ward-bonding–back-bonding Co–As$_2$–Co interaction which concomitantly results in a decrease of the As–As valence-bond order from *three* (as a neutral species) to approximately *two*. Similar considerations of the corresponding synergic bonding mechanism in Fe$_2$(CO)$_6$S$_2$ suggest a resultant S–S total valence-bond order decrease from *two* (as neutral free S$_2$) to a value near *one* in this Fe$_2$S$_2$ complex.[26] Further synthetic and structural work is in progress to appraise and amplify these bonding conclusions.

Acknowledgment. We are pleased to acknowledge the National Science Foundation (GP-4919) for their financial support of this work. The use of the CDC 3600 and 1604 computers at the University of Wisconsin Computing Center was made possible by the partial support of NSF and WARF through the University Research Committee. One of us (M. S. F.) is grateful to NSF (Grant GY-4404) for a summer undergraduate NSF Trainee Fellowship.

Alan S. Foust, Michael S. Foster, Lawrence F. Dahl
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706
Received April 3, 1969

Trifluoroacetolysis of Simple Primary Alkyl Toluenesulfonates[1]

Sir:

In earlier work, EtOH, AcOH, and HCOOH proved to be instructive and useful solvents in probing the competition between anchimerically assisted ionization (k_Δ) and anchimerically unassisted ionization (k_s) in solvolysis of simple alkyl systems.[2,3] The solvent sequence of k_Δ/k_s ratios in solvolysis of marginal systems, such as 2-phenyl-1-ethyl,[2b,c] is EtOH < AcOH < HCOOH. With the simplest primary alkyl toluenesulfonates,[3a] the observed MeOTs–EtOTs–*i*-BuOTs–neopentyl-OTs (neoPenOTs) sequence of solvolysis rates at 75° changed from a steeply descending one, 4000:1750:80:1, in EtOH to 10:9:2.8:1 in AcOH, and finally to the relatively flat sequence, 0.56:1.0:1.22:1.0, in HCOOH. Formolysis of MeOTs and EtOTs was judged to be far from the Lim. category; in other words, it occurs with substantial nucleophilic solvent participation.

The formolysis rate of neoPenOTs, just as high as that of EtOTs in spite of the very large steric hindrance to backside solvent entry, was most simply explained as due to anchimeric assistance from carbon participation.[3a] In the case of *i*-BuOTs, the formolysis rate was judged to be consistent with at least some successful competition with k_s from k_Δ due to hydrogen participation.[3a] Since our earlier remarks regarding neopentyl solvolysis, various other discussions[4] have appeared pro and con with the idea of anchimeric assistance to neopentyl ionization.

Quite recently, CF$_3$COOH, with its very low nucleophilicity and relatively high ionizing power, has become recognized as an important solvolyzing solvent which gives rise to k_Δ/k_s ratios much higher than in HCOOH.[5] We have found this solvent to be very instructive in the case of the simplest primary alkyl systems, and in this communication we report the trifluoroacetolysis of the Me, Et, *n*-Pr, *i*-Bu, and neoPen series of *p*-toluenesulfonates.

The solvolyses in CF$_3$COOH were followed using the absorption of the alkyl tosylate at 273 mμ.[6] The first-order solvolysis rate constants (k_t) listed in Table I were measured in the absence of CF$_3$COONa. In the case of MeOTs, EtOTs, and *n*-PrOTs, k_t increases substantially on addition of CF$_3$COONa. The increase in k_t at 100° can be fit with second-order rate constants equal to 6.1×10^{-5}, 4.9×10^{-5}, and 4.2×10^{-5} M^{-1} sec^{-1}, for MeOTs, EtOTs, and *n*-PrOTs, respectively. For *i*-BuOTs and neoPenOTs, no sensitivity of k_t to CF$_3$COONa addition was detected.

The products of reaction were followed by nmr. MeOTs and EtOTs produce the corresponding ROCOCF$_3$ quantitatively. No deuterium scrambling (<2%) was observed when β-d_3-EtOTs was solvolyzed. Propyl tosylate produces 11.4% *n*-PrOCOCF$_3$ plus 88.6% *i*-PrOCOCF$_3$ at 100° and 10.3% *n*-PrOCOCF$_3$ plus 89.7% *i*-PrOCOCF$_3$ at 125°. The solvolysis of 2,2-d_2-1-PrOTs at 100° yields 83.7% *i*-PrOCOCF$_3$ containing <0.05 α proton (δ 4.75, based on CH$_2$Cl$_2$ at δ 5.30) and 5.03 β protons (δ 1.03). Thus, the *i*-PrOCOCF$_3$ does not arise from solvent addition to propene[7] and there is no extensive equilibration of the protons. The remaining 16.3% product is *n*-PrOCOCF$_3$. In the solvolysis of 1,1-d_2-1-PrOTs no α proton signals were evident (<0.05 proton) in the residual *n*-PrOTs or the *n*-PrOCOCF$_3$ product. Thus, the solvolysis is not appreciably accompanied by 1,3-hydride shifts[8] or formation and reopening of cyclopropane.[9] The solvolysis of *i*-BuOTs yields only a rearranged product, this being mainly *t*-BuOCOCF$_3$ accompanied by as much as 20% 2-BuOCOCF$_3$. Quantitative product analysis is difficult in this case since the product is unstable even in the presence of CF$_3$COONa. *t*-AmOCOCF$_3$ is produced quantitatively from neoPenOTs.

As seen in Table I the relative rates in CF$_3$COOH at 75.0° show a steeply rising trend for the primary tosylates, the MeOTs–EtOTs–*n*-PrOTs–*i*-BuOTs–neoPenOTs sequence being 1:13:93:3060:5970, in sharp contrast to the sequences previously observed[3a] in EtOH, AcOH,

---

[1] Research sponsored by the National Science Foundation.

[2] S. Winstein, *et al.*: (a) *Bull Soc. Chim. Fr.*, **18**, 55 (1951); (b) *J. Amer. Chem. Soc.*, **75**, 147 (1953); (c) *ibid.*, **78**, 4801 (1956); (d) *ibid.*, **79**, 3105, 3114 (1957); (e) *Helv. Chim. Acta*, **41**, 807 (1958); (f) *J. Amer. Chem. Soc.*, **87**, 3504 (1965).

[3] (a) S. Winstein and H. Marshall, *ibid.*, **74**, 1120 (1952); (b) S. Winstein, *et al.*, *ibid.*, **74**, 1113 (1952); (c) S. Winstein and J. Takahashi, *Tetrahedron Lett.*, **2**, 316 (1958).

[4] (a) W. A. Sanderson and H. S. Mosher, *J. Amer. Chem. Soc.*, **88**, 4185 (1966); (b) W. G. Dauben and J. L. Chitwood, *ibid.*, **90**, 6876 (1968); (c) G. J. Karabatsos, *et al.*, *ibid.*, **86**, 1994 (1964); (d) J. E. Nordlander, *et al.*, *ibid.*, **88**, 4475 (1966); (e) J. E. Nordlander and W. J. Kelly, *J. Org. Chem.*, **32**, 4122 (1967); (f) G. M. Fraser and H. M. R. Hoffman, *Chem. Commun.*, 561 (1967).

[5] (a) A. Diaz and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 4300 (1969); (b) A. Diaz, I. Lazdins, and S. Winstein, *ibid.*, **90**, 6546 (1968); (c) J. E. Nordlander and W. G. Deadman, *Tetrahedron Lett.*, 4409 (1967), *J. Amer. Chem. Soc.*, **90**, 1590 (1968); (d) R. J. Jablonski and E. I. Snyder, *Tetrahedron Lett.*, 1103 (1968).

[6] C. G. Swain and C. R. Morgan, *J. Org. Chem.*, **29**, 2097 (1964).

[7] The 2-Pr product formed in the HgO-catalyzed formolysis of *n*-PrBr in 90% aqueous HCOOT contains no tritium, supporting an intramolecular reaction: J. S. Coe and V. Gold, *J. Chem. Soc.*, 4940 (1960).

[8] The AlBr$_3$-catalyzed isomerization of *n*-PrBr to *i*-PrBr proceeds by an essentially irreversible 1,2-hydride shift: G. J. Karabatsos, J. L. Fry, and S. Meyerson, *Tetrahedron Lett.*, 3735 (1967).

[9] Addition of CF$_3$COOD to cyclopropane gives *n*-PrOCOCF$_3$ with one D statistically distributed: N. C. Deno, *et al.*, *J. Amer. Chem. Soc.*, **90**, 6457 (1968).

Table I. Rates of Trifluoroacetolysis of Some Primary RCH_2OTs[a]

RCH_2	Temp, °C	10^5k_t, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Rel rate	$\frac{-\Delta \log k,}{\Delta\sigma^*}$ 75°
Me	75.0[b]	0.00181			1	
	100.0	0.0164 ± 0.0012	22.0 ± 0.7	-31.0 ± 2.0		
	125.0	0.113 ± 0.008				2.2
Et	75.0	0.0226 ± 0.0012			12.5	
	100.0	0.204 ± 0.003	21.8 ± 0.7	-26.7 ± 2.0		9.6
	125.0	1.35 ± 0.04				
n-Pr	75.0	0.169 ± 0.005			93.3	
	100.0	1.80 ± 0.07	23.7 ± 0.3	-17.2 ± 0.8		16.6
i-Bu	75.0	5.54 ± 0.15			3060	
	100.0	60.0 ± 1.7	23.9 ± 0.3	-9.7 ± 0.8		2.5
neoPen	50.0	0.692 ± 0.013				
	75.0[c]	10.8 ± 0.4			5970	
	100.0	114 ± 3	23.8 ± 0.5	-8.9 ± 1.3		

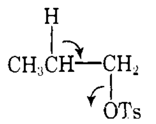
[a] *Ca.* 0.04 *M* ROTs. [b] Extrapolated from data at other temperatures. [c] Reported 8.5×10^{-5} sec^{-1} by Dauben[4b] in buffered trifluoroacetic acid.

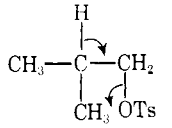
Table II. Summary of Rate Constants for *n*-Propyl and Isobutyl Tosylates at 75°

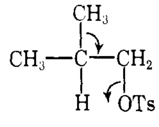
Solvent	10^6k, sec^{-1} k_t	k_Δ	k_s	% k_Δ	k_t, 100.0° α-H/α-D	β-H/β-D	β-H/β-D, 100.0° k_Δ	k_s
				n-PrOTs				
EtOH	19.5	3.8×10^{-4}	19.5	0.002[c]				
AcOH	0.61[a]	1.03×10^{-3}	0.61	0.168[d]		1.06		1.06
HCOOH	13.2[b]	0.10	13.1	0.763				
CF_3COOH	1.69	1.48	0.21	87.4[e]	1.29[j]	1.77	1.85	1.15[k]
				i-BuOTs				
EtOH	1.33[f]	0.05	1.28	4.8[g]		1.12		
AcOH	0.234[f]	0.185	0.049	79.0[h,m]		1.67	1.78	1.28[l]
HCOOH	23.1[f]	22.3	0.80	96.5[m]				
CF_3COOH	55.4	55.4	0.017[i]	99.97	1.15	1.92		

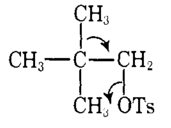
[a] Interpolated value, 10^7k, sec^{-1}, = 66 (100°) and 3.55 (70°) (W. Pritzkow and K. H. Schöppler, *Chem. Ber.*, **95**, 834 (1962). [b] H. M. R. Hoffman, *J. Chem. Soc.*, 6762 (1965). [c] Extrapolated value from log k_Δ *vs.* log k_t for neophyl-OTs in Figure 1. [d] Extrapolated from data at higher temperatures; 2-PrOAc product at 100.0 and 125.0° is 0.32 and 0.56%, respectively. [e] Extrapolated from data at higher temperatures; 2-PrOCOCF_3 product at 100.0 and 125.0° is 88.6 and 89.7%, respectively. [f] Reference 3a. [g] Extrapolated from data at higher temperatures; *i*-BuOEt product at 100 and 125° is 89.5 and 76.5%, respectively. [h] Extrapolated from data at higher temperatures; *i*-BuOAc product at 100.0 and 125.0° is 17.0 and 14.1%, respectively. [i] Extrapolated value from log k_s for *i*-BuOTs *vs.* log k_t for EtOTs. [j] The k_H/k_D values for EtOTs (125.0°) and neoPenOTs (100.0°) are 1.09 and 1.13, respectively. [k] For comparison, k_H/k_D for EtOTs at 125.0° is 1.16. [l] Acetolysis of β-*d*-*i*-BuOTs at 100.0° produces 21.9% *i*-BuOAc. [m] CH_3 participation is less important in these solvents than in CF_3COOH, the $k_\Delta^H/k_\Delta^{CH_3}$ ratios being *ca.* 40 in AcOH and 20 in HCOOH.

and HCOOH. The plot of log k for the RCH_2OTs series *vs.* Taft's σ^* for R[10] is not linear.[4d] Instead, it is S-shaped, the slope being small between MeOTs and EtOTs, large between EtOTs and *n*-PrOTs, larger between *n*-PrOTs and *i*-BuOTs, and small between *i*-BuOTs and neoPenOTs. The data are certainly suggestive of a change in mechanism between EtOTs and *n*-PrOTs, namely, from the k_s type to the k_Δ type. On the basis of discrete k_Δ and k_s processes, a formulation which successfully accounts for the behavior of other primary and simple secondary systems,[5a,b] we can dissect k_t for the present series of tosylates into k_Δ and k_s components. For *n*-PrOTs solvolysis, the *n*-Pr product is assigned to k_s and the *i*-Pr product to k_Δ due to H participation (see I). On this basis, k_t for *n*-PrOTs in CF_3COOH at 75.0° is 87.4% k_Δ and 12.6% k_s. The derived k_Δ and k_s values are listed in Table II. Also included in the table are deuterium isotope effects for k_t and the derived isotope effects for k_Δ and k_s. For comparison with the results in CF_3COOH, the small amounts of rearrangement accompanying solvolysis of *n*-PrOTs in AcOH and HCOOH were also determined, and the results are given in Table II.


I


IIa


IIb


III

Just as in the 2-phenyl-1-ethyl,[5b] 1-phenyl-2-propyl,[5a] and other cases,[5a,b] a crucial test of the k_Δ and k_s dissection based on discrete processes may be based on the quantitative trends shown by the derived k_Δ and k_s values as the solvent is varied. On the basis of the

---

(10) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, p 556 ff.

mechanistic significance assigned to k_Δ, we should expect a correlation of k_Δ values with solvolysis rates (k_t) of neophyl-OTs,[5b] for which ionization occurs with phenyl participation at a rate equal to k_t and dependent on solvent ionizing power but not nucleophilicity. On the other hand, the k_s process should depend on a blend of nucleophilicity and ionizing power for which the simple EtOTs should be a rather good model.[5b] Thus, k_s would be expected to correlate rather well with k_t values for EtOTs.

As illustrated in Figure 1, a good linear free-energy correlation exists between log k_Δ for n-PrOTs and log k_t for neophyl-OTs. The slope of the least-squares line is 0.846 with a mean deviation of 0.08 log unit for the fit of the AcOH, HCOOH, and CF_3COOH points. Similarly, log k_s is linear in log k_t for EtOTs. The slope is 0.925 with a mean deviation of 0.01 log unit for the four solvents. With the aid of the log k_Δ plot 0.002% k_Δ is estimated in EtOH.

For i-BuOTs solvolysis in EtOH, AcOH, and HCOOH, k_s was approximated by assigning the yield of unrearranged i-Bu solvolysis product to the k_s route, the remainder being assigned to k_Δ due to H participation as in IIa and CH_3 participation as in IIb. Listed in Table II are the k_t, k_s, and composite k_Δ values. A good correlation exists between log k_s for i-BuOTs and log k_t for EtOTs at 75°. The slope of the least-squares line is 0.86, with a mean deviation of 0.02 log unit for the fit of the EtOH, AcOH, and HCOOH points.

Solvent correlations for n-PrOTs and i-BuOTs strongly support the interpretation of solvolysis on the basis of discrete k_Δ and k_s processes in EtOH, AcOH, HCOOH, and CF_3COOH. Isotope effects are also reasonable.[3c] For k_Δ the β-deuterium isotope effects are *ca.* 1.8, while for k_s the range is 1.06 to 1.28. The $\Delta S^{\ddagger}$ values seem to be characteristically lower[2c] for MeOTs and EtOTs, which solvolyze by the k_s route, than for i-BuOTs and neoPenOTs, which solvolyze mainly by the k_Δ route.

It is clear that the major shift from k_s to k_Δ in the solvolysis of n-PrOTs occurs in going from HCOOH to CF_3COOH. For i-BuOTs, the shift occurs between EtOH and AcOH. For neoPenOTs, k_Δ is dominant even in EtOH where the 92.7% rearranged products[4f] are ascribed to the k_Δ process due to CH_3 participation (see III) and the 7.3% neoPenOEt[4f] is assigned to k_s. In AcOH, k_t for neoPenOTs is already >99.97% k_Δ.[11] The least-squares line for the plot of log k_Δ for neoPenOTs at 75° *vs.* neophyl-OTs has a slope of 0.833 for the solvents EtOH, AcOH, HCOOH, and CF_3COOH. The mean deviation for the fit of the points is 0.25 log unit.

It is interesting to examine the k_Δ and k_s rate constants for the primary alkyl tosylates as regards their variation with structure. For k_Δ the ROTs structure sequence is PhEt $\gtrsim$ i-Bu $\gtrsim$ neoPen > n-Pr, while for k_s the ROTs structure sequence is Et $\simeq$ n-Pr > PhEt > i-Bu > neoPen.

Trifluoroacetic acid is certainly an effective solvent for bringing out k_Δ. Even more effective is FSO_3H, and in the following communication[12] we report the results of a study of solvolysis of the simple primary alkyl tosylates in this solvent.

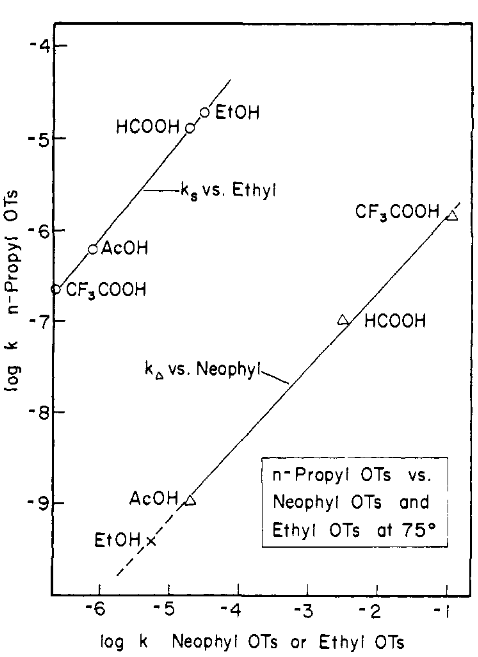


Figure 1. Trifluoroacetolysis of simple primary alkyl toluenesulfonates.

I. Lazdins Reich, A. Diaz, S. Winstein
Contribution No. 2412, Department of Chemistry
University of California, Los Angeles, California 90024

Received June 9, 1969

Solvolysis of Primary Tosylates in Fluorosulfuric Acid[1]

Sir:

As reported in the preceding communication,[2] CF_3COOH is quite effective in increasing k_Δ/k_s ratios in solvolysis of simple primary tosylates. Another such solvent is concentrated H_2SO_4, as is reported by Myhre in an accompanying communication.[3a] In this communication we report on the solvolysis of primary tosylates in FSO_3H. This solvent, with its extremely low nucleophilicity and tremendously high ionizing power, is even more effective in promoting high k_Δ/k_s ratios. In FSO_3H, even n-PrOTs reacts completely by the anchimerically assisted k_Δ route, as do i-BuOTs and neoPenOTs.

Solvolyses in FSO_3H were followed directly by nmr[4] in nmr tubes[5] at preset probe temperatures determined before and after the run from the temperature-sensitive chemical shifts of MeOH. The solvolysis of n-PrOTs was followed using the disappearance of the signals for the α-H at δ 4.28 and the γ-H at δ 0.85 as n-PrOTs forms isopropyl product. The p-methyl and aromatic proton signals were used as standards. Good first-order rate constants (k_t) were observed between 5 and 90% reaction, and the infinities were 100%. Added $KFSO_3$ reduces k_t, k_t being *ca.* inversely proportional

---

[11] The acetolysis of neoPenOTs at 125° in the presence of 0.036 M NaOAc yields 0.03 ± 0.007% neoPenOAc. However, all the evidence indicates that most of this small amount can be ascribed to the reaction with NaOAc.

[12] A. Diaz, I. L. Reich, and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 5637 (1969).

[1] Research sponsored by the National Science Foundation.

[2] I. L. Reich, A. Diaz, and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 5635 (1969).

[3] (a) P. C. Myhre and E. Evans, *ibid.*, **91**, 5641 (1969); (b) P. C. Myhre and K. S. Brown, *ibid.*, **91**, 5639 (1969).

[4] All chemical shifts are relative to CH_2Cl_2 at δ 5.30.

[5] After the initial nmr spectrum was recorded, MeOTs, EtOTs, and n-PrOTs could be recovered from the reaction solution in 90, 91, and 75%, yield, respectively.