to give 0.01 M excess. Lithium perchlorate in these high concentrations was found to catalyze the reaction of acetic anhydride with water (as does strong acid), so that it was not necessary to heat the solution to hasten completion of the dehydration.

Acetic acid, 0.100 M in p-toluenesulfonic acid and 0.01 M in acetic anhydride, was similarly prepared from the monohydrate of p-toluenesulfonic acid and acetic anhydride.

Acetic acid, 0.100 M in lithium p-toluenesulfonate and 0.01 M in acetic anhydride, was prepared by dissolving the calculated amounts of lithium carbonate, p-toluenesulfonic acid monohydrate and pure acetic anhydride in acetic acid and holding the solution at near reflux for 24 hours. The resulting solution was very slightly on the acid side.

Acetic acid containing diphenylguanidinium perchlorate and/or acetate was prepared by dissolving the calculated amounts of diphenylguanidinium perchlorate[16] (m.p. 161.5–162.5°) and/or diphenylguanidine in anhydrous acetic acid.

Kinetic Measurements.—The usual sealed ampoule technique was used. The halides were followed by an extraction procedure[15] and Volhard analysis for halide ion. The arylsulfonates were followed by acidimetric titration[17] with *ca.* 0.02–0.04 M sodium acetate in acetic acid, using brom phenol blue indicator. The presence of high concentrations (0.10 M) of lithium perchlorate, lithium p-toluenesulfonate and p-toluenesulfonic acid was found to diminish appreciably the sharpness of the end-points; the addition of 10-25 ml. of dioxane to the solution being titrated helped only slightly.

The data reported in Table I were based on an average of six points per run, followed past 60–90% reaction.

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[16] C. Hanson, Thesis, U.C.L.A., 1943, p. 27.

[17] 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]

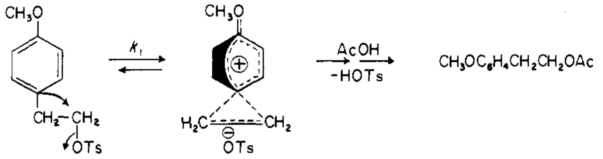
Salt Effects and Ion Pairs in Solvolysis and Related Reactions. V. Special Salt Effect in Acetolysis of 2-Anisylethyl *p*-Toluenesulfonates

BY ARNOLD H. FAINBERG AND S. WINSTEIN

RECEIVED NOVEMBER 17, 1955

The effects of lithium perchlorate on acetolysis rate of *o*- and *p*-anisylethyl *p*-toluenesulfonates have been contrasted with those observed with the phenylethyl, neophyl and *p*-methoxyneophyl esters. With the *o*- and *p*-anisylethyl derivatives, lithium perchlorate exerts both "special" and "normal" salt effects. The former designation refers to a very steep rise in titrimetric rate constant, k_t, from the base value, k_t^0, due to low concentrations of lithium perchlorate. The latter refers to the linear increase in k_t at somewhat higher lithium perchlorate concentrations, the magnitude of this effect being approximately equal to that observed with the neophyl analogs. The special salt effect may be characterized by the quantities: (i), k_{ext}^0, an extrapolated rate constant at zero salt concentration, which includes the special but excludes the normal salt effect; (ii), $(LiClO_4)_{1/2}$, the salt concentration which produces one-half of the total special salt effect equal to $2\text{–}3 \times 10^{-4}$ M in the present cases; (iii), (k_{ext}^0/k_t^0), a measure of the magnitude of the special salt effect, equal to *ca.* 3 in the present work. Regarding the origin of the special salt effects, the indications are that these are concerned with suppression of ion-pair return. On this basis, k_{ext}^0 is a better approximation than k_t^0 to the ionization rate. The use of k_{ext}^0 for acetolysis rate modifies substantially EtOH:AcOH rate ratios, useful in certain discussions of mechanism.

In the previous paper[1] were reported the effects of various salts on rates of acetolysis of neophyl and p-methoxyneophyl arylsulfonates, substances which are ideal for the elucidation of the pattern of normal salt effects on rates of ionization. The reason for this is that ionization is anchimerically assisted and any ion pair return accompanying acetolysis is without effect on the observed solvolysis rate, since the product of ion pair return is, for practical purposes, instantaneously solvolyzed. The present paper deals mainly with the effect of lithium perchlorate on acetolysis rate of 2-o- and p-anisylethyl p-toluenesulfonates. The acetolysis of these substances resembles that of the p-methoxyneophyl analog in one respect; ionization involves anisyl participation,[2] p-anisylethyl toluenesulfonate (I), for example, giving rise to ion pair II. However, ion pair return,[3] if it occurs in acetolysis of I or its o-methoxy isomer, will cause a corresponding decrease in solvolysis rate. Any salt effect on acetolysis rate would include, not only the salt effect on ionization rate, but also the salt effect on ion pair return. The main purpose of the measurements reported in the present paper was to disclose any possible contrast between salt effects in acetolysis of I and its o-methoxy isomer, on the one hand, and the neophyl analogs on the other.



I II

In Table I are summarized the first-order rate constants at two temperatures for the solvolysis of 2-phenylethyl, 2-o-anisylethyl and 2-p-anisylethyl p-toluenesulfonates in ethanol and in acetic acid containing various concentrations of lithium perchlorate. The observed kinetics for the 2-phenylethyl ester, as well as for the 2-anisylethyl esters in ethanol and in acetic acid containing the higher concentrations of lithium perchlorate, were first order within the average deviations listed with these rate constants. However, the slight downward drifts in rate during solvolysis of the 2-anisylethyl esters in pure acetic acid previously noted[2] were confirmed in the present work; such drifts were also noted in the acetolyses involving the lower concentrations of lithium perchlorate. These rate depressions are obviously common ion effects, dealt with for other systems in a previous paper in this series.[3] In the present work they were treated empirically, as described in the Experimental section, to obtain the initial rate constants reported in

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[1] A. H. Fainberg and S. Winstein, THIS JOURNAL, **78**, 2763 (1956).

[2] S. Winstein, C. R. Lindegren, H. Marshall and L. L. Ingraham, *ibid.*, **75**, 147 (1953).

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

TABLE I

SUMMARY OF ACETOLYSIS RATES

Compound	$[RX] \times 10^2$, M	$LiClO_4$ concn. $\times 10^2$, M	10^5k (sec.$^{-1}$) 50.0°	10^5k (sec.$^{-1}$) 75.0°	$\Delta H^\ddagger$ at 50°, kcal./mole	$\Delta S^\ddagger$ at 50°, e.u.
$C_6H_5CH_2CH_2OTs$	2.4–4.1[b]	..	0.00164[f]	0.340[f,g]	24.95[f]	−17.1[f]
	3.14[h]	3.12		0.496[g,h]		
	2.3[a,b]	..		0.708[a,b]		
	3.18[a]	3.11	.0632 ± 0.0004[a]	0.760 ± 0.002[a]	21.6	−20.2
o-$CH_3OC_6H_4CH_2CH_2OTs$	3.05	..	.032[c]	0.68	26.7[c]	−5.8[c]
	3.12	0.0100	.0595	1.13	25.7	−7.7
	3.10	0.100	.088	1.66	25.6	−7.1
	3.01	1.00	.115 ± .002	2.20	25.7	−6.2
	3.01	3.00	.141 ± .001	2.66	25.6	−6.2
	3.04	6.00	.1820 ± .0009	3.28 ± .01	25.21	−6.9
	2.98	10.0	.236 ± .003	4.21 ± .02	25.11	−6.7
	2.97	30.0	.55 ± .01	9.0 ± .1	24.3	−7.7
p-$CH_3OC_6H_4CH_2CH_2OTs$	2.06	..	.0456[d]	0.91	26.1[d]	−7[d]
	2.08	0.00100	.0503	1.02	26.3	−6.2
	2.09	0.0100	.075 ± .001	1.39	25.4	−8.0
	2.22	0.0400	.103	1.82	25.0	−8.6
	2.18	0.100	.1188 ± .0008	2.08	24.95	−8.6
	2.17	1.00	.156 ± .001	2.60 ± .05	24.51	−9.4
	2.05	3.00	.201 ± .004	3.29 ± .03	24.33	−9.4
	2.00	6.00	.255 ± .002	4.13 ± .03	24.25	−9.3
	2.03	10.0	.321 ± .004	5.04 ± .06	23.96	−9.7
	3.35[a]	..	.0985 ± .0005[a]	1.358 ± .005[a,e]	22.83	−15.5
	3.05[a]	3.11	.1066 ± .0009[a]	1.520 ± .005[a]	23.11	−14.5

[a] In EtOH. [b] Reported by S. Winstein, *et al.*, THIS JOURNAL, **75**, 147 (1953). [c] Extrapolation to 50.0° of data reported[b] at other temp. gives $10^5k = 0.0344$, $\Delta H^\ddagger = 26.15$, $\Delta S^\ddagger = -7.3$. [d] Extrapolation to 50.0° of data reported[b] at other temp. gives $10^5k = 0.0455$, $\Delta H^\ddagger = 25.4$, $\Delta S^\ddagger = -9.0$. [e] Previously reported[b] $10^5k = 1.35$. [f] Calcd. from data reported[b] at 75.01 and 99.62°. [g] At 99.92°. [h] Data of R. Heck.

Table I. The table also lists the values of the thermodynamic quantities of activation $\Delta H^\ddagger$ and $\Delta S^\ddagger$.

The inclusion of low concentrations of lithium perchlorate in acetolysis of the 2-anisylethyl esters gave rise to a two-stage acceleration of rate, as shown in Fig. 1 for the *o*-isomer at 50.0°: (i) an initial, very steep rise in the first-order titrimetric rate constant, k_t, from the value in the absence of salt, k_t^0; (ii) a subsequent small increase in k_t, nearly perfectly linear in salt concentration ($LiClO_4$). This latter linear portion recalls the normal salt effect of lithium perchlorate previously demonstrated[1] in acetolysis of neophyl and *p*-methoxyneophyl *p*-toluenesulfonates. A short extrapolation of the linear part of the plot of k_t *vs.* ($LiClO_4$) to zero salt concentration yields the intercept k_{ext}^0, as shown in Fig. 1. The linear part of the plot may be expressed by equation 1, where *b* is the slope of the linear plot

$$k_t = k_{ext}^0\,[1 + b(LiClO_4)] \qquad (1)$$

physically the per cent. increase in rate constant over k_{ext}^0 per 0.01 *M* increment of lithium perchlorate. This is the same form previously employed[1] to fit the normal salt effects shown by the neophyl systems in acetolysis. In Table II are listed the values of K_{ext}^0 and *b* for the least squares fits of the linear portions of the plot for both the *o*- and *p*-anisylethyl esters at two temperatures. The value of *b* at 50.0° for the *o*-isomer is 13.1, and for the *p*-isomer is 11.4; these compare with a value of 12.2 for *p*-methoxyneophyl *p*-toluenesulfonate at 50.0°. As in the case of the neophyl derivatives,[1] the values of *b* in acetolysis of the anisylethyl esters decrease as temperature increases; again, they appear to be roughly proportional to the inverse square of the absolute temperature.

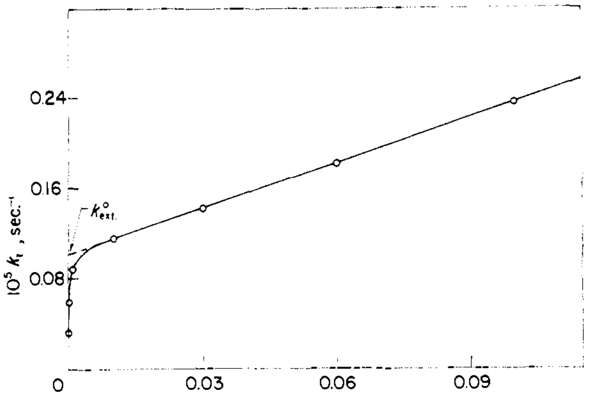

Fig. 1.—Plot of k_t for acetolysis of *o*-anisylethyl *p*-toluenesulfonate at 50.0° *vs.* [$LiClO_4$].

It is convenient to refer to the steep initial rise in solvolysis rate on addition of lithium perchlorate as a "special" salt effect. The nature of the dependence of the special salt effect on salt concentration is shown in Fig. 2 for acetolysis of *p*-anisylethyl toluenesulfonate, using a greatly expanded scale for lithium perchlorate concentration. From this plot, as well as from the data in Table I, it is apparent that considerable acceleration of rate is brought about by concentrations of lithium perchlorate in the range of 10^{-5} to 10^{-4} *M*. Using the terminology of equation 1, the initial special salt effect corresponds to an initial value of *b* of the order of 10^4.

TABLE II

SUMMARY OF LITHIUM PERCHLORATE EFFECTS IN SOLVOLYSIS

Compound	Solvent	Temp., °C.	$10^5 k_{ext}^0$ (sec.$^{-1}$)	b	$(LiClO_4)_{1/2}$ $\times 10^4$, M	k_{ext}^0/k_t^0	Linear fit: No. of points	Linear fit: Av. fit, % of k_{ext}^0	Linear fit: Salt range, M
$C_6H_5CH_2CH_2OTs$	EtOH	75.0	0.708	3.0		1.0	2		0 to 0.031
	AcOH	99.9	0.34[a]	14[a]		1.0	2		0 to 0.031
o-$CH_3OC_6H_4CH_2CH_2OTs$	AcOH	50.0	0.102[d]	13.1	2	3.2	4	±0.3	0.01 to 0.10[c]
	AcOH	75.0	1.98[d]	11.1	2	2.9	4	±0.5	0.01 to 0.10[c]
p-$CH_3OC_6H_4CH_2CH_2OTs$	EtOH	50.0	0.0985	2.6		1.0	2		0 to 0.031
	EtOH	75.0	1.358	3.6		1.0	2		0 to 0.031
	AcOH	75.0	2.3 ± 0.4[b]	2 ± 2[b]		2.5 ± 0.4	2		0.046 to 0.070
	AcOH	50.0	0.150[e]	11.4	3.4	3.3	3	±0.4	0.03 to 0.10
	AcOH	75.0	2.6[e]	9.7	3.4	2.9	3	±1.4	0.03 to 0.10

[a] Based on data of R. Heck. [b] Salt is KOAc; based on data of S. Winstein, *et al.*, THIS JOURNAL, **75**, 147 (1953). [c] Extrapolated value at 0.300 M $LiClO_4$ is 9% low at 50°, 5% low at 75°. [d] $\Delta H^{\ddagger} = 25.87$ kcal./mole; $\Delta S^{\ddagger} = -6.0$ e.u. [e] $\Delta H^{\ddagger} = 24.86$ kcal./mole; $\Delta S^{\ddagger} = -8.4$ e.u.

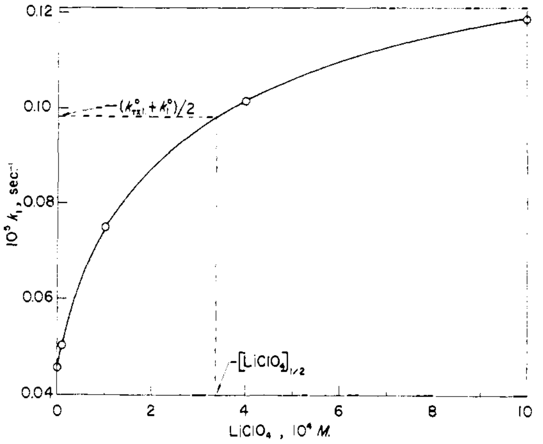

Fig. 2.—Plot of k_t for acetolysis of p-anisylethyl p-toluene sulfonate at 50.0° *vs.* $[LiClO_4]$.

In Fig. 2 is illustrated one of the convenient ways to characterize the special salt effect, namely, by means of the quantity $(LiClO_4)_{1/2}$. This is defined as the concentration of lithium perchlorate which produces one-half of the total special salt effect, *i.e.*, the concentration at which the titrimetric rate constant equals $(k_{ext}^0 + k_t^0)/2$. Values of this quantity, which has theoretical implications which will be brought out in later papers of this series, are listed in Table II.

From the foregoing definitions, it is clear that the extrapolated rate constant k_{ext}^0 is the titrimetric rate constant, at zero salt concentration, which includes the special salt effect of lithium perchlorate, but excludes its normal salt effect. Thus, the ratio of rate constants, k_{ext}^0/k_t^0 measures the magnitude of the full special salt effect. Values of this ratio, listed in Table II, are of the order of 3, and these are seen to decrease slightly as temperature rises.

Regarding the origin of the special salt effect of lithium perchlorate, the indications are that such special salt effects are concerned with suppression of ion pair return.[3] The salt effects observed in acetolysis of the phenylethyl, anisylethyl and p-methoxyneophyl[1] esters lead to such a conclusion. Thus, 2-phenylethyl p-toluenesulfonate does not show an appreciable special salt effect; the increase in acetolysis rate arising from the addition of 0.0311 M lithium perchlorate is of the magnitude expected for the normal salt effect. Consistently, the titrimetric acetolysis rate cannot be seriously affected by ion pair return, since phenyl participation, which could lead to a returnable ion pair, is not of much importance in acetolysis of the phenylethyl ester.[2,4] On the other hand, the anisylethyl esters, which do exhibit the special salt effect, do involve anisyl participation[2,4] in acetolysis and production of intermediates that can be involved in ion pair return. Finally, p-methoxyneophyl p-toluenesulfonate, the acetolysis of which involves the same participating anisyl group, does not show the special salt effect. For this system the observed titrimetric rate constant is unaffected by ion pair return.

While this whole situation will be considered at greater length in subsequent papers in this series, it is already evident that k_{ext}^0 is a better approximation to the ionization rate constant, k_1, than is k_t^0. The use of k_{ext}^0 for the acetolysis rate constant revises considerably the EtOH:AcOH rate ratio which is a useful quantity for certain discussions of mechanism.[2] While the data listed in Table I on the effect of added lithium perchlorate on ethanolysis of 2-phenyl- and 2-p-anisylethyl p-toluenesulfonates are scanty, they suffice to show that any special salt effects are negligible. The small effect of 0.031 M lithium perchlorate on the ethanolysis rates of these compounds, virtually the same for both materials, rules out any appreciable special salt effect. The EtOH:AcOH rate ratio at 75° for p-anisylethyl toluenesulfonate, based on k_t^0 in ethanol and k_{ext}^0 in acetic acid, is 0.52 instead of 1.6 on the old basis.[2]

Experimental Part

Toluenesulfonates.—Phenylethyl, o-anisylethyl and p-anisylethyl p-toluenesulfonates were available from previous work.[2]

Solvents.—The preparation of acetic acid, 0.01 M in acetic anhydride and containing various concentrations of lithium perchlorate, has been described previously.[1,5] Anhydrous ethanol was prepared by the method of Lund and Bjerrum.[6] Solutions of lithium perchlorate in ethanol were prepared with anhydrous lithium perchlorate obtained by stepwise quantitative vacuum dehydration at 77° and 111° of lithium perchlorate trihydrate.

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(4) R. Heck, unpublished work.

(5) A. H. Fainberg and S. Winstein, THIS JOURNAL, **78**, 2770 (1956).

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

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

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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

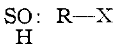
This paper is one of a series concerned with a detailed examination of the basis, scope and limitations of the linear free energy relationship for the correlation of solvolysis rates, $\log k = \log k_0 + mY$. Solvolysis data for *t*-butyl chloride at 25.0°, and the Y values derived therefrom, are reported 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 mY 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

$$\log k = \log k_0 + mY \qquad (1)$$

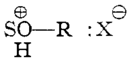
k and k_0 are the first order solvolysis rate constants for a certain substance in a solvent and in the standard solvent, 80% aqueous ethanol, respectively, and m is the compound parameter measuring sensitivity of solvolysis rate to **Y**, the measure of ionizing power of the solvent.

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°.



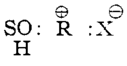
$\underset{H}{SO}\!:\ R—X$

I



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

II



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

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.