Correlation of Solvolysis Rates. IX. p-Methoxyneophyl Toluenesulfonate in a Variety of Solvents. Ionizing Power of Hydroxylic and Non-hydroxylic Solvents[1,2]

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Rates of ionization of p-methoxyneophyl p-toluenesulfonate have been measured in a series of solvents, both hydroxylic and non-hydroxylic. In the common solvolyzing solvents, the rates of ionization of p-methoxyneophyl toluenesulfonate are well correlated by the mY relation with separate lines for the different binary solvent pairs. Taking hydroxylic and non-hydroxylic solvents together, the present data provide a useful scale of solvent polarity based on ionization rate of an alkyl arenesulfonate. Such a scale is useful in correlating rates of various reactions which are solvent-sensitive, and this is illustrated for three rearrangements, a substitution reaction and a keto–enol equilibrium.

For various studies of solvolysis involving ion pair return[3], merging ion pair and cyclic mechanisms,[4] etc., it was desirable to have a scale of solvent polarities for both hydroxylic and non-hydroxylic solvents based on ionization rate of some alkyl arenesulfonate. Such a scale of solvent ionizing power is useful in correlating the ionization rate constant, k_1, which it is necessary to know in ascertaining the importance of ion pair return in certain solvolyses. Also, such a scale of ionizing power would be useful in quantitatively gauging the sensitivity of certain processes to ionizing power.

It is clear[5] that p-methoxyneophyl toluenesulfonate (I) tends to undergo anchimerically assisted ionization with specific rate constant k_Δ, as opposed to anchimerically unassisted reaction with specific rate constant k_s. Ion pair return of cationic intermediates II to the covalent condition would give rise to a very reactive tertiary derivative III which would survive only briefly. Therefore, observed first-order rate constants, k_t, for destruction of p-methoxyneophyl toluenesulfonate (I) are actually rate constants for anchimerically assisted ionization, k_Δ. For this reason, p-methoxyneophyl toluenesulfonate is uniquely suitable[6] as a substrate system on which to base a scale of solvent ionizing power for arenesulfonates. Rates of reaction of p-methoxyneophyl toluenesulfonate (I) have thus been measured in a spectrum of hydroxylic and non-hydroxylic solvents, and the data obtained are reported and discussed in the present article. A few correlations based on this scale of solvent polarity are also presented.

Results

Common Solvolyzing Solvents.—First-order rate constants for solvolysis of p-methoxyneophyl

toluenesulfonate in aqueous dioxane, acetone, methanol, ethanol and acetic acid solvents and acetic acid–formic acid mixtures are summarized in Table I. As is clear from the table, good first-order kinetics were observed in these solvents.

Other Solvents.—In Table II are summarized first-order rate constants for formation of toluenesulfonic acid from p-methoxyneophyl toluenesulfonate in a variety of other solvents. Two of the solvents consist of acetic acid diluted with either dioxane or acetic anhydride. In these solvents relatively satisfactory first-order behavior was observed. Another of the solvents is octanoic acid, a much less ionizing carboxylic acid than is acetic acid. In this solvent integrated first-order rate constants tended to increase as reaction progressed, and thus the rate constant was calculated from the initial slope of a plot of log $(a - x)$ vs. time.

Non-hydroxylic Solvents.—Even in the non-hydroxylic solvents listed in Table II, p-methoxyneophyl toluenesulfonate developed toluenesulfonic acid which could be titrated. Several of the solvents, namely, dimethylformamide, acetone, ethyl acetate and tetrahydrofuran, tended to produce weakly acidic substances which buffered the titration end-points quite seriously. In acetone highly colored material was formed, and the solu-

(1) Research sponsored by the Office of Ordnance Research, U. S. Army.
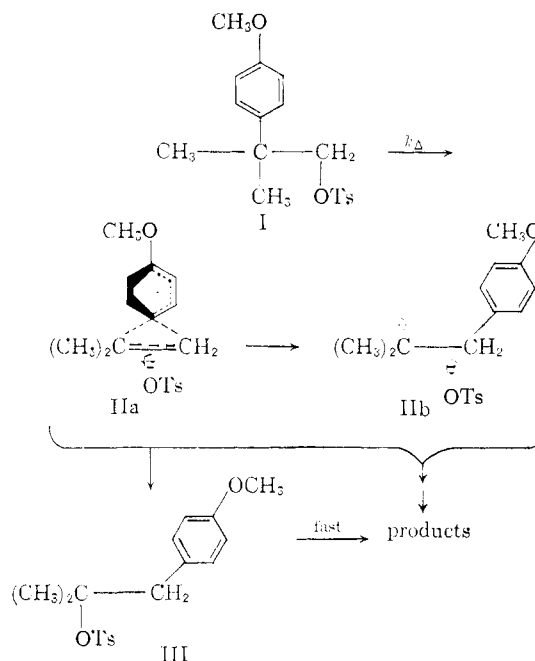
(2) Research supported by the National Science Foundation.

(3) (a) W. G. Young, S. Winstein and H. L. Goering, THIS JOURNAL, **73**, 1958 (1951); (b) S. Winstein and D. Trifan, *ibid.*, **74**, 1154 (1952); (c) S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2165 (1952); (d) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck and G. C. Robinson, *ibid.*, **78**, 328 (1956).

(4) (a) C. A. Grob and S. Winstein, *Helv. Chim. Acta*, **35**, 782 (1952); (b) S. Winstein and G. C. Robinson, THIS JOURNAL, **80**, 169 (1958); (c) Discussion, "Symposium on Molecular Rearrangements," Queen Mary College, Univ. of London, April 6, 1954; see *Chem. Eng. News*, **32**, 1898 (1954); *Nature*, **173**, 898 (1954).

(5) (a) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse, THIS JOURNAL, **74**, 1113 (1952); (b) S. Winstein and R. Heck, *ibid.*, **78**, 4801 (1956); (c) R. Heck and S. Winstein, *ibid.*, **79**, 3432 (1957).

(6) (a) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2763 (1956); (b) A. H. Fainberg and S. Winstein, *ibid.*, **79**, 1608 (1957).

TABLE I

SOLVOLYSIS RATES OF *p*-METHOXYNEOPHYL *p*-TOLUENE-
SULFONATE[a] IN SOME COMMON SOLVOLYZING SOLVENTS

Solvent, vol. %[b]	$10^5 k$, sec.$^{-1c}$ 25.0°	50.0°	$\Delta H^{\ddagger}$, kcal./ mole (50°)	$\Delta S^{\ddagger}$, e.u. (50°)
EtOH–H₂O				
100	0.179	4.23	23.56	−5.8
80	1.406	26.2	21.75	−7.8
60	3.75			
MeOH–H₂O				
100	0.510	11.4	23.12	−5.2
80	2.87	50.5	21.31	−7.8
60		143[d]		
AcOH–HCOOH				
100	0.537	11.9	23.09	−5.2
75	5.5			
50	17.2			
HCOOH[e,b]	83.1			
AcOH + 8.00 *M* H₂O[f]	4.60	74.5[d]	20.7	−9
Dioxane–H₂O				
80	0.160			
70	0.400			
60	1.08			
50	2.66			
Me₂CO–H₂O				
96.8		3.22[g]		
93.8		7.39[g]		
90		16.1[g]		
80		53.0[g]		

[a] Initial concentration: 0.01 − 0.03 *M*. [b] *X* vol. % A–B means *x* volumes of A plus 100 − *x* volumes of B, both at 25° before mixing. [c] Unless otherwise indicated, the average deviation of these rate constants ranged from ±0.2 to ±1.0%, the over-all average deviation being ± 0.7%. [d] Average deviation ±2%. [e] Contained 0.0302 *M* NaOCHO. [f] Contained 0.068 *M* LiOAc. [g] Temp. 75.0°.

TABLE II

RATES OF REACTION OF *p*-METHOXYNEOPHYL *p*-TOLUENE-
SULFONATE IN A VARIETY OF SOLVENTS

Solvent	Temp., °C.	[ROTs], 10^2 *M*	$10^5 k_1$, sec.$^{-1}$
50% AcOH–Ac₂O	50.0	2.01	6.43 ± 0.01
Me₂SO	49.9	2.48	1.35 ± .01[d]
Me₂SO	75.0	2.50	18.2 ± .2
MeNO₂	75.0	2.01	12.3[a]
C₇H₁₅COOH	50.0	2.00	0.434[a,c]
C₇H₁₅COOH	75.0	2.01	7.26[a]
MeCN	75.0	2.02	6.01[a,c]
HCONMe₂	75.0	2.50	4.96 ± 0.07[b,c]
Ac₂O	75.0	2.02	3.41 ± .02
C₅H₅N	75.0	2.06	2.14 ± .04
C₅H₅N	100.0	2.01	20.4 ± .5[a]
12.5% AcOH–dioxane	75.1	2.50	1.21 ± .02
Me₂CO	75.0	2.03	.857 ± 0.012[a,c]
EtOAc	75.0	2.01	.113[a,c]
(CH₂)₄O	75.0	2.02	.0847 ± .0023[a,c]
Et₂O	75.0	2.03	ca. .005[c]

[a] Initial rate constant; first-order rate constant drifts up. [b] Initial rate constant; first-order rate constant drifts down. [c] Calculated on the basis of the theoretical infinity titer. [d] $\Delta H^{\ddagger}$ = 22.5 kcal./mole, $\Delta S^{\ddagger}(75°)$ = −11.3 e.u. [e] $\Delta H^{\ddagger}$ = 22.6 kcal./mole, $\Delta S^{\ddagger}(75°)$ = −15.4 e.u.

tion was almost black by 60% reaction. In these solvents it was not possible to obtain an experimental infinity titer, and the rate constants were calculated on the basis of the theoretical value.

In dimethyl sulfoxide, acid production from *p*-methoxyneophyl toluenesulfonate followed good first-order kinetics, as is illustrated in Table III. In most of the non-hydroxylic solvents acceleration of rate due to accumulation of toluenesulfonic acid during a run was evident, and thus integrated first-order rate constants drifted up in a run. The magnitude of this drift is summarized in Table IV for a number of solvents and illustrated for nitromethane and chloroform in Tables V and VI. In such cases the rate constants listed in Table II were determined from the initial slope of a plot of log (*a* − *x*) *vs.* time.

TABLE III

RATE OF REACTION OF 0.0250 *M* *p*-METHOXYNEOPHYL
TOLUENESULFONATE IN DIMETHYL SULFOXIDE AT 75.0°

Time, 10^{-3} sec.	Titer, ml.[a]	Acid, %	$10^4 k_1$, sec.$^{-1}$
. . .	0.100	2.9	. .
0.60	.449	12.8	1.85
1.20	.755	21.6	1.83
1.92	1.076	30.8	1.82
2.70	1.391	39.8	1.83
3.60	1.700	48.6	1.83
4.50	1.965	56.2	1.84
6.60	2.430	69.5	1.84
11.10	2.980	85.2	1.83
70.80	3.400	97.3	
70.80	3.395	97.1	
70.80	3.440	98.4	

Mean 1.83 ± 0.01

[a] 0.03605 *M* sodium methoxide per 5.037-ml. aliquot; theoretical infinity titer, 3.496 ml.

TABLE IV

UPWARD DRIFTS IN INTEGRATED FIRST-ORDER RATE CON-
STANTS FOR *p*-METHOXYNEOPHYL TOLUENESULFONATE IN
VARIOUS SOLVENTS AT 75°

Solvent	(ROTs) 10^2 *M*	% increase in integ. k_1 at 50% rn.	k_2, 1./mole-sec.
n-C₇H₁₅COOH	2.01	2	
Me₂CO	2.03	6	
MeCN	2.02	7	
HCONMe₂	2.50	7[a]	
(CH₂)₄O	2.02	7	
EtOAc	2.01	29	
MeNO₂	2.01	42	ca. 6.2 × 10⁻³
Et₂O	2.03	150	1.6 × 10⁻⁵
CHCl₃	2.01	ca. 650	4.69 × 10⁻²
C₆H₆	2.51		1.84 × 10⁻²

[a] % decrease.

Pyridine.—From *p*-methoxyneophyl toluenesulfonate in pyridine at 75°, only 77.6% of the theoretical infinity acid titer was observed. The corresponding figure was 83% after 20 half-lives at 100°. Evidently, titratable acid is produced only by elimination and not substitution, which must also compete. Excellent first-order rate constants for disappearance of *p*-methoxyneophyl toluenesulfonate were obtained on the basis of the experimental infinity titers.

Nitromethane and Ether.—As illustrated in Table V, integrated first-order rate constants for acid production from *p*-methoxyneophyl toluenesulfonate in nitromethane drift up rapidly during a run. This drift may be ascribed to the contri-

TABLE V

RATE OF REACTION OF 0.0201 M p-METHOXYNEOPHYL TOLUENESULFONATE IN NITROMETHANE AT 75.0°

Time, 10^{-2} sec.	Acid, %	$10^4 k_1$, sec.$^{-1}$	
		Instant.	Integ.
....	2.2	1.26	..
1.95	4.5	1.29	1.20
4.20	7.2	1.33	1.23
6.60	9.9	1.36	1.24
9.60	13.6	1.43	1.32
13.20	18.2	1.51	1.37
16.80	22.9	1.60	1.43
24.00	32.4	1.83	1.55
30.00	39.9		1.64
36.00	47.8		1.72
45.00	57.3		1.87
59.40	70.5		2.05
78.60	82.7		2.27
330.00	98.7		
330.00	98.7		

TABLE VI

REACTION OF 0.0201 M p-METHOXYNEOPHYL TOLUENESULFONATE IN CHLOROFORM AT 75.0°

Time, 10^{-2} sec.	Acid, %	Integrated $10^5 k_1$, sec.$^{-1}$	Integrated $10^2 k_2$, 1./mole-sec.
....	1.3	..	..
3.00	2.1	2.8	(8.6)
6.00	2.1	1.5	(4.4)
9.00	3.0	2.0	(4.9)
12.00	3.5	2.0	(4.3)
15.00	5.1	2.7	4.75
18.00	6.6	3.1	4.72
24.00	10.4	5.1	4.64
30.00	17.0	5.9	4.62
36.00	26.8	8.5	4.65
42.00	39.3	11.8	4.66
48.00	54.4	16.5	4.72
57.00	75.6	25.4	4.75
360.00	98.6		
777.00	98.3		

Mean 4.69 ± 0.05

bution of a toluenesulfonic acid-catalyzed term to the instantaneous first-order rate constant, $[(dx/dt)/(a - x)]$, as in eq. 1. In this equation, x

$$[(dx/dt)/(a - x)] = k_1 + k_2 x \qquad (1)$$

and $(a - x)$ denote concentrations of toluenesulfonic acid and alkyl toluenesulfonate, respectively, and k_2 is a second-order rate constant for the toluenesulfonic acid-catalyzed reaction. In accordance with eq. 1, the instantaneous first-order rate constant does increase linearly with x at low x-values, but it tends to rise more steeply at higher values. The intercept at $x = 0$ from a plot of $[(dx/dt)/(a - x)]$ $vs.$ x leads to a value of 1.23×10^{-4} sec.$^{-1}$ for k_1, while the slope of the initial linear portion of the plot leads to a k_2-value of $ca.$ 6.2×10^{-3} 1./mole-sec.

In diethyl ether at 75°, acid production from p-methoxyneophyl toluenesulfonate was followed to 83%. In this range an integrated first-order rate constant climbs from an initial value of 5×10^{-8} to 18.5×10^{-8} sec.$^{-1}$. A plot of $[(dx/dt)/(a - x)]$ $vs.$ x is roughly linear, and the intercept and slope of this plot lead to a value of 5×10^{-8} sec.$^{-1}$ for k_1 and 1.6×10^{-5} 1./mole-sec. for k_2.

Chloroform and Benzene.—In chloroform at 75.0° p-methoxyneophyl toluenesulfonate produced one equivalent of acid relatively rapidly. However, an integrated first-order rate constant increased from 2.0×10^{-5} sec.$^{-1}$ at 3% reaction to 25.4×10^{-5} sec.$^{-1}$ at 75.6% reaction. A plot of $[(dx/dt)/(a - x)]$ $vs.$ x passes essentially through the origin so that k_1 may be omitted in eq. 1. In fact, a good second-order rate constant is obtained from the integrated form of eq. 1 omitting k_1. This is illustrated in Table VI.

In benzene, acid production from p-methoxyneophyl toluenesulfonate is very strongly autocatalytic. Sealed ampoules could not be employed for rate measurements because erratic induction periods for the formation of acid were encountered. However, acid formation could be followed by titration of aliquots from a single reaction flask. As is clear from the data summarized in Table VII, a plot of the instantaneous first-order rate constant $vs.$ the instantaneous concentration of developed acid curves up after $ca.$ 30% reaction. This behavior is reflected in Table VII by the upward

TABLE VII

REACTION OF 0.0251 M p-METHOXYNEOPHYL TOLUENESULFONATE IN BENZENE AT 75.0°

Time, 10^{-4} sec.	Acid, %	Instant. $10^4 k_1$, sec.$^{-1}$	Integ. $10^2 k_2$, 1./mole-sec.	Integ. k_3, 1.^{2}/mole^2. sec.
...	0.03	..	..	..
0.900	1.8	..	..	..
1.260	8.1	0.3	1.84	
1.440	16.4	1.1	1.84	
1.500	22.1	1.5	1.86	
1.560	28.9	2.1	1.88	3.55
1.590	33.3	2.7	1.90	3.50
1.656	44.9	4.3	1.95	3.28
1.710	56.2	5.9	2.01	3.12
1.770	67.1	7.6	2.06	2.90
1.800	73.4	9.4	2.11	2.88
1.830	78.4	11.0	2.16	2.84
1.860	79.3		2.14	2.64
1.896	85.5		2.25	2.73
1.944	90.5		2.50	2.98
3.300	92.1			
3.720	91.9			
4.230	92.3			

drift in k_2 calculated from the integrated form of eq. 1 neglecting k_1. Further, a plot of the instantaneous first-order rate constant $vs.$ the square of the developed toluenesulfonic acid concentration curves down slightly. This is evident from the downward drift in the values of k_3 calculated from the integrated form of eq. 2. There are difficulties with the application of the integrated forms of eq. 1 and 2 to small values of x. Therefore, in the calculation of k_3 in Table VII, t_0 was shifted as in eq. 3 to the point where $x_0 = 0.850$ ml. Although k_3 drifts down during the run, it is more constant than k_2 after $ca.$ 20 or 30% reaction.

$$[(dx/dt)/(a - x)] = k_3 x^2 \qquad (2)$$

$$k_3 = \frac{1}{a(1 - t_0)}\left[\frac{1}{x_0} - \frac{1}{x} + \frac{2.303}{a}\left(\log\frac{a - x_0}{x_0} - \log\frac{(a - x)}{x}\right)\right] \qquad (3)$$

Neophyl Toluenesulfonate.—The behavior of neophyl toluenesulfonate was examined briefly in several of the non-hydroxylic solvents employed with the p-methoxy derivative. The pertinent first-order rate constants are summarized in Table VIII. In dimethyl sulfoxide, good first-order

TABLE VIII

RATE OF REACTION OF NEOPHYL TOLUENESULFONATE IN SEVERAL SOLVENTS

Solvent	Temp., °C.	(ROTs) $10^2 M$	$10^5 k_1$, sec. $^{-1}$
Me$_2$SO	75.0	2.50	0.151 ± 0.001
C$_5$H$_5$N	100.0	2.00	$.137 \pm 0.002$
Me$_2$CO	75.0	2.51	$.0040^{a,b}$
(CH$_2$)$_4$O	75.0	1.99	ca. $.0005^b$
Et$_2$O	75.0	1.98	ca. $.0001^b$

^{a} Initial rate constant; first-order rate constant drifts up. ^{b} Calculated on the theoretical infinity.

kinetics of acid formation were observed. In pyridine at 100°, acid production was followed as far as 63.5% of theoretical, and a steady first-order rate constant was obtained on the basis of the same infinity acid titer observed with p-methoxyneophyl toluenesulfonate. In acetone, tetrahydrofuran and ether, it was possible to follow the rate of acid production only a short way, so the rate constants are based on the first 7, ca. 2 and 1.8% of acid formation in the three solvents, respectively. Especially in tetrahydrofuran and ether, these rate constants are very rough.

Discussion

*m*Y Fits.—The correlation of the rates of solvolysis of p-methoxyneophyl toluenesulfonate in the common solvolyzing solvents with the linear free energy *m*Y relation[7] (4) is summarized in Table IX. In this correlation, solvent ionizing power, Y, is based on t-butyl chloride as the standard substrate. Relation 4 is equivalent to the linear relation 5 between log $(f_{RX}/f_{\pm})$ for the substrate, RX, and that of the standard substrate, BuCl, $(f_{RX}/f_{\pm})$ being the ratio of activity coefficients for ground state and transition state, respectively.

$$\log k = \log k_0 + m\mathbf{Y} \tag{4}$$

$$\Delta \log \left(\frac{f_{RX}}{f_{\pm}}\right)_{RX} = m\Delta \log \left(\frac{f_{RX}}{f_{\pm}}\right)_{BuCl} \tag{5}$$

Plots of log k $vs.$ Y[8] display the now familiar dispersion[8,9] into separate lines for different binary solvent pairs. As summarized in Table IX, treatment of the binary solvent pairs separately leads to satisfactory *m*Y correlations over the solvent ranges explored, the *m*-values ranging from 0.42 to 0.58 at 25°.

p-**Methoxyneophyl–Neophyl Comparison.**—When we turn to a consideration of the non-hydroxylic solvents, summarized in Table II, the question legitimately arises whether rate constants in these solvents still reflect anchimerically assisted ionization. Since some of the solvents have very low

(7) (a) E. Grunwald and S. Winstein, THIS JOURNAL, **70**, 846 (1948); (b) S. Winstein, E. Grunwald and H. W. Jones, $ibid.$, **73**, 2700 (1951).

(8) A. H. Fainberg and S. Winstein, $ibid.$, **78**, 2770 (1956).

(9) (a) A. H. Fainberg and S. Winstein, $ibid.$, **79**, 1597 (1957); (b) A. H. Fainberg and S. Winstein, $ibid.$, **79**, 1602 (1957); (c) A. H. Fainberg and S. Winstein, $ibid.$, **79**, 1608 (1957); (d) S. Winstein, A. H. Fainberg and E. Grunwald, $ibid.$, **79**, 4146 (1957).

TABLE IX

CORRELATION OF SOLVOLYSIS RATES WITH Y

Temp., °C.	Solvent range	No. of points	m	log k_0	r
25.0	60–100% EtOH–H$_2$O^a	3	0.421	-4.881	0.024
50.0	80–100% EtOH–H$_2$O^b	2	.390	-3.582	...
25.0	80–100% MeOH–H$_2$O^c	2	.510	-4.736	...
50.0	60–100% MeOH–H$_2$O^d	3	.423	-3.472	0.012
25.0	0–100% AcOH–HCOOH	4	.585	-4.236	0.052
25.0	0–8 M H$_2$O in AcOH	2	.499	-4.433	...
50.0	0–8 M H$_2$O in AcOH	2	.426	-3.210	...
25.0	50–80% dioxane–H$_2$O	4	.560	-5.360	0.028

^{a,b,c,d} Extrapolated rate constants for pure water: ^{a} log $k = -3.410$. ^{b} log $k = -2.220$. ^{c} log $k = -3.493$. ^{d} log $k = -1.994$.

ionizing power, there would be the possibility, at least for the more nucleophilic solvents in this group, that anchimerically unassisted processes involving nucleophilic solvent participation are instead being measured. With other substrates than p-methoxyneophyl toluenesulfonate, nucleophilic solvent participation in the rate-determining process is observed in solvents such as pyridine,[10] dimethyl sulfoxide,[11] dimethylformamide,[12] etc. In the present case an excellent criterion of mechanism is the sensitivity of rate to p-methoxyl substitution in the neophyl system. Since anchimerically assisted ionization is known[5b,c] to be very sensitive to methoxyl substitution and anchimerically unassisted solvolysis is relatively insensitive, the p-methoxyneophyl–neophyl rate ratio indicates whether k_Δ is indeed being measured for p-methoxyneophyl toluenesulfonate.

Summarized in Table X are the p-methoxyneophyl–neophyl ratios in various solvents, based on the present work or the results of another in-

TABLE X

COMPARISON OF REACTION RATES OF p-METHOXYNEOPHYL AND NEOPHYL p-TOLUENESULFONATES IN VARIOUS SOLVENTS

Solvent	Temp., °C.	Rate ratio	Ratio at 50°
HCOOH	25.0	72^a	52^b
80% EtOH	50.0	97^a	97
AcOH	50.0	118^a	118
MeOH	50.0	135^a	135
EtOH	50.0	165^a	165
Me$_2$SO	75.0	121	175^b
Pyridine	100.0	156	341^b
Me$_2$CO	75.0	210	320^b
(CH$_2$)$_4$O	75.0	ca. 170	ca. 250^b
Et$_2$O	75.0	ca. 100	ca. 140^b

^{a} Based on solvolysis rates of neophyl toluenesulfonate determined by A. Fainberg and G. Goldman.[13] ^{b} p-Methoxyneophyl–neophyl ratio corrected to 50°, assuming $\Delta S^\pm$ invariant to p-methoxy substitution.

vestigation.[13] As the summary shows, p-methoxyneophyl toluenesulfonate is more rapid than neophyl toluenesulfonate by factors ranging from ca. 50 to ca. 300 at 50°, the factor tending to increase as one traverses the solvent spectrum from the more reactive toward the less reactive end. This ratio is high even for solvents such as pyridine, acetone and tetrahydrofuran, nucleophilic solvents relatively low in ionizing power, and it becomes

(10) J. A. Vona and J. Steigman, $ibid.$, **81**, 1095 (1959).

(11) S. G. Smith and S. Winstein, $Tetrahedron$, **3**, 317 (1958).

(12) H. K. Hall, Jr., THIS JOURNAL, **78**, 2717 (1956).

(13) A. Fainberg and G. Goldman, unpublished work.

clear that rates of reaction of p-methoxyneophyl toluenesulfonate in the whole spectrum of solvents summarized in Tables I and II reflect anchimerically assisted ionization.

Scale of Solvent Ionizing Power.—Relative rates of ionization of p-methoxyneophyl toluenesulfonate in some twenty solvents compared to acetic acid are summarized in Table XI. These cover a rate range of some 7 powers of ten and provide a useful scale of solvent-ionizing power for correlating rates of certain reactions.

TABLE XI

RELATIVE RATES OF p-METHOXYNEOPHYL p-TOLUENESULFONATE

	Solvent	D, 25°	Ref.	$\log k_1$ 75°	Rel. rate 75°
1	H₂O	78.54	14	−1.180	39[d,g]
2	HCOOH	58[a]	14	−0.929[h]	153[e]
3	80% EtOH–H₂O	67.0	15	−2.505	1.85[d]
4	AcOH	6.2	14	−2.772	(1.00)[d]
5	MeOH	32.63	14	−2.796	0.947[d]
6	50%AcOH–Ac₂O				.540[f]
7	EtOH	24.30	14	−3.204	.370
8	Me₂SO	45	16	−3.738	.108
9	MeNO₂	36.7	14	−3.921	7.3×10^{-2}
10	n-C₇H₁₅COOH	2.4[b]	14	−4.139	4.30×10^{-2}
11	CH₃CN	36.7	14	−4.221	3.56×10^{-2}
12	HCONMe₂	36.71	17	−4.298	2.94×10^{-2}
13	Ac₂O	20.7[c]	14	−4.467	2.02×10^{-2}
14	C₅H₅N	12.3	14	−4.670	1.27×10^{-2}
15	12.5% AcOH–dioxane			−4.910	7.28×10^{-3}
16	Me₂CO	20.7	14	−5.067	5.07×10^{-3}
17	EtOAc	6.02	14	−5.947	6.69×10^{-4}
18	(CH₂)₄O	7.39	18	−6.073	5.0×10^{-4}
19	Et₂O	4.23	14	−7.3	$ca. 3 \times 10^{-5}$

[a] Value at 16°. [b] Value at 20°. [c] Value at 19°. [d] Extrapolated from data at other temperatures. [e] Relative rate at 25.0°. [f] Relative rate at 50.0°. [g] Questionable value since it is based on a rate constant in water obtained by extrapolation of m Y plots for aqueous methanol and ethanol to pure water (Table IX). [h] Extrapolated from 25° assuming $\Delta S^{\neq}$ is the same as for neophyl toluenesulfonate.[13]

The carboxylic acids listed in Table XI, HCOOH, CH₃COOH and C₇H₁₅COOH, constitute an interesting and useful series of relatively poor nucleophilic solvents which cover a 3.6×10^3 range of ionizing power as measured by p-methoxyneophyl toluenesulfonate. As judged by rates of racemization of exo-norbornyl bromobenzenesulfonate in another investigation,[19] propionic and n-valeric acids fill in the gap in ionizing power between acetic and n-octanoic acids.

As regards mixtures of acetic acid with a nonhydroxylic solvent, dilution with dioxane to 12.5% AcOH–dioxane depresses solvolysis rate somewhat more than changing from acetic acid to octanoic acid as a solvent. On the other hand, dilution of acetic acid with acetic anhydride, whose dielectric constant (D) is 20, is only slightly rate-depressing. In this case, the whole rate factor between pure

acetic acid and pure acetic anhydride is only 50. Acetic acid–acetic anhydride mixtures represent an interesting and useful range of solvents of slightly decreasing ionizing power and definitely increasing dissociating power.[20]

Dielectric Constant and Hydrogen Bonding.— Simple electrostatic considerations suggest that $\log (f_{RX}/f_{\pm})$ should follow $[(D - 1)/(2D + 1)]$, and, therefore, that $\log k$ should be linear in $[(D - 1)/(2D + 1)]$. While it is well known that dielectric constant is, in general, a poor guide to ionizing power, it is nevertheless instructive to plot $\log k$ for p-methoxyneophyl toluenesulfonate $vs.$ $[(D - 1)/(2D + 1)]$ for the various pure solvents in Table XI. This plot shown in Fig. 1 emphasizes the failure of dielectric constant as a guide to the behavior of $\log (f_{RX}/f_{\pm})$. For example, acetic acid and tetrahydrofuran have very similar dielectric constants, and yet ionization rate in acetic acid exceeds that in tetrahydrofuran by a factor of 2×10^3.

The most important specific solvation factor which makes dielectric constant a poor guide to ionizing power involves hydrogen bonding between a hydroxylic or similar solvent and the organic substrate ground and transition states. For this reason, the hydroxylic solvents in Table XI and Fig. 1 tend to be relatively high in the scale of ionizing power. Indeed, omitting the hydroxylic solvents, a rough straight line is given by the plot of $\log k$ $vs.$ $[(D - 1)/(2D + 1)]$ for the nonhydroxylic solvents in Fig. 1.

It is worth noting that the most ionizing nonhydroxylic solvents in Table XI, such as dimethyl sulfoxide and nitromethane, are actually more ionizing than octanoic acid and began to rival even ethanol in this respect.

Other Solvents.—There are data in the literature which furnish information on relative ionizing power toward alkyl halides of some solvents not listed in Table XI. With the alkyl halides the situation is less satisfactory than in the p-methoxyneophyl case, since it is not clear exactly what fraction[3,4,21] of the ionization rate is being measured in the investigations in question. Judging by rates of elimination, exchange or solvolysis reactions of t-butyl bromide, the solvent order HCOOH[9b] $\simeq$ SO₂[22] > F₃CCH₂OH[23] > EtOH[9b] > MeNO₂[24] > HCONMe₂[25,26] EtCONHMe[25a] > Me₂CO,[26] is indicated, rates in the first three solvents being very similar. For t-butyl chloride, the sequence, HCOOH[8] > HCONH₂[8] > EtOH[8] > MeNO₂[27] > HCONMe₂[25a], is indicated, solvolysis rate in formamide being nearly equal to that in

(14) A. A. Maryott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids," National Bureau of Standards Circular No. 514, 1951.

(15) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," A.C.S. Monograph, No. 137, 3rd edition, Reinhold Publishing Corp., New York, N. Y., 1958, p. 161.

(16) Technical Bulletin, The Stepan Chemical Company, Chicago, Ill.

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(18) F. E. Critchfield, J. A. Gibson and J. L. Hall, ibid., 75, 6044 (1953).

(19) E. Clippinger, unpublished work.

(20) P. Klinedinst and S. Smith, unpublished work.

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(22) C. A. Bunton, C. H. Greenstreet, E. D. Hughes and C. K. Ingold, J. Chem. Soc., 642 (1954).

(23) F. L. Scott, Chemistry & Industry, 224 (1959).

(24) P. B. de la Mare, E. D. Hughes, C. K. Ingold and Y. Pocker, J. Chem. Soc., 2930 (1954).

(25) (a) S. D. Ross and M. M. Labes, THIS JOURNAL, 79, 4155 (1957); (b) N. Kornblum and R. K. Blackwood, ibid., 78, 4037 (1956).

(26) S. Winstein, S. Smith and D. Darwish, Tetrahedron Letters, 16, 24 (1959).

(27) Y. Pocker, J. Chem. Soc., 1972 (1960).

in 50% AcOH–HCOOH or 70% EtOH–HOH. From solvolysis or racemization rates of α-phenylethyl chloride, the solvent sequence, $HCOOH^{9a,28}$ > $C_3F_7COOH^{9a}$ > SO_2,[29] covers a rate range of approximately one power of ten.

In chloroform and benzene, toluenesulfonic acidcatalyzed ionization of p-methoxyneophyl toluenesulfonate is so important that it was not possible to estimate rate constants for uncatalyzed ionization. This toluenesulfonic acid catalysis, already serious in ether and nitromethane, resembles the similar catalysis by generated benzenesulfonic acid in the alkylation of solvent benzene with benzyl[30a] and other[30b] benzenesulfonates as reported by Nenitzescu.[30] It is analogous to the hydrogen chloride catalysis of ionization of chlorides, such as camphene hydrochloride in nitrobenzene,[31] α-chloroethers in alcohol–benzene,[32] and t-butyl chloride in nitromethane.[27] Also analogous is the benzenesulfonic acid catalysis of alkylation of solvent benzene by benzyl chloride.[33] Such catalysis can be expected to be especially important in the poor anion-solvating solvents, the catalyzed ionization leading to HCl_2^- or its analog in other cases.[34]

In benzene, ionization of p-methoxyneophyl toluenesulfonate is between first and second order in toluenesulfonic acid, and this is analogous to Nenitzescu's report[30,33] that reactions of benzyl benzenesulfonate and benzyl chloride are approximately second order in benzenesulfonic acid. Thus there is a tendency for the benzenesulfonate anion to be associated with more than one benzenesulfonic acid molecule. In fact, the number of benzenesulfonic acid molecules involved is apparently large, since cryoscopic measurements by Nenitzescu[3c] indicated that benzenesulfonic acid is associated into dimers and trimers. Kinetic orders of one to two in benzenesulfonic acid correspond to the involvement of two to six benzenesulfonic acid molecules in the ionization step.

Because the toluenesulfonic acid catalysis of ionization of p-methoxyneophyl toluenesulfonate is so effective in benzene and chloroform, ionization of this substrate actually occurs relatively rapidly in these solvents. Thus, at a toluenesulfonic acid concentration of 0.01 M, ionization proceeds in benzene as rapidly as in dimethyl sulfoxide, and in chloroform about as rapidly as in ethanol.

Z-Values.—Recently, Kosower[35] proposed a measure of solvent polarity based upon the solvent dependence of the position of the charge-transfer absorption maximum of 1-methyl-4-carbomethoxypyridinium iodide. The observed maxima were converted into transition energies and termed Z-values. It was found that Z correlated quite well with available Y-values,[8] the usual dispersion

(28) Bodendorf and Böhme, *Ann.*, **516**, 1 (1935).

(29) E. Bergmann and M. Polanyi, *Naturwiss.*, **21**, 378 (1933).

(30) (a) C. D. Nenitzescu, S. Tzitzeica and V. Ioan, *Bull. soc. chim. France*, 1272 (1955); (b) C. D. Nenitzescu, V. Ioan and L. Theodorescu, *Ber.*, **90**, 585 (1957).

(31) (a) P. D. Bartlett and I. Pöckel, This JOURNAL, **60**, 1585 (1938); (b) H. Meerwein and K. van Emster, *Ber.*, **55B**, 2500 (1922).

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

(33) C. D. Nenitzescu, private communication.

(34) E.g., see H. V. Looy and L. P. Hammett, This JOURNAL, **81**, 3872 (1959).
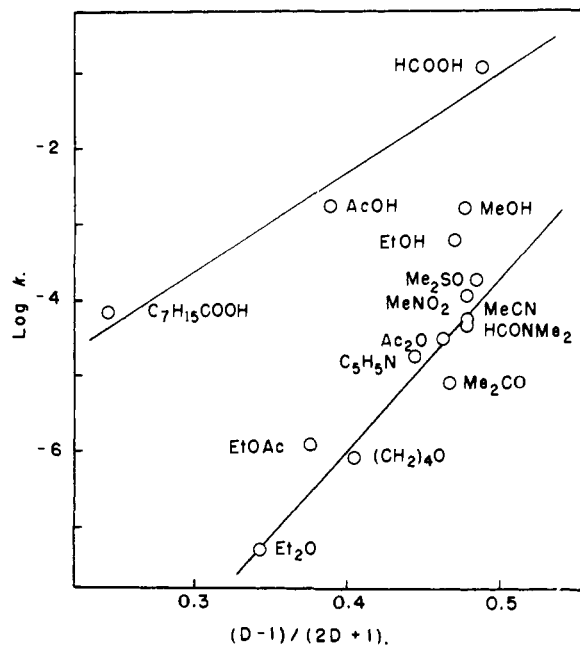
(35) E. M. Kosower, *ibid.*, **80**, 3253, 3267 (1958).

Fig. 1—Plot of log k for p-methoxyneophyl OTs vs. $(D - 1)/(2D + 1)$.

into separate lines for binary solvent pairs being observed. It is now possible to extend the correlation between Z-values and ionization rates to include non-hydroxylic solvents by plotting log k_1 for p-methoxyneophyl toluenesulfonate vs. Z. From Fig. 2 it is clear that the scatter in the plot is not large, and that a fair linear relation exists between the two measures of solvent polarity. The mean deviation of Z from the least squares line of eq. 6 is ± 1.6 kcal./mole.

$$Z = 104.2 + 8.11 \log k_1 \qquad (6)$$

Rearrangements.—Using the scale of solvent ionizing power based on p-methoxyneophyl toluenesulfonate, we can attempt to correlate the response of other reactions to solvent variation with the log k_1 values for the p-methoxyneophyl system. It is clear from the outset that we cannot expect such correlations to have unlimited scope, since there will be limitations to the changes which can be made in the R and X portions of substrate RX molecules which will still leave log $(f_{RX}/f_{\pm})$ linearly related to log $(f_{RX}/f_{\pm})$ for p-methoxyneophyl toluenesulfonate over any specific solvent range.[8,9,36]

Sufficient data are available in the literature to illustrate a linear relation between solvent ionizing power, as given by log k_1 for p-methoxyneophyl toluenesulfonate, and log k for several rearrangements. These are the ionic rearrangement of 9-decalyl perbenzoate,[37] the allylic rearrangement of 1-phenylallyl 3,4,5-tribromobenzoate[38] and the Curtius rearrangement of benzoyl azide.[39] As

(36) S. Winstein and A. H. Fainberg, *ibid.*, **79**, 5937 (1957).

(37) (a) R. Criegee and R. Kasper, *Ann.*, **560**, 127 (1948); (b) P. D. Bartlett and J. L. Kice, This JOURNAL, **75**, 5591 (1953); (c) H. L. Goering and A. C. Olson, *ibid.*, **75**, 5853 (1953).

(38) J. Meisenheimer, W. Schmide and G. Schafer, *Ann.*, **501**, 131 (1933).

(39) M. S. Newman, S. H. Lee and A. B. Garrett, This JOURNAL, **69**, 113 (1947).

TABLE XII

CORRELATION OF VARIOUS REACTIONS WITH IONIZATION OF p-METHOXYNEOPHYL TOLUENESULFONATE

Reaction correlated	Ref.	Temp., °C.	Solvents[a]	—Least square— parameters[b] a	b	Mean dev. in log k
Transition energies for the c-t band of 1-methyl-4-carbomethoxypyridinium iodide (Z-values), kcal./mole	35	25	1, 3, 4, 5, 7, 8, 11, 12, 14, 16	8.11	104.2	1.6[c]
Rearrangement of 9-decalyl perbenzoate; k_1, sec.$^{-1}$	37	40	4, 5, 9, 11, 14, 16, 17	0.690	−1.52	0.16
Rearrangement of 1-phenylallyl 3,4,5-tribromobenzoate; k_1, hr.$^{-1}$	38	137	9, 11, 16, 19	.569	1.834	.05
Curtius rearrangement of benzoyl azide; k_1, hr.$^{-1}$	39	75	4, 9, 11, 14, 16, 17	.119	0.497	.05
Keto-enol equilibrium of ethyl acetoacetate; enol/ketone	40	ca. 20	1, 4, 5, 7	− .756	−3.29	.03
			1, 16, 17, 19	− .344	−2.82	.02
Exchange of MeI with radio −NaI; k_2, l./mole-sec.	42	25	1, 5, 7, 16	−1.06	−4.82	.24

[a] Numbers refer to the solvents in Table XI. [b] Least square parameters for the linear relation 7; log k_1 for p-methoxyneophyl toluenesulfonate at 75°. [c] Mean deviation in Z (kcal./mole).

summarized in Table XII, log k for these rearrangements are correlated quite well by log k_1 for p-methoxyneophyl toluenesulfonate. The least squares slope a and intercept b for the linear
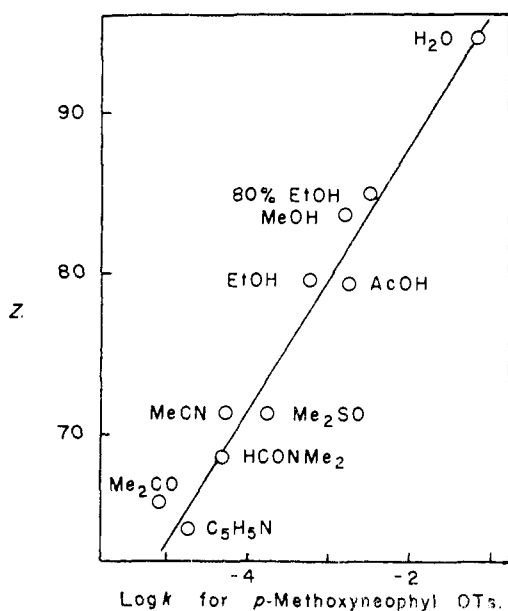

Fig. 2.—Plot of Z vs. log k for p-methoxyneophyl OTs.

relation 7 are listed in Table XII, together with the mean deviation between the predicted and actual log k values.

$$\log k_{reaction} = a \log k_1 + b \qquad (7)$$

The a-value in eq. 7 is a measure of relative sensitivity of a reaction to solvent ionizing power. From the a-values in Table XII, we see that the order of decreasing sensitivity to ionizing power of the different rearrangements is: 9-decalyl perbenzoate > 1-phenylallyl tribromobenzoate > benzoyl azide. In the latter case, the a-value is only 0.119, sensitivity to ionizing power being very low.

Other Reactions.—Meyer showed that the position of equilibrium between the keto and enol forms of ethyl acetoacetate depends upon the nature of the solvent.[40] Powling and Bernstein[41]

attempted to correlate the equilibrium constants with $[(D - 1)/(2D + 1)]$ and observed two lines, one for water and alcohols, and another for non-hydroxylic solvents together with formic and acetic acids. As summarized in Table XII, the correlation of log K with log k for p-methoxyneophyl toluenesulfonate also leads to two lines. However, one line is obtained for the hydroxylic solvents and a second one for the non-hydroxylic ones.

Since log k_1 for p-methoxyneophyl toluenesulfonate 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 would be $(1/D)$. This follows because $[(D - 1)/(2D + 1)]$ is linear in $(1/D)$ except at very low dielectric constants.[8] One such reaction is the exchange reaction between methyl iodide and sodium radio-iodide measured by Swart and LeRoux[42] in several solvents. As summarized in Table XII, their data are correlated quite well with the ionization rate constants for p-methoxyneophyl toluenesulfonate.

Experimental

Toluenesulfonates.—The neophyl p-toluenesulfonate[5a] was kindly furnished by R. Heck.

Part of the p-methoxyneophyl p-toluenesulfonate employed in the present work was the same material, m.p. 44–46°, used previously.[5b] A new preparation of this material gave rise to another crystalline form, m.p. 53–54°. This material had the same infrared spectrum and the same acetolysis rate as did the older preparation. Seeding a solution of the 53–54° modification with the 44–46° material gave toluenesulfonate, m.p. 45–46.5°.

Acetic Anhydride.—Baker and Adamson reagent grade acetic anhydride was distilled through a 4-foot bubble plate column; b.p. 139° (750 mm.), $n^{25}{}_D$ 1.3880 (reported[43] $n^{20}{}_D$ 1.3904).

Acetone.—Reagent grade acetone was dried by allowing it to slowly percolate through a 2-foot column packed with $^1/_{16}''$ pellets of type 4A Linde molecular sieve. The acetone was then distilled from a small amount of powdered type 4A molecular sieve through an 18″ Vigreux column;

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(41) J. Powling and H. J. Bernstein, THIS JOURNAL, 73, 4353 (1951).

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(43) A. Weissberger, E. S. Proskauer, J. A. Reddick and E. E. Toops, Jr., "Technique of Organic Chemistry," Vol. VII, "Organic Solvents," Interscience Publishers, Inc., New York, N. Y., 2nd edition, 1955.

b.p. 56° (750 mm.). The solvent was used immediately after distillation.

Acetonitrile.—Acetonitrile was distilled from phosphorus pentoxide. It was then refluxed over potassium carbonate for a few hours and then again distilled from phosphorus pentoxide; $n^{25}D$ 1.3420 (reported[43] $n^{25}D$ 1.34163).

Benzene.—This solvent was dried by distillation from calcium hydride[44]; $n^{25}D$ 1.4977 (reported[43] $n^{25}D$ 1.4979).

Chloroform.—This solvent was washed with two portions of concentrated sulfuric acid, three portions of water, and dried over potassium carbonate. After filtering, the chloroform was distilled from powdered type 4A Linde molecular sieves; $n^{25}D$ 1.4442 (reported[43] $n^{16}D$ 1.44854).

Diethyl Ether.—Mallinckrodt reagent grade ether was distilled from lithium aluminum hydride.

Dimethylformamide.—Matheson, Coleman and Bell dimethylformamide was dried over calcium hydride for 2 days. Nitrogen was then bubbled through the mixture overnight. The solvent was then decanted from the excess calcium hydride and further dried by passing through a 2-foot column of $^1/_{16}''$ type 4A Linde molecular sieves followed by distillation; b.p. 58° (24 mm.), $n^{25}D$ 1.4280 (reported[43] $n^{25}D$ 1.4269).

Dimethyl Sulfoxide.—Stepan Chemical Co. dimethyl sulfoxide was dried with type 4A molecular sieves and distilled immediately before use; b.p. 63° (8 mm.), m.p. 18.0–18.5° (reported[45] 18.45°), $n^{25}D$ 1.4765.

Ethyl Acetate.—Eastman Kodak Co. ethyl acetate was dried over potassium carbonate and distilled through a 4-foot bubble plate column. A portion of the center cut was dried immediately before use with molecular sieves followed by simple distillation; $n^{25}D$ 1.3696 (reported[43] $n^{25}D$ 1.36979).

Nitromethane.—Nitromethane was washed with a solution of sodium bicarbonate and sodium bisulfite followed by water, 5% sulfuric acid, water, and finally dilute sodium bicarbonate. It was then dried over Drierite followed by percolation through a 2-foot column packed with $^1/_{16}''$ pellets of type 4A Linde molecular sieve, followed by distillation from powdered type 4A molecular sieve; b.p. 58° (160 mm.). The resulting solvent was neutral to brom phenol blue in ethanol; $n^{25}D$ 1.3792 (reported[43] $n^{25}D$ 1.37949).

n-Octanoic Acid.—Eastman Kodak Co. *n*-caprylic acid was cooled in an ice-bath until it was almost entirely crystallized. The slush was decanted and the solid melted. After three such crystallizations, the product was dried with type 4A Linde molecular sieve and distilled, b.p. 144–145° (27 mm.), m.p. 15.7–16.4° (reported[43] 16.63°), $n^{25}D$ 1.4261 (reported[43] 1.4263).

Pyridine.—Eastman Kodak Co. "white label grade" pyridine was dried with type 4A Linde molecular sieves and fractionally distilled through an 18″ Raschig ring packed column, b.p. 115° (750 mm.), $n^{25}D$ 1.5059 (reported[43] $n^{25}D$ 1.5067).

Tetrahydrofuran and Dioxane.—These solvents were purified as described by Fieser.[46]

Karl Fischer Titrations.—Karl Fischer reagent was added to 30–40 ml. of methanol in a 100-ml. ground glass stoppered volumetric flask until a permanent light brown color was obtained. The addition of 10 ml. of the dried solvents used in kinetic runs (except acetic anhydride and acetone) did not change the color of the solution. Dry acetone gave no reaction to Karl Fischer reagent when the titration solvent was 20 ml. of methanol and 20 ml. of pyridine.

Kinetic Measurements.—Except for benzene, all reactions were carried out in sealed ampoules. At appropriate times 5-ml. aliquots were analyzed for developed toluenesulfonic acid. In anhydrous acetic acid, 50% AcOH–Ac₂O, 12.5% AcOH–dioxane and acetic anhydride, aliquots were analyzed for toluenesulfonic acid by titrating with standard sodium

acetate in acetic acid to the yellow end-point of brom phenol blue. This end-point was considerably sharper in the presence of acetic anhydride than in pure acetic acid. This effect has been previously noted by Fritz[47] in the potentiometric titration of sodium acetate with perchloric acid in acetic acid containing 5–50% acetic anhydride. The rate of the reaction in octanoic acid was followed in the same manner except that 10 ml. of dioxane was added to the 5-ml. aliquot to improve the end-point.

Solvolyses in aqueous acetic or formic acids and acetic-formic mixtures were usually carried out in the presence of excess base (lithium acetate and/or lithium formate); these were followed by titration with *ca.* 0.02–0.04 *M* perchloric acid in anhydrous dioxane, which was standardized against sodium acetate in acetic acid. Aliquots were titrated in 25 to 50 ml. of anhydrous dioxane, the addition of which sharpens up the end-point markedly[48]; brom phenol blue in acetic acid was the indicator employed.

The presence of lithium formate in formic acid was found to slow down the rate of decomposition of the solvent markedly, allowing the runs in the sealed ampoules to be followed much further.

In the solvolyses in anhydrous and aqueous alcohols, aliquots were titrated with *ca.* 0.04 *M* sodium methoxide in methyl alcohol, using 0.1% alcoholic brom thymol blue as indicator. However, the latter was found unsuitable for the aqueous dioxane solutions, apparently because of the buffering effect of the weak acids which were produced by the solvent. For these titrations, 0.1% alcoholic brom phenol blue was more satisfactory.

Aliquots from reactions run in dimethyl sulfoxide, nitromethane, acetonitrile, dimethylformamide, acetone, ethyl acetate, tetrahydrofuran, diethyl ether and chloroform were diluted with 20 ml. of absolute ethanol and titrated with standard sodium methoxide to the blue end-point of brom phenol blue.

Solvent decomposition in acetonitrile, dimethylformamide, acetone, ethyl acetate and tetrahydrofuran to produce weakly acidic substances which tend to buffer the end-point was serious. In these solvents it was not possible to obtain an experimental infinity titer.

The rate of acid formation in pyridine was followed by titrating aliquots directly with standard sodium methoxide in methanol using thymol blue as an indicator. It is necessary to protect the titration flask from atmospheric carbon dioxide during this titration. This was conveniently accomplished by attaching the titration flask directly to the buret with a small rubber stopper which had an air vent protected with a soda-lime tube. Titration of weighed samples of benzoic acid in pyridine by the above procedure gave accurate results.

In benzene, when the reaction was run in the usual sealed ampoules, a different induction period was observed for each tube. This behavior has been noted by Nenitzescu[30] in the reaction of benzyl benzenesulfonate with benzene. When the reaction was followed in a ground glass stoppered volumetric flask so that the entire solution began reacting at the same time, the titers increased uniformly with time. When aliquots were taken from the volumetric flask, the developed toluenesulfonic acid crystallized in the pipet. This disturbance was minimized by warming the pipet before taking a sample from the reaction flask and by washing out the entire contents of the pipet with a stream of acetone injected through the air vent of the automatic pipet into 20 ml. of acetone. The developed acid was titrated with sodium methoxide using brom phenol blue as the indicator.

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(45) T. B. Douglass, THIS JOURNAL, **68**, 1072 (1946).

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