with ethyl ether, the ether evaporated, and 50 ml. of 50% aqueous ethanol added to the residues in glass-stoppered erlenmeyer flasks. Addition of an aqueous ethanolic solution of sodium 3,5-dinitrobenzoate to one flask yielded benzyl 3,5-dinitrobenzoate, m.p. 108–110.8° (111.1–112.0° after recrystallization from alcohol). Volhard titration of the other 21 days later showed 100.3% chloride ion. This is evidence for benzyl chloride. From a third aliquot the dibenzyl sulfide was precipitated out of the ether layer by extraction with an alcoholic solution of mercuric chloride. The dibenzyl sulfide–mercuric chloride complex was filtered and dried in a desiccator, yield 88.4%, m.p. 134.6–135.5°.[17]

Kinetic Measurements.—All rates were measured by the usual sealed ampoule technique with about 6 ml. of solution in soft glass tubes. Zero time was taken after the tubes had been in the thermostat for about five minutes, at which time the initial concentration was determined by titration. For reaction of tribenzylsulfonium chloride, tubes were quenched in ice-water and an accurate 5-ml. aliquot of the contents added to a separatory funnel containing 10 ml. of ethyl ether. About 15 ml. of distilled water was added and the sample shaken thoroughly to remove benzyl chloride. When the emulsifying properties of the sulfonium salts prevented a clear separation of layers, a 5% solution of sodium acetate was used instead of distilled water to overcome this difficulty. The aqueous layer and two extracts of the ether layer were combined and titrated for chloride ion by the Volhard method (with nitrobenzene) with a blue (daylight) lamp bulb to facilitate recognition of the end-point. Titrations of samples of the reaction mixture for acid at the start of the reaction and at the end were made in order to check on any hydrolysis of benzyl chloride. No hydrolysis was detectable during the period of time of decomposition of the sulfonium salt. In the runs with perchlorate salts and no added chloride ion, titrations for acid were made to follow the reaction. Typical kinetic runs are given in Tables II and III.

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(17) Reported as 136° by L. Bermejo and J. J. Herrera, *Anales soc. españ. fis. quim.*, **32**, 682 (1934); *C. A.*, **28**, 6709 (1934).

[Contribution from the Department of Chemistry, Massachusetts Institute of Technology]

Mechanisms of Decomposition of Neutral Sulfonium Salts in Solution. II. t-Butyldimethylsulfonium Salts[1-3]

By C. Gardner Swain, Laura E. Kaiser and Terence E. C. Knee

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The hydrolysis of *t*-butyldimethylsulfonium chloride is not significantly faster than that of the perchlorate in 90% acetone–10% water solution at 50°. Therefore anions do not appear to be involved in the mechanism. Of 15 solvents and solvent-mixtures studied, 90% acetone–10% water gave the largest first-order rate constant for solvolysis and 100% water the smallest, but the range was less than a factor of four. The rate constant for solvolysis in 100% acetic acid is only slightly (28%) larger than that for hydrolysis in 100% water. This relatively low rate in 100% acetic acid suggests that the rate-determining step is reaction of acetic acid with trimethylcarbonium ion.

The decomposition of neutral *t*-butyldimethylsulfonium salts in 90% acetone–10% water solution is a solvolysis not involving a nucleophilic displacement on carbon by the anion, in contrast to the decompositions of trimethyl- and tribenzyl-sulfonium salts described in the previous paper.[2] Measurements[4] at 50° and 0.01 *M* ionic strength gave relative first-order rate constants of 1.00 for *t*-butyldimethylsulfonium perchlorate *vs.* 1.17 for the chloride, 1.12 for the bromide and 1.13 for the iodide. This less than 20% variation is in contrast to the greater than thousand-fold difference between perchlorate and chloride salts of trimethyl- and tribenzyl-sulfonium ions.[2,5] In agreement with this, previous workers[6] have reported first-order kinetics for *t*-butyldimethylsulfonium chloride in 80% ethanol and water from 50° to 80°. However, their kinetic study did not bear on the role of the anion, because the reaction of trimethylsulfonium ion with chloride ion, shown to be a direct one-step process in part I,[2] also gave first-order kinetics under the conditions of varying ionic strength which they employed. This perchlorate experiment establishes that the mechanism is not a slow reaction with anion followed by a fast solvolysis.

There are striking differences in the relative rates of solvolysis of *t*-butyl chloride and *t*-butyldimethylsulfonium ion in different solvents. *t*-Butyl chloride reacts less than a hundred thousandth *as fast* in either 90% acetone–10% water or 100% acetic acid as in 100% water. However *t*-butyldimethylsulfonium ion hydrolyzes more than three times *faster* in 90% acetone than in pure water, in spite of the fact that the water is ten times more dilute. Also its solvolysis in acetic acid is slightly faster than in water. Table I gives first-order rate constants for 15 different solvents and solvent mixtures. The rates of solvolysis of *t*-butyl chloride and *t*-butyldimethylsulfonium ion happen to be

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(1) Supported by the Office of Naval Research. Reproduction permitted for any purpose of the United States Government.

(2) *Cf.* Paper 1, C. G. Swain and L. E. Kaiser, This Journal, **80**, 4089 (1958).

(3) For further details, *cf.* T. E. C. Knee, Ph.D. Thesis in Organic Chemistry, M.I.T., September, 1956.

(4) L. E. Kaiser, Ph.D. Thesis in Organic Chemistry, M. I. T., February, 1951.

(5) We are indebted to Mr. David A. Kuhn for the observation that the variation is even less when a larger excess of inert salt is used. Thus the rate of solvolysis of 0.010 *M* sulfonium perchlorate at 50° in 90% acetone containing 0.11 *M* sodium perchlorate was the same as with 0.10 *M* sodium perchlorate and 0.010 *M* sodium chloride within 1%. Also the rate of 0.005 *M* sulfonium perchlorate at 50° in 100% acetic acid containing 0.012 *M* sodium acetate and 0.11 *M* sodium perchlorate was the same as with 0.012 *M* sodium acetate, 0.10 *M* sodium perchlorate and 0.010 *M* sodium chloride within 1%. The rate in acetic acid was unaffected by the concentration of sodium acetate (0.010 *M* sodium perchlorate, 0.010–0.021 *M* sodium acetate, no other salt). Increasing the ionic strength from 0.01 to 0.12 *M* with sodium perchlorate depressed the rate in these two solvents only very slightly. It is probable that the 17% variation with different anions noted above may be experimental error, caused, for example, by release of slight and variable amounts of water by the ion exchange resin used in the preparation of those salts, in spite of attempts to dry the resin thoroughly before use.

(6) K. A. Cooper, E. D. Hughes, C. K. Ingold and B. J. MacNulty, *J. Chem. Soc.*, 2038 (1948); K. A. Cooper, M. L. Dhar, E. D. Hughes, C. K. Ingold, B. J. MacNulty and L. I. Woolf, *ibid.*, 2043 (1948).

TABLE I

RATES OF SOLVOLYSIS OF 0.006–0.013 *M* *t*-BUTYLDIMETHYLSULFONIUM CHLORIDE AT 50.4°

Solvent, vol. %^{a}		k,^{b} sec.$^{-1}$ × 10^6	$\log(k/k^0)^c$	$D_{25°}{}^d$	$D_{50°}$	Y^e	$d_1{}^f$	$d_2{}^f$
EtOH	100	16.6	0.16	24.3	20.9	−2.03	−0.53	−1.03
	90	12.7	.04	29.2	25.1	−0.75	− .01	−0.54
	80	11.5	.00	34.9	30.1	0.00	.00	0.00
	60	9.15	− .10	46.7	40.7	+1.12	− .22	+1.34
	50	7.94	− .16	52.6	46.2	+1.66	+ .12	+1.33
	40	6.97	− .22	58.4	51.4	+2.20	− .26	+2.13
MeOH	100	14.7	.11	31.5	27.4	−1.09	− .05	−0.73
	96.7	13.6	.06	33.1	28.7	−0.82	− .11	−0.05
	69.5	9.44	− .09	47.9	41.3	+1.01	− .06	+1.32
Me_2CO	90	21.1	.26	25.3	22.4	−1.86	− .53	−1.52
	80	15.6	.13	32.1	28.3	−0.67	− .45	−0.68
	70	12.6	.04	38.9	34.3	+0.13	− .09	− .75
	50	9.55	− .08	52.0	46.2	+1.40	− .25	+ .97
H_2O	100	6.52	− .25	78.5	69.8	+3.49	− .44	+4.01
AcOH	100	8.33^g	− .14	6.2	6.4	−1.64	−4.82	+3.12

^{a} *N* vol. % A means *N* ml. of A at 25° per 100 − *N* ml. of water at 25° before mixing; EtOH = ethanol, MeOH = methanol, Me_2CO = acetone, AcOH = acetic acid. ^{b} First-order rate constant, $0.693/t_{1/2}$. ^{c} Decimal logarithm of rate constant relative to that in 80% ethanol. ^{d} Dielectric constant at 25° interpolated from data of G. Åkerlöf, THIS JOURNAL, **54,** 4125 (1932), or (for acetic acid) of C. P. Smyth and H. E. Rogers, *ibid.*, **52**, 1824 (1930), for weight % values calculated from first column using densities of 0.997, 0.785, 0.787 and 0.787 for water, ethanol, methanol and acetone at 25°. ^{e} Solvent "ionizing power."[7] ^{f} Solvent parameters for solvolysis of alkyl halides and esters.[8] ^{g} Used 0.019–0.022 *M* sulfonium chloride and 0.056–0.062 *M* sodium acetate in acetic acid.

the same in acetic acid at 50° within a factor of two.[7]

We attempted to correlate the observed changes in rates of solvolysis in different solvents with various solvent parameters including reciprocal[9] and logarithm[7] of dielectric constant (D), solvent "ionizing power" based on *t*-butyl chloride (Y),[7] and two solvent parameters based on a wider variety of alkyl halides and esters ($c_1d_1 + c_2d_2$, where c_1 and c_2 are each adjusted for the best fit).[8] For each of these parameters (P), values α and β in

$$\log(k/k^0) = \alpha P + \beta \qquad (1)$$

were determined from data for all 15 solvents by the method of least squares, and a simple measure of the goodness of the fit (Φ)[10] was calculated. Table II gives the results.[11]

TABLE II

CORRELATION OF LOG (k/k^0) FOR SOLVOLYSIS OF *t*-BUTYLDIMETHYLSULFONIUM CHLORIDE WITH VARIOUS SOLVENT PARAMETERS BY EQUATION 1

Parameter	α	β	Φ, %
$1/D_{50°}$	+0.143	−0.021	0
$\log D_{25°}$	− .084	+ .113	8
$\log D_{50°}$	− .106	+ .142	12
Y	− .107	+ .000	51
d_1,d_2	−0.031, −0.094	+ .024	71

None of the correlations are very good. In the best of them, *viz.*, the ones *vs.* Y or d_1 and d_2, the observed rate for acetic acid is much too small to agree with the calculations. Thus the rates do not appear to be determined primarily by any one of the following variables: dielectric constant, combined cation and anion solvating power, solvent nucleophilicity or solvent electrophilicity (anion solvating power).

For the water–alcohol solvents, it seems likely that these log (k/k^0) values determined with *t*-butyldimethylsulfonium ion are dependent primarily on the cation-solvating power of the solvent. For pure ethanol, methanol and water they decrease in the same fashion that the free energy of solvation for silver ion increases.[12] In contrast to the strongly-solvated anionic leaving group in the solvolysis of *t*-butyl chloride, the leaving group from *t*-butyldimethylsulfonium ion is an uncharged molecule (dimethyl sulfide), in much less need of electrophilic solvation. Consequently variations in rate from one solvent to another should be principally due to differences in ability of the different solvents to solvate cations. The positive charge is more concentrated in the reactant sulfonium ion than in the transition state, where it is distributed over sulfur, carbon and nine hydrogens. Hence the most polar solvents or best cation-solvating solvents retard the reaction by stabilizing the reactant more than the transition state. Rate constants are greatest in the least polar solvents where the electrostatic advantage of charge dispersal is greatest. One can then understand much of the scatter in the correlations, because none of the parameters in Table II is primarily a measure of cation-solvating power.

However, the failure of acetic acid to be the fastest of the group is unexpected even on the basis of cation-solvating power, because acetic acid would be expected to be the poorest at solvating cations. It has by far the lowest dielectric constant, dipole moment and basicity of any of the solvents or solvent components studied. Its dielectric constant is 6.4 *vs.* 20 or more for all of the others. Its dipole moment (liquid, 25–50°) is zero,[13] in contrast to water, the alcohols and acetone which are all

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(7) A. H. Fainberg and S. Winstein, THIS JOURNAL, **78**, 2770 (1956); E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948).

(8) C. G. Swain, R. B. Mosely and D. E. Bown, *ibid.*, **77**, 3731 (1955).

(9) G. Scatchard, *J. Chem. Phys.*, **7**, 657 (1939).

(10) C. G. Swain, D. C. Dittmer and L. E. Kaiser, THIS JOURNAL, **77**, 3740 (1955).

(11) We are indebted to Mrs. Inka Allen for these calculations.

(12) F. K. V. Koch, *J. Chem. Soc.*, 279 (1928).

(13) C. P. Smyth and H. E. Rogers, THIS JOURNAL, **52**, 1824 (1930).

above 2.5 Debye units. The pK_A of its conjugate acid is −6.2 in contrast to a less negative value for acetone and much less negative values for water and the alcohols.[14] For all of these reasons the cleavage of sulfonium cation to the *t*-butyl cation should be faster in acetic acid than in any of the other solvents.

We interpret the relatively low rate in acetic acid as evidence that there is significant covalent bonding between acetic acid and the *t*-butyl group in the transition state. Acetic acid is the weakest nucleophile of the hydroxylic reagents that we have used. Hence it is very likely that the rate-determining step in acetic acid is the reaction of acetic acid with trimethylcarbonium ion, rather than the formation of trimethylcarbonium ion.

Experimental

Reactants.—For the aqueous alcohol solvents, U. S. I. absolute ethanol or Fisher reagent grade methanol was used without further purification. For 100% ethanol, the ethanol was dried by addition of excess sodium metal and ethyl formate more than equivalent to the water but less than equivalent to the sodium. After refluxing for four hours, distillation gave ethanol containing less than 0.01% water.[15] Methanol was dried by refluxing with calcium hydride for five hours before distilling. Acetone was reagent grade, dried over Drierite, distilled, and the middle fraction used. Dry acetic acid was prepared from Mallinckrodt reagent (dichromate test) glacial acetic acid by refluxing for three days with an amount of analytical reagent acetic anhydride equivalent to three to four times the amount of water present. The acetic acid was then separated from the anhydride by distilling through a four-foot glass-helices column, b.p. 118.0–118.2°. The concentration of anhydride in the acetic acid was shown to be less than 0.1% by the anthranilic acid test.[16]

A sodium hydroxide carbonate-free solution (0.0155 *M*) was made by filtering 50% aqueous sodium hydroxide and diluting with boiled distilled water. Sodium carbonate reagent grade was dried at 260–270° for half an hour and cooled in a desiccator. Standard solutions of sodium acetate in acetic acid prepared by dissolving weighed quantities of sodium carbonate in purified acetic acid were used to standardize the 0.031 *M* toluenesulfonic acid (Eastman Kodak Co. white label) in acetic acid using a saturated solution of brom phenol blue in acetic acid as indicator.[17]

t-Butyldimethylsulfonium iodide was prepared by reaction of equimolar amounts of dimethyl sulfide (Eastman Kodak white label, b.p. 37–37.5°) and *t*-butyl iodide (b.p. 33° at 75 mm.) in nitromethane solution for three days. The product was filtered, recrystallized from 95% ethanol, washed with ether and dried, dec. p. 160–161° (T.E.C.K.), 164.5–166° (L.E.K.), 160° (literature[18]).

t-Butyldimethylsulfonium chloride was prepared by shaking an aqueous solution of the iodide with an excess of freshly prepared silver chloride until no iodide could be detected in the solution. The test used for the iodide ion was oxidation with a drop of chlorine water and extraction of the iodine into chloroform, where its characteristic color was most easily detected. Evaporation under reduced pressure gave a white solid, dec. p. 135–138°, 99% pure by Volhard titration for chloride ion. *t*-Butyldimethylsulfonium bromide and perchlorate were prepared by passing the iodide in 90% acetone over a Nalcite anion-exchange resin column containing exchangeable bromide or perchlorate ion.[19] These compounds were used without isolation from the eluate. Chloride obtained by this method and used for kinetics in 90% acetone without isolation from the eluate gave a rate constant for decomposition in 90% acetone identical within experimental error to that obtained from the filtrate of a suspension of silver chloride and sulfonium iodide in 90% acetone shaken for 12 hours.

Kinetic Measurements.—For work in solvents containing 10% or more of water, a quantity of aqueous stock solution of *t*-butyldimethylsulfonium chloride was diluted with distilled water and organic solvent to give an approximately 0.01 *M* solution. Sealed glass ampoules containing about 6 ml. each were placed in a 50.4 ± 0.15° thermostat. After about 10 minutes in the thermostat, timing was begun and a "zero time" tube withdrawn. Each tube was quenched in ice, brought to room temperature and a 5-ml. aliquot titrated with the sodium hydroxide using brom thymol blue as indicator. The initial concentration was obtained from an "infinity time" tube after ten or more half-lives. For work in less aqueous solvents, the same procedure was used except that solid *t*-butyldimethylsulfonium chloride was weighed out and dissolved in the desired solvent. A weighed excess of sodium acetate, dried by fusing reagent grade trihydrate at 140° for three hours, was added to the acetic acid solutions, and reaction followed by titration of acetate by toluenesulfonic acid in acetic acid using brom phenol blue as indicator.

First-order rate constants were obtained graphically from semi-logarithmic plots of percentage unreacted *vs.* time by reading $t_{100\%}$ and $t_{50\%}$ off the best straight line fitted by eye and using them in the formula $k_1 = 0.693/(t_{100\%} - t_{50\%})$. Each first-order rate constant reported is the average of two (or more) constants, from kinetic runs with different initial concentrations of sulfonium salt, agreeing to better than 5%. This suggests that the log (k/k^0) values are probably reliable to ±0.02 (±5% in k/k^0). No study was made of the effect of ionic strength on rate constant, but it would be expected to be much smaller in this reaction than in the decomposition of tribenzylsulfonium chloride[2] (which destroys charges) or the hydrolysis of *t*-butyl chloride (which creates charges).

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(14) M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 40 (1957). Although acetone itself has not been measured, its position can be estimated by using the measured values for benzoic acid (−7.4) and acetophenone (−6.1).

(15) G. R. Robertson, "Laboratory Practice of Organic Chemistry," The Macmillan Co., New York, N. Y., 1943, pp. 178, 296.

(16) S. Kilpi, *C. A.*, **35**, 2445 (1945).

(17) S. Winstein, E. Grunwald and L. L. Ingraham, THIS JOURNAL, **70**, 827 (1948).

(18) E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 1571 (1933).

(19) For the work described in footnote 5, *t*-butyldimethylsulfonium perchlorate was prepared from the sulfonium iodide and just equivalent silver perchlorate. The filtered water solution, which gave no tests for iodine, halide and silver ions, was concentrated in a rotatory vacuum evaporator at room temperature. The white crystals were filtered, dried under vacuum over phosphorus pentoxide and crystallized from methanol, dec. p. 178.5–179°. *Anal.* Calcd. for C_6H_{15}-$SClO_4$: C, 32.95; H, 6.91; S, 14.66; Cl, 16.21. Found: C, 32.72; H, 6.90; S, 14.81; Cl, 16.08.