butenoic acid,[6] 2- and 4-chloro-3-phenyl-3-butenoic acids[4] and 2-phenyl-3-butenoic acid[7]) with acetic anhydride and with thionyl chloride, (3) the reaction of an α,β-unsaturated acid chloride (crotonyl chloride) with triethylamine,[8] (4) reactions of β,γ-unsaturated acid chlorides (4-phenyl-3-butenoyl chloride, vinylacetyl chloride[9] and 2-chloro-3-phenyl-3-butenoyl chloride) with triethylamine,[8] and (5) a silver oxide-catalyzed rearrangement of a vinyldiazoketone[8] (diazomethyl α-styryl ketone, obtained from the reaction of atropyl chloride[10] and diazomethane).

Experimental

2-Chloro-3-phenyl-2-cyclobutenone.—A solution of 0.4 g. of 2-chloro-3-phenyl-3-butenoic acid (IV) in 4.0 ml. of acetic anhydride was refluxed for 30 min. The reaction mixture was poured into 5% sodium bicarbonate solution containing crushed ice and stirred at room temperature for 3 hr. Extraction with ether, evaporation, sublimation and recrystallization from cyclohexane gave 0.08 g. of the ketone V, m.p. 63–65°, which was identified by its m.p., mixed m.p. and infrared spectrum.

The following experiment is reasonably typical of many of the attempted ring closures. A solution of 0.3 g. of α-fluoro-β-methylcinnamic acid[4] (VII) in 3 ml. of acetic anhydride was refluxed for 30 min. The reaction mixture was poured into 5% sodium bicarbonate solution and extracted with ether. Acidification of the sodium bicarbonate solution gave 0.20 g. of unchanged VII, m.p. and mixed m.p. 128–129.5°. The ethereal solution was dried over magnesium sulfate, filtered and the ether evaporated. The infrared spectrum of the residue indicated it to be a mixture of anhydrides. The mixture was dissolved in sodium bicarbonate solution and subsequent acidification gave 0.04 g. of the starting acid, m.p. and mixed m.p. 129–130°, which was also identified by its infrared spectrum.

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(6) R. P. Linstead and L. T. D. Williams, *J. Chem. Soc.*, 2735 (1926).

(7) H. Gilman and S. A. Harris, THIS JOURNAL, **53**, 3541 (1931).

(8) W. E. Hanford and J. C. Sauer in Roger Adams, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, pp. 123–126.

(9) Prepared from thionyl chloride and vinylacetic acid in the usual manner. For the preparation of the acid, see L. Talaise and R. Frognier, *Bull. Soc. Chim. Belg.*, **42**, 427 (1933).

(10) A. McKenzie and J. K. Wood, *J. Chem. Soc.*, **115**, 828 (1919).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Mechanisms of Decomposition of Neutral Sulfonium Salts in Solution. I. Trimethyl- and Tribenzyl-sulfonium Salts[1-3]

BY C. GARDNER SWAIN AND LAURA E. KAISER

RECEIVED MARCH 3, 1958

The decomposition of trimethyl- and tribenzyl-sulfonium salts in 90% acetone–10% water solution at 50–100° in the absence of strong bases involves neither carbonium ion formation nor solvolysis in the rate-determining step, but instead a reaction with the anion. The kinetics appears first order only because of exactly compensating salt effects. When a relatively inert anion (perchlorate) is used, no reaction occurs under the same conditions.

The decomposition of tri-*n*-alkylsulfonium salts in solution in the absence of strong bases has been found to be a first-order reaction. Halban studied the decomposition of triethylsulfonium bromide into ethyl bromide and diethyl sulfide by following the disappearance of bromide ion by a Volhard titration.[4] He found that the reaction was first order in 17 different solvents and solvent mixtures, including tetrachloroethane (studied from 18–70°), nitrobenzene (18–70°), acetone (30–60°), 90% acetone–10% water (70–90°), acetic acid and five alcohols. Essex and Gelormini[5] and Corran[6] also found first-order kinetics for this compound in various solvents. Gleave, Hughes and Ingold studied the decomposition of trimethylsulfonium salts in water, 60, 80 and 100% ethanol at 100°.[7] The chloride, bromide and carbonate gave constant and identical first-order rate constants in 100% ethanol within experimental error (7.3×10^{-5}, 7.8×10^{-5} and 7.4×10^{-5} sec.$^{-1}$, respectively, by Volhard titration for chloride and bromide ions and acid titration for carbonate ion), whereas calculated second-order rate constants varied by more than a factor of two in the course of a run. Added carbonate ion (as tetraethylammonium carbonate) did not alter the rate of decomposition of trimethylsulfonium carbonate. It was concluded that the reaction was unimolecular, with

$$(CH_3)_3S^{\oplus} \longrightarrow CH_3^{\oplus} + (CH_3)_2S \qquad (1)$$

as the rate-determining step.

On the other hand, the strongly basic sulfonium salts, trimethylsulfonium phenoxide and hydroxide, gave second-order kinetics.[7] The appreciable effect of ionic strength was noted, and rate constants were compared at concentrations in the neighborhood of 0.1 M (0.013 M^{-1} sec.$^{-1}$ for phenoxide and 0.74 M^{-1} sec.$^{-1}$ for hydroxide in 100% ethanol). The reaction with hydroxide was 20,000 times faster in 100% ethanol than in water, but the kinetics was second-order in both solvents. The reactions with phenoxide and hydroxide ions were interpreted by a single-stage bimolecular mechanism

$$RO^{\ominus} + (CH_3)_3S^{\oplus} \longrightarrow ROCH_3 + (CH_3)_2S \quad (2a)$$

The authors concluded that they had observed a "point of mechanistic change" between the carbonate and phenoxide ions.

Since a methyl cation is an especially high-energy carbonium ion, three possibilities in addition

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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 II, C. G. Swain, L. E. Kaiser and T. E. C. Knee, THIS JOURNAL, **80**, 4092 (1958).

(3) For complete experimental details, *cf.* L. E. Kaiser, Ph.D. Thesis, M. I. T., February, 1954.

(4) H. v. Halban, *Z. physik. Chem.*, **67**, 129 (1909).

(5) H. Essex and O. Gelormini, THIS JOURNAL, **48**, 882 (1926).

(6) R. F. Corran, *Trans. Faraday Soc.*, **23**, 605 (1927).

(7) J. L. Gleave, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 236 (1935); C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, pp. 336, 339; Y. Pocker, *J. Chem. Soc.*, 525 (1958).

TABLE I

DECOMPOSITION OF SULFONIUM SALTS IN 90% ACETONE–10% WATER

Sulfonium salt	Concn., *M*	Addend	Concn., *M*	Temp., °C.	k_2, M^{-1} sec.$^{-1}$
$(CH_3)_3SClO_4$	0.0196	None	....	100.3	<0.0001[a]
$(CH_3)_3SClO_4$	.0110	LiCl	0.0118	100.3	.272
$(C_6H_5CH_2)_3SClO_4$	.0144	None	....	50.0	< .0001[b]
$(C_6H_5CH_2)_3SCl$	.0093	$NaClO_4$	.0126	50.0	.0276
$(C_6H_5CH_2)_3SCl$	.0076	NaCl	.0099	50.0	.0263
$(C_6H_5CH_2)_3SCl$	.0072	$NaNO_3$	.0095	50.0	.0273
$(C_6H_5CH_2)_3SCl$	.0190	$NaClO_4$	.0228	50.0	.0219
$(C_6H_5CH_2)_3SCl$	.0174	$(C_2H_5)_3NH_3Cl$	.0216	50.0	.0207
$(C_6H_5CH_2)_3SCl$	.0170	$NaClO_4$	.0643	50.0	.0104
$(C_6H_5CH_2)_3SCl$	.0158	$NaClO_4$	.131	50.0	.0056
$(C_6H_5CH_2)_3SCl$	.0017	$NaClO_4$	.138	50.0	.0057

[a] Less than 1% hydrogen ion formed in 4830 min. [b] Less than 6% hydrogen ion formed in 1285 min.

to equation 1 for the rate-determining step in decomposition of trimethylsulfonium chloride, bromide and carbonate seem worthy of consideration: (2) the mechanism might still involve the anion in these cases with the participation of the anion extraordinarily well obscured by very large salt

$$X^{\ominus} + (CH_3)_3S^{\oplus} \longrightarrow XCH_3 + (CH_3)_2S \qquad (2)$$

effects, or (3) the rate-determining step might involve reaction with the solvent

$$ROH + (CH_3)_3S^{\oplus} \longrightarrow ROHCH_3^{\oplus} + (CH_3)_2S \quad (3)$$

followed by a fast reaction of the oxonium ion with the anion (X^-), or (4) the mechanism might always involve the anion yet give first-order kinetics if the salts used were predominantly in the form of ion-pairs in solvents such as 90% acetone and 100% ethanol.[8]

$$[X^{\ominus}\,(CH_3)_3S^{\oplus}] \longrightarrow XCH_3 \qquad (4)$$

We therefore examined the conductivity of sulfonium salts and studied salt effects on the decomposition of trimethyl- and tribenzyl-sulfonium salts in 90% acetone at 50–100° in some detail to decide which of these four mechanisms is operative.

Conductivities in 90% Acetone–10% Water Solution.—The equivalent conductances of tribenzylsulfonium chloride and of sodium perchlorate were measured in 90% acetone at 25°. Plots of equivalent conductance *vs.* square root of concentration of salt were linear for each in the range employed below for kinetic studies, and the measured values of equivalent conductance agreed closely with ones calculated by the theoretical equation of Onsager[9] for strong electrolytes. Hence it appears that ion-pair formation is of negligible importance in this range. This excludes the ion-pair mechanism represented by equation 4 for tribenzylsulfonium chloride in 90% acetone.

Dependence of Rate on the Anion.—Table I shows that trimethylsulfonium perchlorate does not liberate hydrogen ion at a significant rate in 90% acetone at 100°.[10] Perchlorate ion is known to be considerably less nucleophilic than chloride, bromide and carbonate.[11] However, when lithium chloride was added, the chloride ion was consumed rapidly with good second-order kinetics. This proves that the anion is involved in the rate-determining step. It excludes the mechanisms represented by equations 1 and 3. The confusing evidence in the literature on the kinetics of sulfonium salt decompositions stems from the fact that previous investigators underestimated the magnitude of salt effects.

Thus a reaction with the anion appears to be the rate-determining step in all previous kinetic studies of trimethylsulfonium ion. In 90% acetone the reactants are dissociated ions (equation 2). In solvents like pure acetone, tetrachloroethane, etc., they are probably mostly ion-pairs (equation 4) or even larger aggregates.

Tribenzylsulfonium perchlorate also failed to liberate hydrogen ion at a significant rate in 90% acetone at 50°. Most of the subsequent work was done using tribenzylsulfonium chloride as the reactant in 90% acetone at 50°.

Kinetics at Constant Ionic Strength.—In order to minimize variations in rate due to varying salt concentration, a large amount of sodium perchlorate was added to most of our kinetic runs to keep the ionic strength effectively constant. This device was not used in previous kinetic studies of the decomposition of sulfonium salts. Table I records some of the results. In runs where the ionic strength was more than four times the concentration of sulfonium ion, the average deviation of second-order rate constants within runs was under 5%, whereas first-order rate constants showed a very large decrease as the reaction proceeded. Table II gives the results of a typical kinetic run. When sodium chloride was substituted for sodium perchlorate, the second-order rate constant, calculated using the total concentration of chloride ion, changed by only 5%.

Correlation of Salt Effects by the Limiting Brönsted–Debye Equation.—With tribenzylsulfonium chloride in 90% acetone at 50° with no added salt to maintain constant ionic strength, first-order rate constants were roughly constant to 80% reaction, whereas second-order constants increased about threefold. Table III gives the re-

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[8] F. M. Beringer and E. M. Gindler, THIS JOURNAL, **77**, 3200 (1955).

[9] S. Glasstone, "Textbook of Physical Chemistry," 2nd ed., D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 905.

[10] Methyl perchlorate is too reactive a compound to accumulate under these reaction conditions. Mr. Karl H. Lohmann has measured its reactivity under a variety of conditions. In a similar medium, 81% acetone–10% benzene–9% water, its rate constant for solvolysis at 25° is 1.2×10^{-3} sec.$^{-1}$, corresponding to a half-life of less than 10 minutes at 25°.

[11] J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 140.

TABLE II

DECOMPOSITION OF 0.0158 M TRIBENZYLSULFONIUM CHLORIDE IN 90% ACETONE–10% WATER WITH 0.131 M SODIUM PERCHLORATE AT 50°

Time, sec.	Titer, KSCN,[a] ml. 0.0251 M	Reaction, %	$k_1 \times 10^5$, sec.$^{-1}$	k_2, M^{-1} sec.$^{-1}$
0	1.56	0.0	..	.....
1740	1.98	13.3	8.20	0.00558
4380	2.43	27.6	7.47	.00540
7440	2.83	40.3	6.91	.00575
11100	3.12	49.6	6.15	.00552
15180	3.39	58.1	5.72	.00573
20340	3.60	64.8	5.09	.00565
30540	3.88	73.6	4.37	.00572
40320	4.04	78.8	3.84	.00571
49140	4.13	81.6	3.45	.00560
1503640	4.71	100.0	..	Av. 0.0056

[a] After addition of 5 ml. of 0.0237 M $AgNO_3$ to the 5-ml. aliquot.

sults of a typical kinetic run. However, it can be shown that this variation in second-order rate constants is very close to that predicted by the limiting form of the Brönsted–Debye rate equation. Decimal logarithms of the instantaneous second-order rate constants (slopes from a plot of $1/(R_3S^+)$ *vs.* t) were plotted *vs.* square root of ionic strength ($\sqrt{\mu} = \sqrt{(R_3S^+)}$ at the time where the slope was measured) for five kinetic runs.[3] The 26 points in the concentration range 0.001–0.01 M determine a straight line

TABLE III

DECOMPOSITION OF 0.0165 M TRIBENZYLSULFONIUM CHLORIDE IN 90% ACETONE–10% WATER AT 50°

Time, sec.	Titer, KSCN,[a] ml. 0.0251 M	Reaction, %	$k_1 \times 10^4$, sec.$^{-1}$	k_2, M^{-1} sec.$^{-1}$
0	1.53	0.0	..	....
400	2.04	15.5	4.16	0.0270
885	2.65	34.0	4.69	.0351
1216	2.99	44.2	4.76	.0391
1830	3.51	60.0	5.00	.0495
2465	3.86	70.5	4.97	.0588
3220	4.11	78.1	4.73	.0672
4712	4.41	87.3	4.38	.0876
276300	4.83	100.0	..	....

[a] After addition of 5 ml. of 0.0237 M $AgNO_3$ to the 5-ml. aliquot.

$$\log k_2 = -0.549 - 7.03\sqrt{\mu}$$

with Φ (measure of fit[12]) = 90% ("excellent" fit). The theoretical slope is −6.08, using a value of 22 for the dielectric constant of 90% acetone at 50°, obtained by interpolation from data of Åkerlöf.[13] This differs less than 15% from the value observed (−7.03).

Experimental

Reactants.—Acetone was Mallinckrodt analytical reagent. By "90% acetone" we mean 90 ml. of acetone at 25° per 10 ml. of water at 25° before mixing. Sodium perchlorate was anhydrous reagent grade from G. F. Smith Chemical Co. Other reagents used were generally reagent grade except where noted below. Melting points are corrected.

Tribenzylsulfonium chloride was prepared from dibenzyl sulfide (Eastman Kodak Co. white label grade) and anhydrous aluminum chloride in benzene solution by the method of Lee and Dougherty,[14] m.p. 82.8–84.0°.

Trimethylsulfonium iodide was prepared by allowing equimolar proportions of dimethyl sulfide and methyl iodide (both Eastman Kodak Co. white label) to interact at room temperature. After filtration, the salt was purified by recrystallization from absolute ethanol, decomposition point 211–212.5°.

Tribenzylsulfonium perchlorate was prepared by passing a solution of tribenzylsulfonium chloride in 90% acetone through a column of Nalcite S B R resin (National Aluminate Corp., Chicago) containing exchangeable perchlorate ion. The compound was used without isolation from the eluate. Trimethylsulfonium perchlorate was prepared similarly from trimethylsulfonium iodide. One ml. of resin holds approximately one milliequivalent of exchangeable anion. The resin was packed tightly in 10-ml. burets, keeping the column flooded at all times to prevent channeling. Anions were put on by passing an aqueous solution containing excess sodium perchlorate (or other anion) slowly through the column. The column was washed several times with carbonate-free water until all the adsorbed anion was removed, then repacked with 90% acetone as solvent. A 90% acetone solution of the sulfonium salt equivalent to less than 15% of the capacity of the column was passed through at one drop every 3–4 sec. After all the solution had passed through, the column was washed several times and the washings and eluate combined. Conductivity tests on the eluate showed that the conversion under these conditions was essentially quantitative in 90% acetone, 80% ethanol and mixtures of higher water content. However the conversion in 100% ethanol is not satisfactory.

Conductivity Measurements.—The conductivity bridge was model RC-1B from Industrial Instruments, Inc. The cell constant was 0.1 as determined from the conductivity of 0.1 M and 0.01 M solutions of potassium chloride at 25°. Theoretical equivalent conductances were calculated from,

$$\Lambda = \Lambda_0 - \left[\frac{82.4}{(DT)^{1/2}\eta} + \frac{8.20 \times 10^5}{(DT)^{3/2}}\Lambda_0\right]\sqrt{c}$$
$$= \Lambda_0 - (A + B\Lambda_0)\sqrt{c}$$

where Λ (cm.^{2} ohm^{-1}) is the equivalent conductance at concentration c (M), Λ_0 is the equivalent conductance at infinite dilution, D is the dielectric constant (27.0[15]), T is 298.2°, η is the viscosity (5.16×10^{-3}),[16] B is 1.14 and A is 178. Both the found and calculated values of Λ_0 for tribenzylsulfonium chloride were 72; for sodium perchlorate they were 128 (Table IV).

TABLE IV

EQUIVALENT CONDUCTANCE OF SOLUTIONS IN 90% ACETONE–10% WATER AT 25°

Concn., M	$\sqrt{\text{Concn.}}$, $M^{1/2}$	$\Lambda_{obs.}$, cm.^{2} ohm^{-1}	$\Lambda_{calcd.}$, cm.^{2} ohm^{-1}
	$(C_6H_5CH_2)_3SCl$		
0.0469	0.217	29.2	15.6
.00940	.0970	44.2	46.7
.00607	.0779	50.6	51.7
.00188	.0436	58.0	60.7
.000607	.0246	67.5	65.7
.000367	.0194	70.6	67.1
	$NaClO_4$		
0.104	0.323	67.1	23.0
.0506	.225	80.0	54.8
.0104	.102	93.9	94.6
.00206	.0454	110.3	112.8
.00104	.0323	115.2	117.1
.000401	.0200	124.7	121.0

Product Identification.—A 0.0268 M solution of tribenzylsulfonium chloride in 90% acetone was left at 50° for 30 hours. Two 10-ml. aliquots were then separately extracted

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

[13] G. Åkerlöf, *ibid.*, **54**, 4125 (1932).

[14] S. W. Lee and G. Dougherty, *J. Org. Chem.*, **4**, 51 (1939).

[15] "International Critical Tables," Vol. 6, p. 101.

[16] *Ibid.*, Vol. 5, p. 22.

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 puпose of the United States Government.

[2] *Cf.* Paper I, 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).