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The Nature of Nucleophilic Assistance to Ion-Pair Formation. Solvolyses of Cyclohexyl p-Toluenesulfonate*

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The solvolysis of cyclohexyl tosylate has been shown previously both to proceed with nucleophilic assistance from the solvent and to give among the substitution and elimination products those which involve a 1,2-hydride shift. In the present report, specific rate data for solvolysis in 18 solvents at 25.0 °C are shown to give an excellent correlation, using the two-term Grunwald-Winstein equation, against N_T solvent nucleophilicity values and Y_{OTs} solvent ionizing power values, with an l value of 0.35 and a m value of 0.85. This indicates that sensitivities to changes in solvent nucleophilicity (l values) of as large as 0.35 can reflect nucleophilic solvation of a developing carbocation, rather than bimolecular (S_N2 + E2) attack. The temperature dependencies of the l and m values are given consideration.

Recently, we have presented[1] a scale of solvent nucleophilicity (N_T values) based on the solvolysis of the S-methyldibenzothiophenium ion. This scale can be applied to the solvolysis of other RX$^+$ substrates, with neutral molecule leaving groups, using equation (1) where k and k_o are the specific rates of solvolysis in a given solvent and

$$\log (k/k_o) = l\,N_T \tag{1}$$

in 80% ethanol, respectively, and l is the sensitivity of the solvolysis of the substrate to changes in solvent nucleophilicity.[2] For application to solvolyses of initially neutral substrates, with anionic leaving groups, the two-term Grunwald-Winstein equation[3] is required (equation 2), where the additional term involves the sensitivity of the sol-

$$\log (k/k_o) = l\,N_T + m\,Y_x \tag{2}$$

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* Dedicated to Professor Dionis E. Sunko on the occasion of his seventieth birthday.

volysis of the substrate (m) to changes in solvent ionizing power (Y_x); for solvolysis of RX, a series of Y_x scales are available.[4]

We are currently evaluating the efficiency of equation (2) for correlating the specific rates of solvolyses proceeding with nucleophilic assistance. An interesting sub-group involves solvolyses believed to proceed with both nucleophilic assistance and carbocationic intermediates. For example, the solvolyses of the *tert*-butyldimethylsulfonium ion[5] and of *tert*-butyl chloride[6] can be correlated by equations (1) and (2), respectively, with appreciable l values (0.3 to 0.4).

For solvolysis of cyclohexyl p-toluenesulfonate (tosylate), both the parent system and also variously substituted derivatives have been extensively studied, in terms of both kinetics and products. Based on early studies, it was recognized that the nucleophilicity of the solvent was an important factor.[7] In reaction of the bromide with iodide ion in acetone, where nucleophilic attack was of prime importance, reaction was about 100 times slower than for isopropyl bromide. Under solvolytic conditions, the rates were similar to those of the corresponding isopropyl derivative and appreciably less than those of the cyclopentyl derivative. Brown proposed that increase in I strain (internal strain) was an important factor in the observation that nucleophilic substitution reactions of cyclohexyl derivatives proceed slower than those of either cyclopentyl or cycloheptyl;[8] the acetolysis of cyclohexyl tosylate was proposed to proceed with a slow rate-determining ionization (S_N1 mechanism).[9] D. D. Roberts and Chambers considered the solvolysis of the chloride to be in the $S_N1 - S_N2$ borderline region in 50% aqueous ethanol but probably involving ionization[10] and this view was supported by D. D. Roberts who proposed an S_N1 mechanism over a range of solvents but also mentioned a slight dependence on solvent nucleophilicity.[11]

Fainberg and Winstein found that addition of lithium perchlorate to the acetolysis of cyclohexyl tosylate led to only a normal salt effect, with no evidence for a special salt effect, which would have indicated ion pair return from a solvent separated ion pair.[12] It has been proposed, however, that a special salt effect does apply in the product forming steps since the extent of hydride shift during acetolysis changes appreciably upon addition of lithium perchlorate.[13] However, a major problem in proposing product formation at the solvent separated ion pair stage is that, in acetolysis of deuterated derivatives, complete inversion of configuration has been observed in the unrearranged acetate product for both cyclohexyl[14] and 4,4-dimethylcyclohexyl[15] tosylates. It has been suggested[16] that hydride shifts start from different carbocationic intermediates than those for substitution.

The solvolyses of cyclohexyl p-toluenesulfonate can lead to appreciable amounts of elimination. Indeed in 2,2,2-trifluoroethanol (TFE) only 4% of reaction at 90 °C is with substitution and this value falls to an even lower value of 2% in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP).[16] Acetolyses at 50 °C leads to 15% substitution and 85% elimination.[10] Ethanolysis in the presence of calcium carbonate gave cyclohexene in 50–60% yield at 50 °C and 65–68% yield at 75 °C.[17a]

By appropriate deuterium labeling, in addition to showing inversion of configuration, Lambert was able to demonstrate[14] that in acetic acid the substitution product was formed 80% by direct displacement with inversion of configuration and 20% by attack after a hydride shift. In formic acid and trifluoroacetic acid, the amounts of substitution product formed after hydride shift were 40% and 50%, respectively. It was concluded that direct displacement involved nucleophilic attack on a tight ion pair. In all three solvents, formation of cyclohexene (70–80%) was the dominant pathway. In

acetolysis only about 5% of the cyclohexene was formed after rearrangement, increasing to 10–15% in formic acid and to about 50% in trifluoroacetic acid. The possibility of a hydrogen-bridged species as an intermediate in trifluoroacetic acid (k_Δ process) was mentioned.

A MINDO/3 calculation suggested that a hydrogen bridging species was slightly more stable than either chair or boat cation but it was realized that interactions with surrounding solvent could change the ordering of stabilities.[17b] Hydrogen-bridged cations have been suggested as intermediates in solvolyses of 4-*tert*-butylcyclohexyl tosylates.[18] However, since use of a *tert*-butyl label distorts the ground state and excludes certain transition state geometries because of steric strain, it is dangerous to directly transfer conclusion reached for solvolyses in the presence of this label to the parent compound.[14] The hydride shifts observed during acetolysis of the 4,4-dimethylcyclohexyl tosylate involved retention of configuration at the migration origin and, within the 17% substitution product formed, 13% of the product was with 1,2-migration to give 3,3-dimethylcyclohexyl acetate.[15] In TFE, 7% of the elimination product and 8% of the substitution product was after a 1,2-hydride shift and, in HFIP, the corresponding values were 5% and 27%.[16] In particular, in both solvents, only negligible 1,3-hydride shifts were observed; the 1,3-shifts were, however, strongly promoted by a *cis*-3-methyl group due to generation of a relatively stable tertiary carbocation.

Solvolysis of cyclohexyl *p*-toluenesulfonate was one of the original compounds studied, using the extended Grunwald-Winstein equation (equation 2), in the pioneering studies of Schadt, Bentley and Schleyer.[19] After developing the N_{OTs} scale based on methyl tosylate solvolysis and the Y_{OTs} scale based on 2-adamantyl tosylate solvolysis, they showed that several secondary alkyl *p*-toluenesulfonates, including cyclohexyl, has moderate dependencies on solvent nucleophilicity accompanying a rather higher dependence on solvent ionizing power. For eight solvents including ethanol, 50 and 80% aqueous ethanol, acetic and formic acids, 70 and 97% TFE, and 97% HFIP, they found a *l* value of 0.33, *m* value of 0.74, and correlation coefficient of 0.989. They considered the mechanism to be an example of what they designated as the S_N2 (intermediate) mechanism,[20] in which there is evidence both for an intermediate and nucleophilic assistance from the solvent. Actually, the description developed is in excellent accord with Ingold's original concept of the S_N1 reaction: »in the unmolecular substitution of an alkyl halide, both of the ions which are formed in the initial heterolysis, have to be solvated«.[21] Unfortunately, the solvation of the developing cation had been largely neglected[22,23] prior to its reemphasis by Bentley and Schleyer.[20,24,25] Essentially, it was proposed that the S_N1 designation should be used only when the solvation of the developing cation is after the transition state and the new S_N2 (intermediate) designation should be used for those (previously considered S_N1) reactions involving nucleophilic solvation of the developing cation before the transition state.

The k_s/k_c rate ratio has been put forward[19] as a useful measure of nucleophilic assistance from the solvent. A way of arriving at minimum estimate for this quantity was presented (k_s and k_c are the specific rates of solvolysis with nucleophilic solvent assistance and *via* the unsolvated carbocation, respectively). The values are relative to an assumed value of unity in trifluoroacetic acid (hence the minimum aspect of the reported values)[25] and they were found to rise with solvent nucleophilicity with, for solvolysis of cyclohexyl tosylate, values of below ten in solvent rich in fluorinated alcohol, of 28 in acetic acid, and of 256 in ethanol. It should be emphasized that these treatments are of overall solvolysis, with no partition into substitution and elimination

components. Deviations from a supposedly limiting plot, based on solvolyses of cyclohexyl tosylate in trifluoroacetic acid and HFIP, present an alternative way of arriving at an estimate of the k_s/k_c rate ratio.[26]

A procedure for obtaining evidence for nucleophilic solvent participation in a qualitative manner, without rigid application of the extended Grunwald-Winstein equation, involves plotting the logarithms of specific solvolysis rates in TFE-H_2O and EtOH-H_2O mixtures against Y_x values.[27,28] When there is substantial nucleophilic assistance from the solvent two lines are obtained (k_s process) and when this is absent only one line is obtained. A plot with cyclohexyl p-bromobenzenesulfonate as the substrate shows the two lines characteristic of a k_s process. A related study using ethanol-water and acetic acid-formic acid mixtures as the two solvent systems also led to assignment (of the tosylate solvolysis) as a k_s process.[29]

The Foote-Schleyer correlation[30,31] relates acetolysis rates of secondary substrates to the infrared carbonyl stretching frequencies of the corresponding ketones. In these correlations, cyclohexyl arenesulfonates are taken as the standards. It has been pointed out[32] that it is surprising that these correlations are as good as observed because they incorporate acetolyses of all three types (k_s, k_c, and k_Δ). More recently,[33] this type of approach has been applied in terms of strain changes between the substrate and the corresponding ketone, with strain changes obtained by force-field calculations and equilibration of alcohols and ketones. The model reproduces the solvolytic behavior of substrates reacting by k_c pathways to give unstrained carbenium ions. Again, acetolysis rates are considered relative to cyclohexyl tosylate, possibly a rather inappropriate choice because of its apparent k_s behavior.[19,25-29]

RESULTS AND DISCUSSION

Cyclohexyl p-Toluenesulfonate Solvolysis

Values have been extracted from the literature for specific rates of solvolysis in 18 solvent systems at 25 °C; for 12 of these systems values are available, or can be obtained by interpolation or extrapolation, at both 50.0 and 75.0 °C. The data are presented in Table I as log (k/k_o) values together with the relevant N_T[1] and Y_{OTs}[4] values. In four instances, where the reported Y_{OTs} values were obtained using 1-adamantyl tosylate as the substrate, the values were adjusted by multiplying by 0.868 and adding 0.027.[34] The unadjusted values are given in parentheses. Calculations have been carried out incorporating either the adjusted or unadjusted values and very little variation in sensitivity values, intercept, or correlation coefficient is observed.

The values obtained for l, m, intercept, and correlation coefficient from a series of calculations involving the extended Grunwald-Winstein equation (equation 2) are presented in Table II. The first two entries are obtained from the simple equation (equation 2 without the first term). It can be seen that the rather low m values using the simple equations result from an appreciable nucleophilic component and, for all 18 solvents at 25 °C, values of 0.35 for l, and 0.85 for m are obtained using the extended (two-term) equation. It is of interest to compare these values with those for tert-butyl chloride solvolysis.[6] Using the identical 18 solvents and the associated N_T and Y_{OTs} values and log (k/k_o) values for tert-butyl chloride, we obtain values of 0.27 ± 0.07 for l, 1.08 ± 0.07 for m, -0.02 ± 0.32 for the intercept, and a correlation coefficient of 0.980. In principle, the most appropriate Y_x scale would be Y_{Cl} but several of our 18 solvents do not have directly determined Y_{Cl} values available. It appears that,

TABLE I

Logarithmic ratio of specific rates of solvolysis of cyclohexyl tosylate in indicated solvent relative to that in 80% ethanol at various temperatures (°C), and associated solvent nucleophilicity (N_T) and solvent ionizing power (Y_{OTs}) values.

Solvents[a]	log (k/k_o)			N_T[b]	Y_{OTs}[c]
	25.0	50.0	75.0		
EtOH	−1.21[d]	−1.14[e]	−1.09[e]	+0.37	−1.75 (−1.96)
80% EtOH	0.00[f]	0.00[g]	0.00[g]	0.00	0.00
70% EtOH	0.39[d]	0.40[h]	0.32[h]	−0.20	+0.47
60% EtOH	0.66[d]	0.62[g]	0.63[g]	−0.39	+0.92
50% EtOH	0.99[d]	0.97[g]	0.93[g]	−0.57	+1.29
TFE	0.23[d]	0.19[i]	0.16[i]	−3.93	+1.77
97% TFE	0.35[d]	0.25[h]	0.13[h]	−3.30	+1.83
85% TFE	0.44[d]	0.46[h]	0.46[h]	−2.31[j]	+1.92[j]
70% TFE	0.83[d]	0.77[h]	0.69[h]	−1.98	+2.00
50% TFE	1.24[d]	1.12[h]	1.00[h]	−1.73	+2.14
CH₃COOH	−1.19[d]	−1.02[k]	−0.95[d]	−1.78	−0.74 (−0.88)
HCOOH	1.71[e]	1.69[e]	1.64[d]	−2.44	+3.04
90% EtOH	−0.43[l]			+0.18	−0.58 (−0.77)
40% EtOH	1.57[l]			−0.74	+1.97
MeOH	−0.67[m]			+0.17	−0.77 (−0.92)
60% Acetone	0.51[m,n]			−0.52	+0.66
H₂O	3.08[n,o]			−1.38	+4.1
97% HFIP	1.37[o]			−5.26	+3.61

[a] Volume percentage for aqueous ethanol and aqueous acetone and weight percentage for aqueous TFE and aqueous HFIP. [b] From Ref. 1. [c] From Ref. 4; the negative values have the values from Ref. 4 in parentheses and the regularly tabulated values are adjusted as suggested in Ref. 34 (see text). [d] Extrapolated value, using the Arrhenius equation. [e] Specific rate from Ref. 18. [f] Specific rate from Ref. 11. [g] Specific rate (slight adjustment using Arrhenius equation) from Ref. 20. [h] Specific rate from Ref. 28. [i] Specific rate (slight adjustment using Arrhenius equation) from Ref. 25. [j] Interpolated value. [k] Specific rate from Ref. 9 (values reported at 30.0, 50.0, and 70.0 °C). [l] Specific rate from Ref. 29. [m] Specific rate from Ref. 26. [n] Specific rate adjusted from experimental value for the methanesulfonate ester. [o] Specific rate from Ref. 25.

in the solvolyses of cyclohexyl tosylate, the sensitivity to changes in solvent nucleophilicity is only slightly greater than for *tert*-butyl chloride solvolysis. It should be mentioned that available data in trifluoroacetic acid have been deliberately excluded because of the claim[24] that specific rates in this solvent are difficult to reproduce.

The solvents within which 1,2-hydride shifts have been observed (acetic acid,[13,14] formic acid,[14] TFE,[16] and HFIP[16]) all fall reasonably close to the correlation line (Figure 1) and the solvolysis in these solvents appears to be with essentially the same degree of nucleophilic participation as the other 14 solvents. In particular, HFIP has been represented as the solvent system, among those commonly used in solvolysis studies, where the solvolysis of secondary alkyl tosylates most approaches k_c behavior (even more so than in trifluoroacetic acid).[25] However, omission of 97% HFIP produces only minor changes in the correlation (Table II) and a calculated value for log (k/k_o) of 1.08 (lN value of −1.99 combined with a mY value of 3.07) for solvolysis in 97% HFIP, using the l and m values from the analysis in the other 17 solvents, is in good agreement with the experimental value of 1.37. This suggests that all solvents are well correlated, even the one of lowest nucleophilicity combined with second highest (after water) ionizing power.

TABLE II

*Analyses of the specific rates of solvolyses of cyclohexyl tosylate using the
Grunwald-Winstein equation.[a]*

$T/°C$	n^b	l	m	C^c	r^d
25.0	18		0.61±0.07	−0.20±0.45	0.913
25.0	18[e]		0.59±0.07	−0.15±0.44	0.914
25.0	18	0.35±0.03	0.85±0.03	0.03±0.14	0.992
25.0	18[e]	0.35±0.03	0.81±0.03	0.09±0.15	0.991
25.0	17[f]	0.38±0.03	0.85±0.03	0.05±0.14	0.993
25.0	12	0.35±0.04	0.80±0.04	0.04±0.14	0.989
50.0	12	0.34±0.04	0.75±0.04	0.06±0.14	0.989
75.0	12	0.33±0.04	0.72±0.04	0.06±0.14	0.986

[a] First two entries using log $(k/k_0) = mY_{OTs}$ and the remainder based on equation (2) ($Y_X = Y_{OTs}$).
[b] Number of solvents. [c] Value for intercept. [d] Correlation coefficient. [e] Using the 4 values for Y_{OTs} presented in Table I in parentheses (see text). [f] Omitting 97% HFIP.
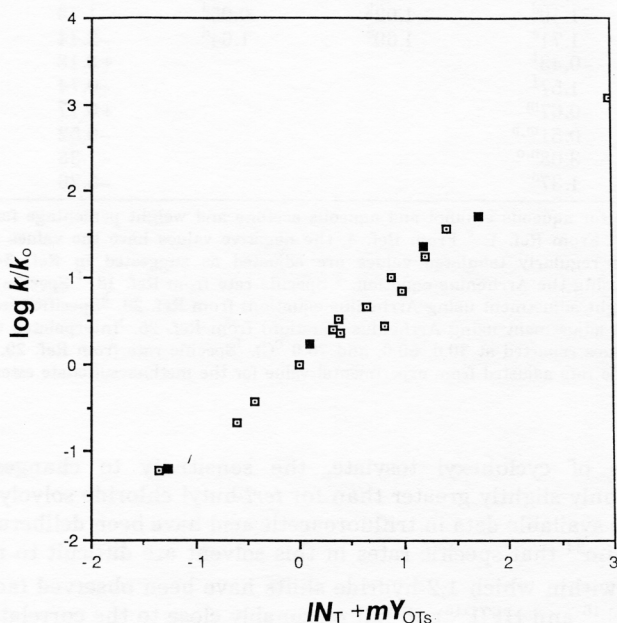

Figure 1. Correlation of log (k/k_0) for cyclohexyl tosylate against $(l\,N_T + m\,Y_{OTs})$, where l and m have values of 0.35 and 0.85, respectively. The solid squares represent the solvent systems (acetic acid, formic acid, TFE, and HFIP, actually 97% HFIP for kinetics) within which 1,2-hydride shifts have been demonstrated.

It can be concluded that an l value as large as 0.35 is consistent with nucleophilic solvation of the developing carbocation within an ionization (S_N1 plus E1) mechanism leading to ion-pair formation and a value of this magnitude does not necessarily indicate covalency changes involving solvent molecules within a bimolecular (S_N2 plus E2) mechanism.

The availability for 12 of the solvent systems of data at three temperature (25, 50, and 75 °C) affords a rather rare opportunity to assess temperature effects on the *l* and *m* values. In general, sensitivity values fall with increasing temperature,[35] and a modest effect is observed for the cyclohexyl tosylate solvolyses. The increase in temperature from 25 to 50 °C leads to a 4.0% fall off in the *l* value and 6.2% fall in the *m* value. Further increase from 50 to 75 °C results in a further 2.1% fall off in the *l* value and a further 4.8% fall off in the *m* value. This small variation with temperature would suggest that *l* and *m* values obtained at temperatures varying by up to 50 °C from each other can be compared with introduction of only minor inaccuracy. Virtually no fall off was observed in the correlation coefficient over the 50 °C temperature range.

$$N_{OTs} = \log (k/k_o)_{MeOTs} - 0.3\, Y_{OTs} \tag{3}$$

The earlier treatment[19] of cyclohexyl tosylate solvolysis, in terms of the extended Grunwald-Winstein equation, incorporated the original N_{OTs} scale, developed using equation (3). It has since been demonstrated[36] that the N_{OTs} scale should have been developed using a value of 0.55 (not 0.3) as the sensitivity of methyl tosylate solvolysis towards changes in solvent ionizing power. A revised scale (designated N'_{OTs}) has been presented.[1] However, new analyses are not needed to correct correlations previously carried out using the original N_{OTs} values in conjunction with Y_{OTs} values; it has been shown[36] that the *l* values and correlation coefficient remain unchanged when N'_{OTs} values are substituted for N_{OTs} values, and the true *m* value is equal to that previously calculated using N_{OTs} values plus 0.25 *l*. Since the previously calculated *l* value was 0.33, the *m* value changes from 0.74 to 0.82. The revised *l* and *m* values of 0.33 and 0.82 (using N'_{OTs} and Y_{OTs}; 8 solvents) are in excellent agreement with the corresponding values of 0.35 and 0.81 presently calculated, using N_T and Y_{OTs} values (18 solvents; fourth entry of Table II, the four Y_{OTs} values which are based on 1-adamantyl tosylate solvolysis being uncorrected.[19,34] This excellent agreement provides additional support for the belief that the revised N_{OTs} values (N'_{OTs}), or the recently presented N_T values, are the ones which should be used as the measure of solvent nucleophilicity in Grunwald-Winstein correlations.

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SAŽETAK

Nukleofilna asistencija pri nastanku ionskih parova. Solvoliza cikloheksil-*p*-toluensulfonata

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Primjenom Grunwald-Winsteinove jednadžbe korelirane su brzine solvolize naslovnog spoja s nukleofilnošću i ionskom jakošću više otapala: EtOH, EtOH-H_2O, CF_3CH_2OH, CF_3CH_2OH-H_2O, CH_3COOH, HCOOH, CH_3OH, CH_3COCH_3, $(CF_3)_2CHOH$.