Kinetic Measurements.—The usual sealed ampoule technique was employed. Development of *p*-toluenesulfonic acid in acetic acid was followed by titration with sodium acetate in acetic acid, as previously described.[1,7] Ethanolysis rates were followed acidimetrically as previously described.[5] The new data reported in Table I were based on an average of six points per run followed to 70 to 90% completion. The observed kinetics for the runs in ethanol were all first order within experimental error of *ca.* ±1%. However, in a number of the runs in acetic acid the rate constants drifted down slightly in the course of the run. In these cases, a plot of the integrated rate constant k_t *vs.* per cent. reaction was treated as roughly linear. Extrapolation to zero reaction gave the initial rate constants listed in Table I. Table III summarizes the magnitudes of these downward drifts, expressed as the per cent. decrease from k_t^0 per 0.01 M reaction.

TABLE III

DOWNWARD DRIFTS IN RATE CONSTANTS DURING ACETOLYSIS

$(LiClO_4) \times 10^2$, M	% Decrease in k_t per 0.01 M reaction: o-$CH_3OC_6H_4CH_2CH_2$-OTs 50°	75°	p-$CH_3OC_6H_4CH_2CH_2$-OTs 50°	75°
0	4	9	3	7
0.00100			2	9
.0100	10	11	0	7
.0400			1	6
.100	4	6	0	5
1.00	0	2	0	0
3.00	0	2	0	0
6.00	0	0	0	0

LOS ANGELES 24, CALIFORNIA

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[7] S. Winstein, E. Grunwald and L. L. Ingraham, THIS JOURNAL, **70**, 821 (1948).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Correlation of Solvolysis Rates. III.[1] *t*-Butyl Chloride in a Wide Range of Solvent Mixtures[2]

BY ARNOLD H. FAINBERG AND S. WINSTEIN

RECEIVED DECEMBER 1, 1955

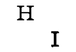
This paper is one of a series concerned with a detailed examination of the basis, scope and limitations of the linear free energy relationship for the correlation of solvolysis rates, $\log k = \log k_0 + m\mathbf{Y}$. Solvolysis data for *t*-butyl chloride at 25.0°, and the **Y** values derived therefrom, are reported for a greatly extended range of solvent composition. The solvents include mixtures of water with ethanol, methanol, formic acid, acetic acid, dioxane and acetone, and mixtures of formic acid with acetic acid and dioxane. They cover the complete range of composition for each binary pair. For interpolation, the **Y** values are expressed in analytical form as a function of the mole fraction of the more rapid component of each binary pair. The variation of log k for *t*-butyl chloride with various functions of the dielectric constant of the solvent, including $(D - 1)/(2D + 1)$, $1/D$, and $\log D$, is examined. The superiority of the $m\mathbf{Y}$ correlation over correlations of log k with these functions of dielectric constant is demonstrated for a number of compounds for which suitable solvolysis data were available in the literature.

The development of accurate correlations of the variation of rates of solvolysis of organic halides, benzenesulfonates, etc., with solvent change is important for diagnosing and controlling reaction mechanism in solvolytic substitution and rearrangement. In the first two papers[1] of this series, the linear free energy relation 1 was explored. In this equation

$$\log k = \log k_0 + m\mathbf{Y} \qquad (1)$$

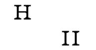
k and k_0 are the first order solvolysis rate constants for a certain substance in a solvent and in the standard solvent, 80% aqueous ethanol, respectively, and m is the compound parameter measuring sensitivity of solvolysis rate to **Y**, the measure of ionizing power of the solvent.

Our previous discussion[1b] of solvolysis was based on a continuous spectrum of transition states depending on structure and solvolytic conditions, structures I, II and III contributing to the hybrid transition state for the *first* step of a solvolysis. The solvolysis of *t*-butyl chloride in the common solvents was regarded as limiting (Lim.[1b]); in other words, the contribution of II to the hybrid transition state was regarded as negligible. This compound was made the standard substance for setting up a scale of **Y** values, these being set equal to log k/k_0 at 25°.



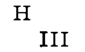
$\underset{\text{H}}{\text{SO}}\text{:}\ \text{R—X}$

I



$\underset{\text{H}}{\overset{\oplus}{\text{SO}}}\text{—R}\ \text{:X}^{\ominus}$

II



$\underset{\text{H}}{\text{SO}}\text{:}\ \overset{\oplus}{\text{R}}\ \text{:X}^{\ominus}$

III

TABLE I

RATES OF SOLVOLYSIS OF *t*-BUTYL CHLORIDE[a] AT 25.0° AND Y VALUES FOR SOLVENTS

Solvent, vol. %[b]	Method[c]	10^5k (sec.$^{-1}$)[d] 25.00 ± 0.02°	Y
EtOH–H_2O			
100	X	0.00860[e]	−2.033
98	X	.0193[v]	−1.681
95	X	.0479[v]	−1.287
90	X	.166[f,v]	−0.747
80	X	.926[g]	0.000
70	X	3.65[h]	0.595
60	X	12.32[i]	1.124
50	X	40.4	
50	H	41.9[j]	1.655
45	H	77.8	1.924
40	X	141	
40	H	145.6[k]	2.196
37.5	H	202	2.338
35	H	275.5	2.473
30	H	488	2.721
25	H	750	2.908
20	H	1043	3.051
15	H	1431	3.189

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[1] Previous papers in this series: (a) (I), E. Grunwald and S. Winstein, THIS JOURNAL, **70**, 846 (1948); (b) (II), S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951).

[2] Research sponsored by the Office of Ordnance Research, U. S. Army.

TABLE I (*Continued*)

Solvent, vol. %[b]	Method[c]	10^5k (sec.$^{-1}$)[d] 25.00 ± 0.04°	Y
10	H	1901	3.312
5	H	2310[w]	3.397
H_2O	H	2880[x]	3.493
$MeOH-H_2O$			
100	X	0.0753[l]	−1.090
90	X	0.464	−0.301
80	X	2.23	0.381
70	X	8.35	0.961
70	H	8.60	
60	X	28.6	1.492
60	H	28.9	
50	X	86.6	1.972
50	H	87.2	
40	H	228	2.391
30	H	525	2.753
20	H	981	3.025
10	H	1760	3.279
AcOH–HCOOH[m]			
100	X	0.0213	−1.639
100[n]		.0196[n]	−1.675[n]
90	X	.109[v]	−0.929
75	X	.62	− .175
50	X	5.3	.757
25	X	27.1	1.466
10	X	67.5	1.862
$HCOOH-H_2O$[m]			
100	X	105[o]	2.054
95	X	135.0	2.163
90	X	155	2.222
80	X	193	2.318
$66^2/_3$	X	265	2.456
50	X	408	2.644
$33^1/_3$	X	828	2.951
25	X	1170	3.100
14.29	X	1627	3.244
$AcOH-H_2O$[m]			
0.50 *M* H_2O	X	0.0369	−1.400
2.00 *M* H_2O	X	.127	−0.863
4.00 *M* H_2O	X	.366	− .404
8.00 *M* H_2O	X	1.45	.193
16.00 *M* H_2O	X	8.93	.984
60	X	30.6	1.519
50	X	80.4	1.938
40	X	190	2.312
25	X	646	2.843
Dioxane–H_2O			
90	X	0.00864[p]	−2.030
80	X	.136[p]	−0.833
70	X	.955	.013
60	X	4.80	.715
50	X	20.8	1.361
50	H	21.8	
40	H	81.6	1.945
30	H	264	2.455
20	H	699	2.877
10	H	1529	3.217
Me_2CO-H_2O			
95.2[q]			−2.76[q]
90	H	0.0131	−1.856
90	X	.0127[v]	
80	H	.197[r]	−0.673
70	H	1.25	.130
70	X	1.25	
60	H	5.80	.796
50	H	22.4	1.398
50	X	23.9	
40	H	88.7	1.981
30	H	281	2.482
25	H	453	2.689
20	H	758	2.913
10	H	1575	3.230
Dioxane–HCOOH[m]			
80	X	0.00469[v]	−2.296
60	X	.195	−0.677
40	X	2.34	.402
20	X	18.1	1.291
Formamide–H_2O			
100	X	3.72	0.604
80	X	22.4	1.383
97.5% $Ac_2O-AcOH$	H	0.00048[s]	−3.29
n-C_3F_7COOH			+1.7[t]
i-PrOH			−2.73[u]
t-BuOH			−3.26[u]

[a] Initial concentration 0.02–0.04 *M* where halide analysis was employed; 0.001–0.005 *M* where acidimetric analysis was used. [b] X vol. % A-B means *x* volumes of A plus 100 − *x* volumes of B, each at 25.0° before mixing. [c] H = acidimetric analysis; X = halide analysis. [d] The average deviation of all of the new rates herein reported that are constant is ±1.0% of *k;* the probable error *r* in log *k* is estimated to be 0.004. [e] Extrapolation to 25.0° of data reported[1a] at other temperatures in EtOH containing several concentrations of KOAc, with simultaneous linear extrapolation to zero salt concentration, gives 0.00916. [f] Previously reported[3] 0.171. [g] Previously reported 0.915,[3] 0.854,[4] 0.917,[5] 0.906,[6] 0.892.[7] [h] Previously reported 3.56,[6] 4.03.[3] [i] Previously reported 12.6.[3] [j] Previously reported 36.7.[3] [k] Previously reported 129.[3] [l] Previously reported 0.0811,[8] 0.0776.[10] [m] Unless otherwise indicated, solutions of AcOH–HCOOH, $HCOOH-H_2O$, dioxane–HCOOH, and $AcOH-H_2O$ contained 0.065–0.068 *M* lithium salts (acetate and/or formate); see Experimental section for details. [n] Estimated value at zero salt concentration. [o] Previously estimated 110.[1a] [p] Initial rate constant; upward drift in the run; see Experimental section. [q] Estimated[9] from data on *t*-butyl bromide[10] in acetone containing 0.170 mole fraction H_2O. [r] Calculation from data reported[3] at other temperatures gives 0.192. [s] Estimated by Grunwald and Winstein[1a] from data at 70.0°. [t] Estimated from data on α-phenylethyl chloride[9] in this solvent. [u] Estimated from data on *t*-butyl bromide[9] in these solvents. [v] Calculated from data at 50 and 75°.[9] [w] Previously reported[11] 2570 ± 300. [x] Previously estimated[1a] 3300.

Since the previous publications[1] on the correlation of solvolysis rates, we have accumulated a substantial body of data probing the basis, scope and limitations of linear free energy correlations. Because of the important position occupied by *t*-butyl chloride in some of the correlations, we have made an especially thorough study of the solvolysis of this substance in a greatly extended range of solvents. The kinetic data at 25° and the now extensive set of **Y** values are presented and applied in the present article. Also reported are the experimental methods employed in the accumulation of the data for this and a number of subsequent members of this series of papers.

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(3) E. D. Hughes, *J. Chem. Soc.*, 255 (1935).

(4) K. A. Cooper, E. D. Hughes, C. K. Ingold, G. A. Maw and B. J. McNulty, *ibid.*, 2049 (1948).

(5) H. C. Brown and R. S. Fletcher, THIS JOURNAL, **71**, 1845 (1949).

(6) H. C. Brown and H. L. Berneis, *ibid.*, **75**, 10 (1953).

(7) V. J. Shiner, Jr., *ibid.*, **76**, 1603 (1954).

(8) A. R. Olson and R. S. Halford, *ibid.*, **59**, 2644 (1937).

(9) A. H. Fainberg, unpublished work.

(10) W. H. Cropper, F. Spieth and A. R. Olson, THIS JOURNAL, **76**, 6248 (1954).

(11) C. G. Swain and S. D. Ross, *ibid.*, **68**, 658 (1946).

Results.—In Table I are summarized the first-order rate constants for solvolysis of *t*-butyl chloride in mixtures of water with ethanol, methanol, formic acid, acetic acid, dioxane and acetone, and in mixtures of formic acid with acetic acid and dioxane. Most of the rate constants in Table I are new, a few representing duplication as indicated in the footnotes. For the first time, these data cover the complete composition range for each of the binary solvent pairs. The very high solvolysis rates in pure water and in the very highly aqueous mixtures were measured by a new technique described in the Experimental section. For the whole body of data in Table I, the probable error r^{12} in the rate constants is estimated to be 0.004 in log *k* or 1% in *k*.

Table I also lists the set of **Y** values for the various solvents based on the new data, as well as a few **Y** values, indirectly derived, for solvents in which the solvolysis rate of *t*-butyl chloride has not been measured. Where the present **Y** values duplicate the previous[1] ones, the revisions are minor, except in the case of the aqueous acetones. For the latter solvents, **Y** values were previously based on *t*-butyl bromide, but Table I lists the set based on *t*-butyl chloride, the present values being different from the previous ones by as much as 0.3.

Y *vs.* **Mole Fraction.**—The variation of **Y** with composition of the binary solvent mixtures is illustrated in Fig. 1 with plots of **Y** *vs.* mole fraction of the more rapid component, water in the case of the aqueous solvent mixtures and formic acid for the acetic–formic acid and dioxane–formic acid mixtures. As mentioned previously,[1a] such plots are convenient for interpolation to obtain **Y** values for solvents of intermediate composition. For this purpose, the curves in Fig. 1 have been fitted by the method of least squares to the power series shown in equation 2, where *N* is the mole fraction of the more rapid solvent component. For mixtures

$$Y = a + bN + cN^2 + dN^3 + eN^4 \qquad (2)$$

of ethanol, dioxane or acetone with water, the three solvent pairs for which the plots of **Y** *vs.* *N* exhibit the most complex behavior, some simplification of the analytical form, as well as an improvement in the fits, were obtained by expressing the curves in two parts, one for the low, and the other for the high water range. The 40 parameters for the resulting eleven equations, summarized in Table II, reproduce the 76 experimental **Y** values with a pooled[12b] probable error[13] of 0.011 in log *k* or 2.5% in *k*. Interpolated values of **Y** of sufficient accuracy for correlation purposes can thus be calculated with these equations. However, it should be noted that the residual errors in these fits are mostly systematic, and that somewhat greater accuracy of interpolation can be obtained (estimated probable error of 0.004 in log *k*) from a large scale plot of **Y** *vs.* *N*.

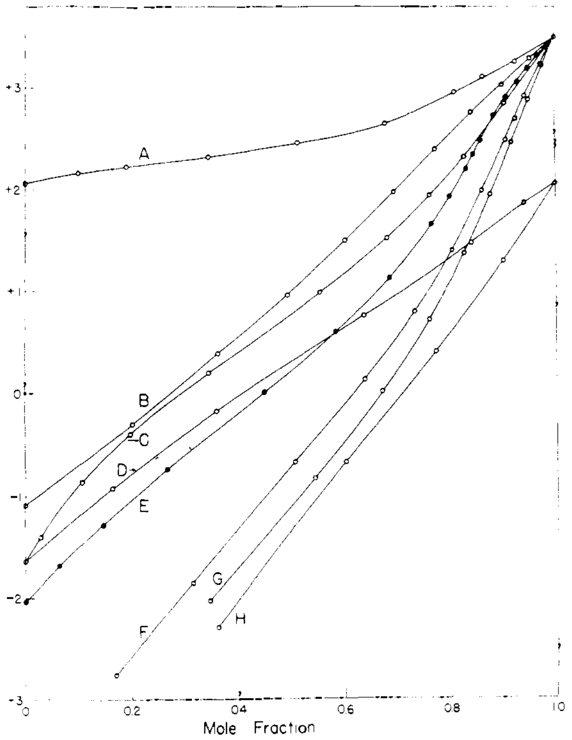

Fig. 1.—Plot of **Y** *vs.* mole fraction of fast component (H_2O or HCOOH) for HCOOH–H_2O (A): MeOH–H_2O (B); AcOH–H_2O (C); AcOH–HCOOH (D); EtOH–H_2O (E); Me_2CO–H_2O (F); dioxane–H_2O (G); and dioxane–HCOOH (H).

The solvent mixtures range from very poorly to highly nucleophilic media of widely varying ionizing power. For example, the series of acetic–formic acid mixtures is one in which ionizing power is varied over a wide range while nucleophilic character is held relatively constant at a level far below that of the aqueous alcohols.[1b] The series of aqueous formic acid mixtures, on the other hand, is one where nucleophilic character varies more than ionizing power. Nevertheless, the variation of **Y** with mole fraction of the more rapid component is remarkably similar for all of the solvent mixtures represented in Fig. 1. Table II lists, for each solvent pair, the composition of solvent at which the curves inflect. All of the curves have at least one inflection, and two of them, for ethanol–water and acetone–water mixtures, show a definite second inflection in the high water region. A second inflection for the dioxane–water curve is not as obvious; however, at the very least, the curve becomes linear in the high water region. Of the six aqueous solvent pairs, the methanol–water set is the only one for which the curve does not show an inflection in the low water region.

The portions of the plots of **Y** *vs.* *N* in the neighborhood of the points of inflection can be treated as linear. Such treatment has actually been applied by Cropper, Spieth and Olson[10] to solvolysis data for *t*-butyl chloride and bromide in a limited range of aqueous acetone mixtures. These authors

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(12) (a) A. H. Margenau and G. M. Murphy, "Mathematics of Physics and Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1943, p. 502; (b) W. J. Youden, "Statistical Methods for Chemists," John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 12, 15.

(13) The probable error of the fit,[12] *r*, is calculated with the equation

$$r = 0.6745\sqrt{\frac{\sum\limits_{i=1,\cdots n} d_i^2}{n-f}}$$

where *d* is the difference between the experimental and calculated values, *n* is the number of pieces of data, and *f* is the number of disposable parameters employed in the equation.

TABLE II

PARAMETERS FOR THE LEAST SQUARES FITS OF **Y** TO THE POWER SERIES, $Y = a + bN + cN^2 + dN^3 + eN^4$

Solvent pair	Range Vol. %	Range N[a]	a	b	c	d	N at inflection[b]	$(n - f)$[c]	r[13]
EtOH–H_2O	100–40	0–0.83	−2.042	6.086	− 6.209	6.024	0.34 .85[e]	6	0.013
EtOH–H_2O	40–0	0.83–1.00	−17.772	37.766	−16.509			7	.006
MeOH–H_2O[d]	100–0	0–1.00	−1.079	3.362	+2.173	−0.944	.77	7	.016
HCOOH–H_2O	100–0	0–1.00	+2.065	0.986	−1.342	1.801	.25	6	.015
AcOH–H_2O	100–0	0–1.00	−1.632	8.448	−13.714	15.205[f]	.40	6	.009
Dioxane–H_2O[d]	90–30	0.34–0.92	−5.641	15.837	−20.374	13.885	.49 .93[e]	3	.005
Dioxane–H_2O	40–0	0.88–1.00	−9.100	12.601				3	.005
Me_2CO–H_2O[d]	90–30	0.31–0.91	−5.101	14.955	−18.542	12.459	.50 .90[e]	3	.007
Me_2CO–H_2O[d]	50–0	0.80–1.00	−7.277	10.784				5	.011
AcOH–HCOOH	100–0	0–1.00	−1.634	4.544	−1.896	1.056	.60	3	.012
Dioxane–HCOOH	80–0	0.36–1.00	−5.777	12.477	−9.666	5.022	.64	1	.005

[a] N is mole fraction of the fast component of each binary pair, H_2O for the aqueous solutions and HCOOH for the AcOH–HCOOH and dioxane–HCOOH mixtures. [b] Unless otherwise noted, calculated from the equations. [c] $(n - f)$ is the number of independent checks of each equation, equal to the number of pieces of data fitted (n) minus the number of parameters (f) employed in the equation. [d] These equations reproduce the data of Cropper, Spieth and Olson,[10] adjusted to 25.0°, for the solvolysis of *t*-butyl chloride in MeOH–H_2O, N = 0–0.60, in dioxane–H_2O, N = 0.70–0.80, and in Me_2CO–H_2O, N = 0.51–0.80, with a probable error of 0.018 in log k. [e] Estimated from the plot of Y *vs.* N. [f] $e = -4.810$.

also cited several other examples of such linear dependence of log k on N. They did, however, recognize that these linear dependencies are the result of inflections in the plots.

Rates *vs.* Dielectric Constant.—The availability of a large body of rate data on *t*-butyl chloride solvolysis provides an opportunity to scrutinize possible correlations based on dielectric constant of the solvent. If we rewrite equation 1 in the form of equation[1] 3, the term m**Y** is replaced by

$$\log k = \log k_0 + \log (f_{RX}/f_{\ddagger}) \qquad (3)$$

$(f_{RX}/f_{\ddagger})$, the ratio of activity coefficients of the solvolyzing molecule and the transition state, respectively. Treating the activity coefficient of a dipole in terms of electrostatic forces, Kirkwood[14] has derived a linear relation between the log of activity coefficient and $(D - 1)/(2D + 1)$, where D is dielectric constant of the solvent. One can express both f_{RX} and $f_{\ddagger}$ in this form. Assuming dipole moments and dimensions of the RX and transition state dipoles to be independent of solvent, and the influence of non-electrostatic terms to be negligible, a linear relation is expected[15,16] between log k and $(D - 1)/(2D + 1)$.

A plot of log k *vs.* $(D - 1)/(2D + 1)$ was made by Laidler and Eyring[15a] for *t*-butyl chloride in 40–90% aqueous ethanol (D = 58 to 29). Similar plots have been made by others, for example, for acetic anhydride,[17–19] benzoyl chloride,[18,20] and benzyl[22] and substituted benzyl[23] *p*-toluenesulfonates in aqueous acetone. Also, such plots have been made for ethylene bromo- and iodohydrins[24] in aqueous ethanol, for *p*-nitrobenzyl bromide[25] in aqueous dioxane, and, recently, for methyl chloromethyl ether[26] in mixtures of ethanol with dioxane, benzene and carbon tetrachloride, and of *n*-butanol with benzene. In most of the cases, the range of dielectric constant examined was not large, so that linearity of the plot was tested over only limited portions of the possible ranges. In spite of this, definite departures from linearity are observable in a number of the plots, and in some, the curvature is considerable.

It becomes of interest to plot log k *vs.* $(D - 1)/(2D + 1)$ for *t*-butyl chloride for all of the data in the solvent mixtures for which dielectric constants are available. These solvent pairs include 0–90% aqueous dioxane (D = 78-6),[27] 0–95% aqueous acetone (D = 78-22),[28] 0–100% aqueous ethanol (D = 78-24)[29] and 0–100% aqueous methanol (D = 78-33).[30] Such plots are shown in Fig. 2, which covers the range of dielectric constant from 78 to 22. This range includes all of the above-mentioned solvent compositions except 65–90% aqueous dioxane (D = 22-6). The portion of this curve which is not shown is very strongly curved.

The breakdown of the simple linear relation be-

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(14) J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).

(15) (a) K. J. Laidler and H. Eyring, *Ann. N. Y. Acad. Sci.*, **39**, 303 (1940); (b) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, p. 419.

(16) A linear relation is similarly expected[15] for a reaction between two dipoles through a polar transition state.

(17) V. Gold, *Trans. Faraday Soc.*, **44**, 506 (1948).

(18) V. Gold, J. Hilton and E. G. Jefferson,[21] *J. Chem. Soc.*, 2756 (1954).

(19) Gold's first plot,[17] covering the 0–50% acetone range, appears to be quite linear; in point of fact, however, considerable curvature was found when an error in the drawing was corrected,[18] and the range was extended to include the 80% acetone point.[18]

(20) B. L. Archer and R. F. Hudson,[21] *J. Chem. Soc.*, 3259 (1950).

(21) These authors plotted log $[k/(H_2O)]$ *vs.* $(D - 1)/(2D + 1)$; these plots show considerable curvature, which is not substantially changed when log k itself is used.

(22) J. K. Kochi and G. S. Hammond, THIS JOURNAL, **75**, 3445 (1953).

(23) J. K. Kochi and G. S. Hammond, *ibid.*, **75**, 3452 (1953).

(24) H. D. Cowan, C. L. McCabe and J. C. Warner, *ibid.*, **72**, 1194 (1950).

(25) J. W. Hackett and H. C. Thomas,[21] *ibid.*, **72**, 4962 (1950).

(26) P. Salomaa, *Ann. Univ. Turkuensis*, **A14** (1953).

(27) F. E. Critchfield, J. A. Gibson, Jr., and J. L. Hall, THIS JOURNAL, **75**, 1991 (1953).

(28) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," A. C. S. Monograph No. 95, 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950.

(29) J. L. Hall, private communication to Professor E. Grunwald of Florida State University.

(30) P. S. Albright and L. J. Gosting, THIS JOURNAL, **68**, 1061 (1946).

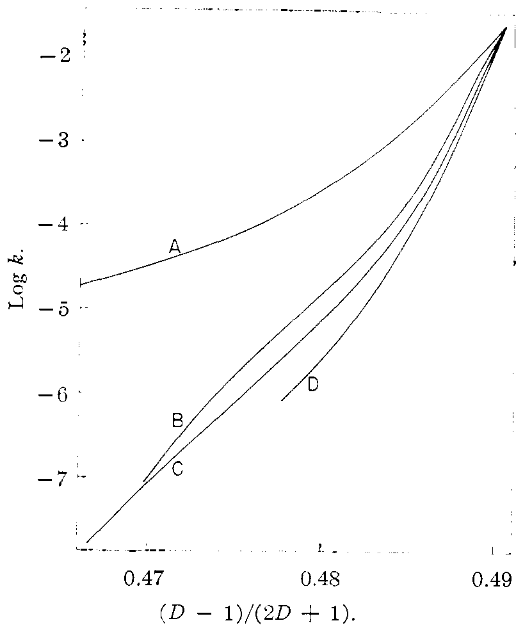

Fig. 2.—Plot of log k *vs.* $(D - 1)/(2D + 1)$ for solvolysis of *t*-butyl chloride at 25.0° in dioxane–H_2O (A); EtOH–H_2O (B); Me_2CO–H_2O (C); MeOH–H_2O (D).

tween log k and $(D - 1)/(2D + 1)$, due to the failure of the approximations involved and also solvent "sorting,"[15,26] is emphasized by two features of the plots in Fig. 2. These features are large dispersion of the plot into separate lines for each solvent pair and curvature of the separate lines. Such dispersion has been noticed, for example, by Salomaa[26] for ethanolysis of methyl chloromethyl ether in ethanol–dioxane and ethanol–benzene mixtures. Further, there are many indications that dielectric constant alone is a poor guide to solvolysis rate[31] of halides such as benzhydryl chloride[35] and benzoyl chloride,[36] and to rates of the Menschutkin reaction[15a] or the reaction of dibutylamine with diisopropyl phosphorochloridate.[37]

The departures from linearity in most of the regions of the curves is considerable. The linear portions of the plots extend only over the ranges of solvent composition of dielectric constant greater than *ca.* 53. These include 0–30% aqueous dioxane and 0–50% aqueous acetone, ethanol and methanol. However, close examination of a large scale plot of the high water region shows that inflections in the curves are responsible for the apparent linearity of the plots for the aqueous ethanol and aqueous acetone mixtures, and that the plot for aqueous dioxane is curved all the way to pure water. A second set of inflections in the low water regions of aqueous ethanol (70–90%) and aqueous acetone (70–95%) is also responsible for the apparent linearity of the curves in these regions.

Using a double spherical ion model for the activated complex, Scatchard[38] plotted log k for solvolysis of *t*-butyl chloride in aqueous methanol and ethanol against another function of dielectric constant, $1/D$. Electrostatic considerations suggest[15] that this is the function of D against which log k should be plotted for reactions between ions, or between ions and neutral molecules. However, it needs to be emphasized that it is impossible to decide between the functions $1/D$ and $(D - 1)/(2D + 1)$ on the basis of linearity of log k plots for dielectric constants greater than *ca.* 8. This can readily be seen by carrying out explicitly the division of $(D - 1)$ by $(2D + 1)$, as shown in equation 4. For $D = 8$, the error involved in neglecting terms in D^2 and higher

$$\frac{D-1}{2D+1} = \frac{1}{2} - \frac{3}{4D} + \frac{3}{8D^2} - \frac{3}{16D^3} + \ldots \qquad (4)$$

powers is less than one per cent. Therefore, $(D - 1)/(2D + 1)$ is linear in $(1/D)$ to an excellent approximation. This is true in *all* solvent mixtures of water with acetone, ethanol and methanol. This approximation would become inexact only for such solvent mixtures as aqueous dioxane containing less than 10% water. It is obvious, therefore, that the plots of log k *vs.* $1/D$ for *t*-butyl chloride show curvature and dispersion just as do the plots *vs.* $(D - 1)/(2D + 1)$ in Fig. 2.

Böhme, *et al.*,[39,40] plotted log k against log D for α-phenylethyl chloride, benzhydryl chloride, methanesulfonyl chloride and benzoyl chloride in mixtures of water with dioxane, tetrahydrofuran, ethylene glycol dimethyl ether and β,β'-dimethoxydiethyl ether. In all cases except benzoyl chloride, the plots were quite linear.

The plots of log k *vs.* log D for *t*-butyl chloride in aqueous dioxane, acetone, ethanol and methanol are complex curves, as is clear from Fig. 3. However, as a result of the numerous inflections, major portions of the curves can be approximated roughly by straight lines. Thus, as far as linearity of plots is concerned, log D is the best function of D so far considered. However, the magnitude of the dispersion of the separate lines remains as large as for the other functions of D.

***mY* Correlations.**—The usefulness of the m**Y** correlation of solvolysis rates becomes apparent when the same data which led to marked curvature of the plots of log k *vs.* $(D - 1)/(2D + 1)$ are replotted against **Y**. Table III lists the parameters m and log k_0 of equation 1, as well as the probable error of the fit,[12,13] r, for all but one[41] of these sets of

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[31] In this connection, the data in heptafluorobutyric acid and in formamide are particularly striking. The dielectric constant for heptafluorobutyric acid must be close to that of acetic acid (Dannhauser and Cole[32] reported $D = 6.2$ for acetic acid, and $D = 8.3$ for trifluoroacetic acid; the value for the latter is probably somewhat higher than that for heptafluorobutyric acid). However, the solvolysis rate of α-phenylethyl chloride in heptafluorobutyric acid exceeds that in acetic acid by four powers of ten.[9] The solvolysis rate of *t*-butyl chloride in formamide ($D = 109.5$)[33] is *ca.* one-thirtieth that in formic acid ($D = 56.1$),[34] and is somewhat less than that in 60% aqueous dioxane ($D = 26.6.$).[27]

[32] W. Dannhauser and R. H. Cole, THIS JOURNAL, **74**, 6105 (1952).

[33] G. R Leader, *ibid.*, **73**, 856 (1951).

[34] J. F. Johnson and R. H. Cole, *ibid.*, **73**, 4536 (1951).

[35] N. T. Farinacci and L. P. Hammett, *ibid.*, **59**, 2542 (1937).

[36] D. A. Brown and R. F. Hudson, *J. Chem. Soc.*, 883 (1953).

[37] I. Dostrovsky and M. Halmann, *ibid.*, 511 (1953).

[38] G. Scatchard, *J. Chem. Phys.*, **7**, 657 (1939).

[39] H. Böhme and H. J. Henning, *Z. Naturforsch.*, **1**, 580 (1946).

[40] H. Böhme and W. Schürhoff, *Chem. Ber.*, **84**, 28 (1951).

[41] Benzoyl chloride hydrolysis has been recently dissected by Gold, *et al.*,[15] into two distinct solvolytic processes, which he regards as separate S_N1 and S_N2 substitutions. Our analysis of the data, which supports the existence of two solvolytic processes, is included in a later paper. Our interpretation, however, is that one of the processes is substitution and the other is addition.

TABLE III

CORRELATION OF SOLVOLYSIS RATES WITH **Y**

Compound	Temp., °C.	Solvent range	No. of points	m	log k_0[a]	r[13]
Acetic anhydride[17,42]	5.0	0–50 wt. % $Me_2CO–H_2O$	5	0.587	−5.226	0.012
	25.0	0–80 wt. % $Me_2CO–H_2O$	7	.579	−4.636	.015
Ethylene bromohydrin[24]	70.0	0–80 wt. % $EtOH–H_2O$	4	.226	−6.245	.033
Ethylene iodohydrin[24]	70.0	0–60 wt. % $EtOH–H_2O$	3	.166	−6.457	.013
1-Chloro-2-methylpropan-2-ol[43]	85.1	0–80 vol. % $EtOH–H_2O$	5	.281	−6.138	.016
	97.1	0–80 vol. % $EtOH–H_2O$	5	.292	−5.646	.016
p-Nitrobenzyl bromide[25]	5.0	50–90 wt. % Dioxane–H_2O	3	.340	−7.554[b]	.024
	60.0	50–90 wt. % Dioxane–H_2O	3	.472	−5.256[b]	.011
Benzyl *p*-toluenesulfonate[22]	25.3	23–71 mole % $Me_2CO–H_2O$[c]	8	.650	−4.711	.019
p-Methylbenzyl *p*-toluenesulfonate[23]	25.3	23–71 mole % $Me_2CO–H_2O$[c]	8	.724	−3.275	.014
p-β-Styrylbenzyl *p*-toluenesulfonate[23]	25.3[d]	38–55 mole % $Me_2CO–H_2O$[c]	3	.669	−2.455	.005
p-Phenylethynylbenzyl *p*-toluenesulfonate[23]	25.3[d]	23–38 mole % $Me_2CO–H_2O$[c]	4	.741	−4.638	.007
Methanesulfonyl chloride[40]	25.0	50–90 wt. % Dioxane–H_2O	9	.465	−4.568	.028
	35.0	50–90 wt. % Dioxane–H_2O	9	.445	−4.141	.026
Ethyl chloroformate[40]	25.0	50–90 wt. % Dioxane–H_2O[e]	9	.405	−4.595	.011
cis-5-Methyl-2-cyclohexenyl acid phthalate[44]	99.85	50–90 vol. % $Me_2CO–H_2O$	4	.429	−4.039[f]	.009
	99.85	50–90 vol. % $Me_2CO–H_2O$	4	.472	−4.193[g]	.001
2,3-Dichlorodioxane[45]	15.0	0–90 vol. % $Me_2CO–H_2O$ 0–75 vol. % Dioxane–H_2O	14	.879	−5.069	.036
	35.0	0–90 vol. % $Me_2CO–H_2O$ 0–75 vol. % Dioxane–H_2O	14	.845	−3.991	.030
	15.0	0–90 vol. % $Me_2CO–H_2O$	10	.873	−5.037	.016
	35.0	0–90 vol. % $Me_2CO–H_2O$	10	.839	−3.964	.017
	15.0	0–75 vol. % Dioxane–H_2O	5	.919	−5.187	.020
	35.0	0–75 vol. % Dioxane–H_2O	5	.877	−4.084	.016
Trimethylsulfonium hydroxide[46]	100.0	0–100% $EtOH–H_2O$	4	– .778	−1.731[h]	.017
Triethylsulfonium hydroxide[46]	100.0	0–80 vol. % $EtOH–H_2O$	3	– .835	−1.709[h]	.026

[a] Unit of k_0, sec.$^{-1}$, unless otherwise specified. [b] Hackett and Thomas[25] reported their results as $k_h = k/(H_2O)$; these were converted to first-order solvolysis rate constants by multiplying by the following calculated water concentrations: 27.8, 17.3 and 5.73 moles/liter for 50, 70 and 90 wt. % dioxane–H_2O, respectively. [c] Kochi and Hammond[22,23] state that the solvent mixtures contained 1.84 *M* $LiClO_4$; from their description of the preparation of the solutions, the actual concentrations employed were *ca.* 0.18 *M*. [d] Temperature not given[23]; assumed to be 25.3°. [e] Values in the range 45 to 0 wt. % dioxane–H_2O fall increasingly below this line. [f] k_α; polarimetric rate constant. [g] k_t; titrimetric rate constant. [h] Bimolecular rate constant, in liters/mole-second.

data. In all cases, there is considerable improvement in the linearity of the fits of log k *vs.* **Y** over that obtained for log k *vs.* $(D - 1)/2D + 1)$. Also listed in Table III are a number of additional cases from the literature which correlate well with **Y**, and, therefore, very poorly with $(D - 1)/(2D + 1)$. In particular, it should be noted that, in the case of 2,3-dichlorodioxane, where data are available in both aqueous acetones and aqueous dioxanes, the enormous dispersion that exists when the data are plotted against $(D - 1)/(2D + 1)$ is reduced very considerably when plotted against **Y**. It is nevertheless true, however, that the fits are still better when separate lines for each of the solvent pairs are used. Such dispersion of lines is treated in subsequent papers of this series. The pooled[12b] probable error of fit for all of the data in Table III, employing separate lines for different solvent pairs, is 0.018 in log k, which corresponds to less than 5% in k. This is typical of the fits which have been obtained with the m**Y** relation.

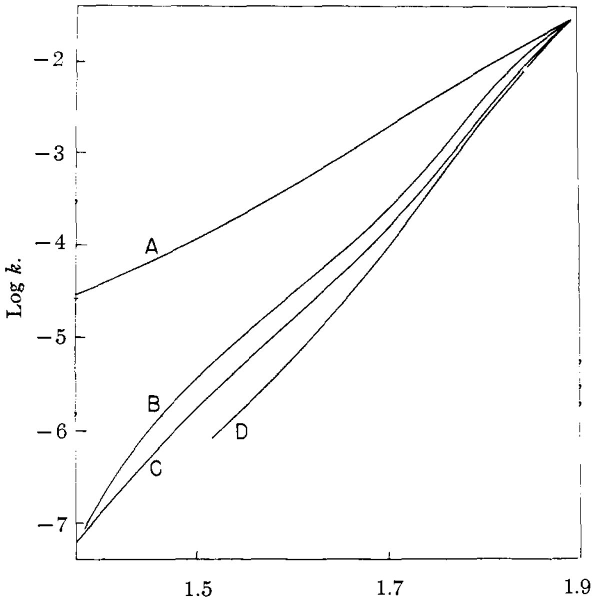

Fig. 3.—Plot of log k *vs.* log D for solvolysis of *t*-butyl chloride at 25.0° in dioxane–H_2O (A); $EtOH–H_2O$ (B); $Me_2CO–H_2O$ (C); and $MeOH–H_2O$ (D).

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(42) A. R. Emery and V. Gold, *J. Chem. Soc.*, 1455 (1950).

(43) G. J. Harvey, N. V. Riggs and V. R. Stimson, *ibid.*, 3267 (1955).

(44) H. L. Goering and E. F. Silversmith, THIS JOURNAL, **77**, 1129 (1955).

(45) P. Salomaa, *Acta Chem. Scand.*, **8**, 744 (1954).

(46) J. L. Gleave, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 236 (1935).

Since **Y** correlates log k for certain reactions for which electrostatic considerations suggest the variable $(D - 1)/(2D + 1)$, it may also be employed to correlate certain reactions for which the suggested variable is $1/D$. This follows because $(D - 1)/(2D + 1)$ is linear in $1/D$. One such reaction is the bimolecular decomposition of trialkylsulfonium hydroxides in aqueous ethanol mixtures.[46] Here, passage to the transition state involves a decrease in charge; hence, change to a more strongly ionizing medium decreases rate of reaction. Laidler and Eyring[15a] plotted the logarithms of the bimolecular rate constants for the decomposition of trimethylsulfonium hydroxide against $1/D$; the resulting plot is markedly curved. In contrast, an excellent correlation with **Y** was obtained, as shown in Table III.

Experimental Part

t-Butyl Chloride.—Treatment of t-butyl chloride with phosphorus pentoxide, followed by fractional distillation, gave a center cut, b.p. 50.8° (760 mm.), $n^{20}\text{D}$ 1.3855, $n^{25}\text{D}$ 1.3819, d^{25}_4 0.8370 (reported b.p. 50.7° (760 mm.),[47] $n^{20}\text{D}$ 1.3855,[48] d^{25}_4 0.8353[47]).

Solvents.—Methanol was dried by the method of Lund and Bjerrum[49]; d^{25}_4 0.78651–0.78658 (reported[50] d^{25}_4 0.7866).

Ethanol was dried by the method of Lund and Bjerrum[49]; d^{25}_4 0.78505–0.78513 (reported[50] d^{25}_4 0.78507).

Acetone was dried by refluxing over Drierite and fractionally distilling therefrom; d^{25}_4 0.7844–0.7847 (reported[50] d^{25}_4 0.7850).

Dioxane was purified by the method described by Fieser[51]; d^{25}_4 1.0261–1.0279 (reported[50] d^{25}_4 1.0280).

Formamide was fractionally distilled, b.p. 99–100° (9.5 mm.), $n^{25}\text{D}$ 1.4445 (reported[50] $n^{25}\text{D}$ 1.4459).

Formic acid (B. and A., C.P. 98–100%) was dried by the method described by Winstein and Marshall[52]; d^{25}_4 1.21381–1.21397 (reported[50] d^{25}_4 1.2140). Lithium formate in dry and aqueous formic acid was prepared by solution of the calculated amount of anhydrous lithium carbonate. A solution 0.068 M in lithium formate therefore contained 0.038 M added water. Such a water concentration is without significant effect on solvolysis rate. Solutions of lithium formate in the dioxane–formic acid mixtures were prepared by dissolving therein the calculated amount of anhydrous lithium formate. The latter was prepared by reaction of equimolar quantities of lithium carbonate and formic acid in aqueous solution, followed by quantitative dehydration of the salt under vacuum at 110°.

Anhydrous acetic acid was prepared by distillation from triacetyl borate,[53] or by addition of the calculated amount of pure acetic anhydride, refluxing for 12 hours, and distillation. The amount of acetic anhydride required was determined by Karl Fischer titration.[54] Acetic acid solutions containing lithium acetate and water or excess acetic anhydride were made up by weighing in the calculated amounts of lithium carbonate and distilled water or pure acetic anhydride. In the case of the acetic anhydride, the resulting solution was refluxed for 12 hours.

Other mixed solvents were prepared by mixing the required volumes of the components which had previously been equilibrated at 25.0°. Density checks on a number of the aqueous methanol and ethanol solvents showed that the compositions agreed with the nominal values within 0.04 wt. %.

Molar concentrations were calculated at 25.0°.

Kinetic Measurements.—The usual sealed ampoule technique, using 5-ml. aliquots, was employed for rate measurements above 25°, and also for the slower rates at 0 and 25°. Special precautions were taken to minimize possible error due to the volatility of the t-butyl chloride. Thus, for the slower rates, in preparing the solvolysis solution, the t-butyl chloride was weighed into a 100 ml. volumetric flask previously made up almost to the mark with solvent at room temperature. After mixing, the flask was cooled to just slightly above the dew point (generally *ca.* 10–15°) and the entire contents were poured into a 100-ml. all-glass hypodermic syringe. The solution was dispensed into the ampoules from the syringe. In this way, the difference in composition between the first and last ampoules was minimized. The vapor space above the solutions in the ampoules was kept as small as possible. With these precautions, the experimental infinity titers obtained after ten half-lives of reaction, or, in the case of very slow rates, the analytically determined initial concentrations (obtained by pipetting an aliquot into 25 ml. of 40% aqueous ethanol, allowing it to solvolyze to completion, and then analyzing for chloride ion), were in most cases found to agree with the calculated value within 1 to 2%.

For most of the fast rates, the solvolysis was carried out directly in the hypodermic syringe immersed in the constant temperature bath, aliquots being taken by forcing the solution up into the pipet. In such cases the vapor space was completely eliminated.

Rates at 0° were carried out by immersing the hypodermic syringe containing the reaction mixture in a mixture of crushed ice and distilled water in a Dewar flask, in a cold room held at 0 ± 2°. In this way, it was possible to employ a pipet which was approximately at the solvolysis temperature.

Aliquots were analyzed for acid by titration with methanolic sodium hydroxide, using brom thymol blue indicator. For fast rates, the aliquots were effectively quenched by pipetting into 25 ml. of acetone. In this solvent, the indicator employed, several drops of a 0.1% neutralized alcoholic solution of brom phenol blue, gave a remarkably sharp end-point at very low acid concentrations (10^{-3} to 10^{-5} M). While this end-point did not correspond exactly to the stoichiometric point (*ca.* 4% low), its position was found to be substantially independent of acid concentration at levels below 0.03 M; this "error" therefore had no appreciable effect on the accuracy of the rate data. Using the acetone quench, satisfactory rates were obtained with concentrations of t-butyl chloride of 0.001 M and lower.

Aliquots were analyzed for chloride ion by a modification of the procedure described by Bateman and Hughes.[55] An aliquot was pipetted into 25 ml. of pentane in a 50-ml. separatory funnel. This solvent is superior to the carbon tetrachloride previously employed[55] because it forms the upper phase, thus simplifying the extraction procedure, and because it separates more rapidly and cleanly from the aqueous phase. The mixture was extracted with two successive 10-ml. portions of water. The procedure was standardized at 40 "shakes" for the first extraction and 30 for the second. The aqueous extracts were combined, acidified with nitric acid, and titrated for chloride ion by the Volhard procedure, nitrobenzene being employed.[56] The extraction procedure was shown to detect at least 99.8% of the halide ion present in the solvolysis solution. Hydrolysis during the aqueous extraction was found to be negligible for t-butyl chloride.

The following technique was developed for the determination of very fast rates with a half-life between several minutes and *ca.* 20 seconds. The material being solvolyzed was roughly measured into the solvent which had previously been equilibrated at the solvolysis temperature. The solution was rapidly mixed, immersed in the thermostat, and the pulling of points started at once. Each aliquot, taken with a fast-draining automatic pipet, was discharged either into 25 ml. of acetone for acid determination, or into a separatory funnel, containing 25 ml. of pentane and 10 ml. of water at the solvolysis temperature, for halide determination. In the latter case, the separatory funnel was then shaken, time being measured at the first "shake." Separa-

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(47) J. Timmermans and Y. Delcourt, *J. Chem. Phys.*, **31**, 98 (1934).

(48) A. Audsley and F. R. Goss, *J. Chem. Soc.*, 873 (1941).

(49) H. Lund and J. Bjerrum, *Ber.*, **64**, 210 (1931).

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(51) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 369.

(52) S. Winstein and H. Marshall, THIS JOURNAL, **74**, 1126 (1952).

(53) W. C. Eichelberger and V. K. La Mer, *ibid.*, **55**, 3633 (1933).

(54) In the Karl Fischer titration of acetic acid, it was found necessary to carry out the titration in the presence of at least a fivefold excess of methanol; otherwise, the reaction with water was erratic, slow and sometimes completely inhibited.

(55) L. C. Bateman and E. D. Hughes, *J. Chem. Soc.*, 1190 (1937).

(56) J. R. Caldwell and H. V. Moyer, *Ind. Eng. Chem., Anal. Ed.*, **7**, 38 (1935).

tion of the aqueous layer and re-extraction of the pentane layer with the second 10-ml. portion of water was deferred until after all of the points were pulled, it having been demonstrated that the reaction was effectively quenched by the first extraction. In this way, the first point could be pulled within 20 to 30 seconds of mixing, and subsequent points could be pulled every 15 to 20 seconds.

A microphone feeding a tape recorder was employed for the time measurement in the fast rates, the quench time for each point being announced orally. The elapsed times between points were later obtained from the tape on playback, using a stopwatch. Accuracy was ensured by reading a time signal into the tape before and after each run, and employing this interval as a calibration time check. In this way, timing accuracy of ±0.2% was readily attained.

The new data reported in Table I were based on an average of six points per run followed past 50 to 90% reaction. The average deviation for all of the rates which were constant was ±1.0%; in only four cases did the average deviation reach ±2%: 50% HCOOH–H_2O at 25.0°, 16 *M* H_2O in AcOH at 50.0°, and 50% AcOH–HCOOH at 25.0 and 50.0°. The observed kinetics were first order within experimental error for all of the solvent compositions employed except 80 and 90 vol. % aqueous dioxane at both 25.0 and 50.0°. In the former solvent, the integrated first order rate constant calculated from the true zero time rose 2.6% for the reaction of the first 0.01 *M* *t*-butyl chloride at both temperatures; in the latter solvent, the corresponding rise was 5.6%.

Equilibrium in Acetolysis of *t*-Butyl Chloride.—The acetolysis of *t*-butyl chloride comes to an equilibrium position far short of completion unless the acetolysis is carried out in the presence of excess base.[1a,57,58] The indications in the present work were that solvolysis of *t*-butyl chloride fell slightly short of completion in acetic acid, formic acid and acetic–formic acid mixtures, even in the presence of a twofold excess of lithium acetate. As shown in Table IV, in the solvolysis of 0.034 *M* *t*-butyl chloride in acetic acid containing 0.068 *M* lithium acetate, the experimental infinity, taken after ten half-lives and accurate to ±1%, was found to be 6.2% smaller than the analytically determined initial concentration of *t*-butyl chloride. A much higher concentration (1 *M*) of lithium acetate was found to suppress the back reaction completely, as did the addition of 2 *M* water. The addition of formic acid was only partly effective. Even in pure formic acid containing 0.068 *M* lithium formate, a measurable equilibrium was observed.

TABLE IV

PER CENT. CHLORIDE ION AFTER 10 SOLVOLYSIS HALF-LIVES UNDER VARIOUS CONDITIONS

Solvent	Temp., °C.	(*t*-BuCl), *M*	(Lithium salt), *M*	% Cl^- after 10 half-lives
AcOH + 0.01 *M* Ac_2O	50.0	0.034	0.068	93.8
AcOH + 0.01 *M* Ac_2O	50.0	.032	1.000	100
AcOH + 2 *M* H_2O	50.0	.033	0.068	99
75% AcOH–HCOOH	50.0	.038	.065	95.6
50% AcOH–HCOOH	25.0	.035	.065	97.3
50% AcOH–HCOOH	50.0	.035	.065	97.1
25% AcOH–HCOOH	0.0	.051	.065	96
25% AcOH–HCOOH	25.0	.051	.065	97.6
HCOOH	25.0	.042	.068	97.8

In computing the rate constants for these solvolyses, the initial analytically determined concentrations of *t*-butyl chloride were employed in place of the experimentally determined infinities. In all cases, the drop in the integrated rate constants as the equilibrium position was approached was not perceptible until 60 to 70% of reaction; later points were not averaged.

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(58) W. G. Young, S. Winstein and H. L. Goering, *ibid.*, **73**, 1958 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Salt Effects and Ion Pairs in Solvolysis and Related Reactions. VI. Additional Examples of Special Salt Effects in Acetolysis[1]

BY ARNOLD H. FAINBERG, GENE C. ROBINSON AND S. WINSTEIN

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trans-2-*p*-Anisylcyclopentyl *p*-bromobenzenesulfonate, *trans*-2-anisylcyclohexyl *p*-bromobenzenesulfonate, 1-*p*-anisyl-2-propyl *p*-toluenesulfonate and *erythro*-3-*p*-anisyl-2-butyl *p*-bromobenzenesulfonate are shown to exhibit the same special salt effect of lithium perchlorate in acetolysis as was previously demonstrated for 2-*o*- and 2-*p*-anisylethyl *p*-toluenesulfonates. The numerical quantities characterizing the magnitude of both the normal and special salt effects are tabulated and compared.

In the preceding paper[2] in this series, it was shown that, in the acetolysis of 2-*o*- and *p*-anisylethyl *p*-toluenesulfonates, lithium perchlorate exerts a special salt effect superimposed on the normal salt effect previously demonstrated[3] for the neophyl esters. In this special salt effect, a steep rise in the titrimetric rate constant, k_t, from the base value, k_t°, is produced by low concentrations of lithium perchlorate. This phenomenon, apparently connected with the reduction of ion pair return,[2,4] has been noted in a number of other cases.[5] In the present paper is reported a study of such salt effects in acetolysis of *trans*-2-*p*-anisylcyclopentyl *p*-bromobenzenesulfonate, *trans*-2-*p*-anisylcyclohexyl *p*-bromobenzenesulfonate, 1-*p*-anisyl-2-propyl *p*-toluenesulfonate, and *erythro*-3-*p*-anisyl-2-butyl *p*-bromobenzenesulfonate. For all of these substances, acetolysis involves predominantly or exclusively anchimerically assisted ionization[5d,6,7] to a bridged carbonium ion, the anisyl group participating as in the 2-anisylethyl cases.[8]

In Table I are summarized the first-order rate

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(1) Research sponsored by the Office of Ordnance Research, U. S. Army.

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(3) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2763 (1956).

(4) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck and G. C. Robinson, *ibid.*, **78**, 328 (1956).

(5) (a) S. Winstein, E. Clippinger, A. H. Fainberg and G. C. Robinson, *ibid.*, **76**, 2597 (1954); (b) S. Winstein, E. Clippinger, A. H. Fainberg and G. C. Robinson, *Chemistry and Industry*, 664 (1954); (c) G. C. Robinson, E. Clippinger and S. Winstein, p. 21-N, Abstracts of Papers, 125th meeting, A.C.S., Kansas City, Mo., March, 1954; (d) G. C. Robinson, unpublished work.

(6) S. Winstein, M. Brown, K. C. Schreiber and A. H. Schlesinger, THIS JOURNAL, **74**, 1140 (1952).

(7) R. Heck, unpublished work.

(8) S. Winstein, C. R. Lindegren, H. Marshall and L. L. Ingraham, THIS JOURNAL, **75**, 147 (1953).