band during hydrolysis of Ia.

one-tenth those for hydrolysis of the dicarbonium ion Ia in the same solvents. Ion II was detected as an intermediate in the hydrolysis of Ia by following the latter reaction, in 90 and 92% acid, at 294 mμ. Absorption started at zero, increased to a maximum, then decreased gradually (see Fig. 1). By treating the system as a series of two consecutive (pseudo) first-order reactions



with $k_1 > k_2$,⁹ both rate constants can be calculated. These values agree well (Table II) with those measured by following each step separately. It should be noted that the ratio of k_2 's in 90 and 92% acid is nearly identical with the ratio of k_1 's in the same solvents,¹⁰ consistent with the view that the nucleophile (presumably water molecules) is the same in both reactions.

One may comment briefly about substituent effects on the hydrolysis rates. There is a large (50-fold) increase in hydrolysis rate when the two *m*-methyl groups of Ia are replaced by hydrogens (compare Ia and Ib in 97.6% sulfuric acid, Table I). This large effect, at some distance from the reaction site, is probably a reflection of two factors. The methyl groups, by electron release mechanisms, undoubtedly lower the energy of Ia relative to Ib. But electron release alone seems insufficient to account for the rate difference, for if one uses $\sigma_m = -0.07$,¹¹ one would calculate a ρ of +12 (using $\log(k/k_0) = \rho(\Sigma\sigma_m)$; $k/k_0 = 1/53$, $\Sigma\sigma_m = -0.14$) which seems rather large for a bimolecular reaction. A second factor which may be operative is the buttressing

(9) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 153.

(10) This is especially so for the values of k_1 and k_2 obtained from the same experiment (Table II, columns 4 and 5) where there is no error due to differences in solvent concentration.

(11) J. Hine, "Physical Organic Chemistry," 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 89.

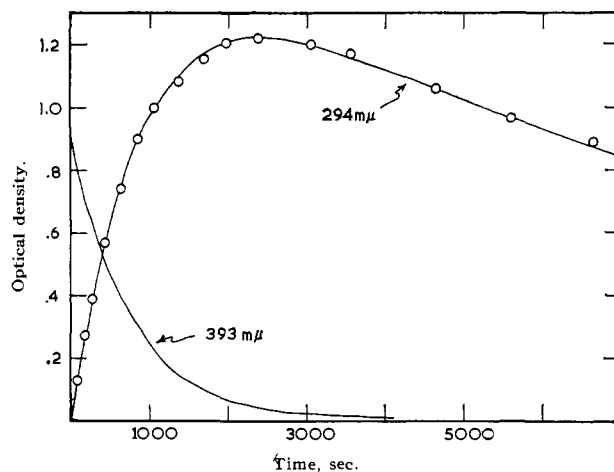


Fig. 1.—Hydrolysis of Ia in 90% sulfuric acid at 25.0° followed at two wave lengths (393 mμ, $3.92 \times 10^{-3} M$; 294 mμ, $2.45 \times 10^{-4} M$). The curve at 294 mμ illustrates the appearance of oxocarbonium ion II as a discrete intermediate. Circles represent experimental points; the solid curve is a fit of those points using data in Table II. The curve at 393 mμ is experimental.

effect of the methyl groups, which would raise the energy of the transition state for Ia relative to Ib. Compound Ic, which has one more methyl group than Ib, nevertheless reacts twice as fast with water molecules, again emphasizing the importance of steric effects on the reaction. Rate studies on other dicarbonium ions in which the steric factor is held constant (for example, 4-substituted 2,3,5,6-tetramethylbenzotrichlorides) should permit us to assess the value of the hydrolysis reaction as a measure of dicarbonium ion stability.

Experimental

Materials.—The polymethyl benzotrichlorides were prepared as described previously³; 100% sulfuric acid was prepared by mixing reagent grade 98% and fuming acid until a maximum freezing point was obtained. Concentrations of diluted acid were determined by titration.

Kinetic Procedure.—Stock solutions of trichloromethyl compound in 100% sulfuric acid were diluted at room temperature with aqueous acid so that the resulting solution had the desired acid composition. The solutions were transferred to stoppered quartz cells and placed in a Beckman DU spectrophotometer equipped with thermostats which maintained the cell housing at $25.0 \pm 0.08^\circ$. Results are given in Table I.

Rates of oxocarbonium ion hydrolysis were obtained in an analogous way, using pentamethylbenzoic acid in place of the benzotrichloride. Results are given in Table II.