ward-bonding-back-bonding Co-As<sub>2</sub>-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  $Fe_2(CO)_6S_2$ 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<sub>2</sub>S<sub>2</sub> complex.<sup>26</sup> 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**<sup>1</sup>

## Sir:

In earlier work, EtOH, AcOH, and HCOOH proved to be instructive and useful solvents in probing the competition between anchimerically assisted ionization  $(k_{\Delta})$  and anchimerically unassisted ionization  $(k_s)$  in solvolysis of simple alkyl systems.<sup>2,3</sup> The solvent sequence of  $k_{\Delta}/k_s$  ratios in solvolysis of marginal systems, such as 2-phenyl-1-ethyl,<sup>2b,c</sup> is EtOH < AcOH < HCOOH. With the simplest primary alkyl toluenesulfonates,3a the observed MeOTs-EtOTs-i-BuOTsneopentyl-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.<sup>3a</sup> In the case of *i*-BuOTs, the formolysis rate was judged to be consistent with at least some successful competition with  $k_s$  from  $k_{\Delta}$  due to hydrogen participation.<sup>3a</sup> Since our earlier remarks regarding neopentyl solvolysis, various other discussions<sup>4</sup> have appeared

(1) Research sponsored by the reactional 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. pro and con with the idea of anchimeric assistance to neopentyl ionization.

Quite recently, CF<sub>3</sub>COOH, with its very low nucleophilicity and relatively high ionizing power, has become recognized as an important solvolyzing solvent which gives rise to  $k_{\Delta}/k_s$  ratios much higher than in HCOOH.<sup>5</sup> 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<sub>3</sub>COOH were followed using the absorption of the alkyl tosylate at 273 m $\mu$ .<sup>6</sup> The firstorder solvolysis rate constants  $(k_t)$  listed in Table I were measured in the absence of CF<sub>3</sub>COONa. In the case of MeOTs, EtOTs, and n-PrOTs,  $k_t$  increases substantially on addition of CF<sub>3</sub>COONa. The increase in  $k_t$  at 100° can be fit with second-order rate constants equal to 6.1  $\times$  10<sup>-5</sup>, 4.9  $\times$  10<sup>-5</sup>, and 4.2  $\times$  10<sup>-5</sup>  $M^{-1}$ sec<sup>-1</sup>, for MeOTs, EtOTs, and *n*-PrOTs, respectively. For *i*-BuOTs and neoPenOTs, no sensitivity of  $k_t$  to CF<sub>3</sub>COONa addition was detected.

The products of reaction were followed by nmr. MeOTs and EtOTs produce the corresponding ROCOCF<sub>3</sub> quantitatively. No deuterium scrambling (<2%) was observed when  $\beta$ -d<sub>3</sub>-EtOTs was solvolyzed. Propyl tosylate produces 11.4% n-PrOCOCF<sub>3</sub> plus 88.6% *i*-PrOCOCF<sub>3</sub> at 100° and 10.3% *n*-PrOCOCF<sub>8</sub> plus 89.7 % i-PrOCOCF<sub>3</sub> at 125°. The solvolysis of 2,2- $d_2$ -1-PrOTs at 100° yields 83.7% *i*-PrOCOCF<sub>3</sub> containing  $<0.05 \alpha$  proton ( $\delta$  4.75, based on CH<sub>2</sub>Cl<sub>2</sub> at  $\delta$  5.30) and 5.03  $\beta$  protons ( $\delta$  1.03). Thus, the *i*-PrOCOCF<sub>3</sub> does not arise from solvent addition to propene<sup>7</sup> and there is no extensive equilibration of the protons. The remaining 16.3% product is *n*-PrOCOCF<sub>3</sub>. In the solvolysis of  $1, 1-d_2-1$ -PrOTs no  $\alpha$ proton signals were evident (<0.05 proton) in the residual n-PrOTs or the n-PrOCOCF<sub>3</sub> product. Thus, the solvolysis is not appreciably accompanied by 1,3-hydride shifts8 or formation and reopening of cyclopropane.9 The solvolysis of *i*-BuOTs yields only a rearranged product, this being mainly t-BuOCOCF<sub>3</sub> accompanied by as much as 20 % 2-BuOCOCF<sub>3</sub>. Quantitative product analysis is difficult in this case since the product is unstable even in the presence of CF<sub>3</sub>COONa. t-AmOCOCF<sub>3</sub> is produced quantitatively from neo-PenOTs.

As seen in Table I the relative rates in CF<sub>3</sub>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<sup>3a</sup> in EtOH, AcOH,

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).

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(8) The AlBr<sub>8</sub>-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  $CF_2COOD$  to cyclopropane gives *n*-PrOCOCF<sub>3</sub> with one D statistically distributed: N. C. Deno, *et al.*, J. Amer. Chem. Soc., 90, 6457 (1968).

<sup>(1)</sup> Research sponsored by the National Science Foundation.

RCH <sub>2</sub>	Temp, °C	$10^{5}k_{t}$ , sec <sup>-1</sup>	$\Delta H^{\pm}$ , kcal/mol	$\Delta S^{\pm}$ , eu	Rel rate	$\frac{-\Delta \log k}{\Delta \sigma^*}$ 75°
Me	75.0%	0.00181			1	
	100.0	$0.0164 \pm 0.0012$	$22.0 \pm 0.7$	$-31.0 \pm 2.0$		
	125.0	$0.113 \pm 0.008$				2.2
Et	75.0	$0.0226 \pm 0.0012$			12.5	
	100.0	$0.204 \pm 0.003$	$21.8 \pm 0.7$	$-26.7 \pm 2.0$		9.6
	125.0	$1.35 \pm 0.04$				
<i>n</i> -Pr	75.0	$0.169 \pm 0.005$			93.3	
	100.0	$1.80 \pm 0.07$	$23.7 \pm 0.3$	$-17.2 \pm 0.8$		16.6
<i>i-</i> Bu	75.0	$5.54 \pm 0.15$			3060	
	100.0	$60.0 \pm 1.7$	$23.9 \pm 0.3$	$-9.7 \pm 0.8$		2.5
neoPen	50.0	$0.692 \pm 0.013$				
	75.0⁰	$10.8 \pm 0.4$			<b>597</b> 0	
	100.0	$114 \pm 3$	$23.8 \pm 0.5$	$-8.9 \pm 1.3$		

Table I. Rates of Trifluoroacetolysis of Some Primary RCH2OTs<sup>4</sup>

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<sup>a</sup> Ca. 0.04 M ROTs. <sup>b</sup> Extrapolated from data at other temperatures. <sup>c</sup> Reported 8.5  $\times$  10<sup>-5</sup> sec<sup>-1</sup> by Dauben<sup>4b</sup> in buffered trifluoroacetic acid.

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

						<i>k</i> <sub>t</sub> , 100.0°		β-H/β-D, 100,0°	
Solvent	$k_{t}$	$k_{\Delta}$	ka	$\% k_{\Delta}$	$\alpha$ -H/ $\alpha$ -D	$\beta$ -H/ $\beta$ -D	$k_{\Delta}$	k,	
			n-	PrOTs		· · · · · ·			
EtOH	19.5	$3.8 \times 10^{-4}$	19.5	0.002°					
AcOH	0.61ª	$1.03 \times 10^{-3}$	0.61	0.168ª		1.06		1.06	
HCOOH	13.2	0.10	13.1	0.763					
CF <sub>3</sub> COOH	1.69	1.48	0.21	87.4°	1.29 <sup>i</sup>	1.77	1.85	$1.15^{k}$	
-			<i>i-</i> ]	BuOTs					
EtOH	1.33/	0.05	1.28	4.80		1.12			
AcOH	0.234/	0.185	0.049	$79.0^{h,m}$		1.67	1.78	1.281	
HCOOH	23.1/	22.3	0.80	96, 5 <sup>m</sup>					
CF <sub>3</sub> COOH	55.4	55.4	$0.017^{i}$	99.97	1.15	1.92			

<sup>a</sup> Interpolated value,  $10^7k$ , sec<sup>-1</sup>, = 66 (100°) and 3.55 (70°) (W. Pritzkow and K. H. Schöppler, *Chem. Ber.*, **95**, 834 (1962). <sup>b</sup> H. M. R. Hoffman, *J. Chem. Soc.*, 6762 (1965). <sup>c</sup> Extrapolated value from  $\log k_{\Delta} vs$ .  $\log k_t$  for neophyl-OTs in Figure 1. <sup>d</sup> Extrapolated from data at higher temperatures; 2-PrOAc product at 100.0 and 125.0° is 0.32 and 0.56%, respectively. <sup>e</sup> Extrapolated from data at higher temperatures; 2-PrOCOCF<sub>3</sub> product at 100.0 and 125.0° is 88.6 and 89.7%, respectively. <sup>e</sup> Extrapolated from data at higher temperatures; *i*-BuOEt product at 100 and 125.0° is 89.5 and 76.5%, respectively. <sup>i</sup> Reference 3a. <sup>e</sup> Extrapolated from data at higher temperatures; *i*-BuOEt product at 100 and 125.0° is 89.5 and 76.5%, respectively. <sup>k</sup> Extrapolated from data at higher temperatures; *i*-BuOEt product at 100 and 125.0° is extrapolated value from log  $k_a$  for *i*-BuOTs vs. log  $k_t$  for EtOTs. <sup>i</sup> The  $k_B/k_D$  values for EtOTs (125.0°) and neoPenOTs (100.0°) are 1.09 and 1.13, respectively. <sup>k</sup> For comparison,  $k_H/k_D$  for EtOTs at 125.0° is 1.16. <sup>i</sup> Acetolysis of  $\beta$ -*d*-*i*-BuOTs at 100.0° produces 21.9% *i*-BuOAc. <sup>m</sup> CH<sub>3</sub> participation is less important in these solvents than in CF<sub>3</sub>COOH, the  $k_{\Delta}H/k_{\Delta}C^{H_3}$  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  $\sigma^*$  for R<sup>10</sup> is not linear.<sup>4d</sup> 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  $k_{\Delta}$  type. On the basis of discrete  $k_{\Delta}$  and  $k_{s}$  processes, a formulation which successfully accounts for the behavior of other primary and simple secondary systems,<sup>5a,b</sup> we can dissect  $k_t$  for the present series of tosylates into  $k_{\Delta}$  and  $k_s$  components. For *n*-PrOTs solvolysis, the *n*-Pr product is assigned to  $k_s$  and the *i*-Pr product to  $k_{\Delta}$  due to H participation (see I). On this basis,  $k_t$  for *n*-PrOTs in CF<sub>3</sub>-COOH at 75.0° is 87.4%  $k_{\Delta}$  and 12.6%  $k_s$ . The derived  $k_{\Delta}$  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  $k_{\Delta}$  and  $k_s$ . For comparison

with the results in CF<sub>3</sub>COOH, 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.



Just as in the 2-phenyl-1-ethyl,<sup>5b</sup> 1-phenyl-2-propyl,<sup>5a</sup> and other cases,<sup>5a,b</sup> a crucial test of the  $k_{\Delta}$  and  $k_s$  dissection based on discrete processes may be based on the quantitative trends shown by the derived  $k_{\Delta}$  and  $k_s$  values as the solvent is varied. On the basis of the

<sup>(10)</sup> 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  $k_{\Delta}$ , we should expect a correlation of  $k_{\Delta}$  values with solvolysis rates  $(k_t)$  of neophyl-OTs,<sup>5b</sup> 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.<sup>5b</sup> Thus,  $k_s$  would be expected to correlate rather well with  $k_{\rm t}$  values for EtOTs.

As illustrated in Figure 1, a good linear free-energy correlation exists between log  $k_{\Delta}$  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<sub>3</sub>COOH 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  $k_{\Delta}$  plot  $0.002 \% k_{\Delta}$  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  $k_{\Delta}$  due to H participation as in IIa and CH<sub>3</sub> participation as in IIb. Listed in Table II are the  $k_t$ ,  $k_s$ , and composite  $k_{\Delta}$  values. A good correlation exists between log  $k_s$  for *i*-BuOTs and log  $k_t$  for EtOTs at 75°. The slope of the leastsquares 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  $k_{\Delta}$  and  $k_{s}$  processes in EtOH, AcOH, HCOOH, and CF<sub>3</sub>COOH. Isotope effects are also reasonable.<sup>3c</sup> For  $k_{\Delta}$  the  $\beta$ -deuterium isotope effects are ca. 1.8, while for  $k_s$  the range is 1.06 to 1.28. The  $\Delta S^{\pm}$  values seem to be characteristically lower<sup>2c</sup> for MeOTs and EtOTs, which solvolyze by the  $k_s$  route, than for *i*-BuOTs and neoPenOTs, which solvolyze mainly by the  $k_{\Delta}$  route.

It is clear that the major shift from  $k_s$  to  $k_{\Delta}$  in the solvolysis of *n*-PrOTs occurs in going from HCOOH to CF<sub>3</sub>COOH. For *i*-BuOTs, the shift occurs between EtOH and AcOH. For neoPenOTs,  $k_{\Delta}$  is dominant even in EtOH where the 92.7% rearranged products<sup>4f</sup> are ascribed to the  $k_{\Delta}$  process due to CH<sub>3</sub> participation (see III) and the 7.3% neoPenOEt<sup>4t</sup> is assigned to  $k_s$ . In AcOH,  $k_t$  for neoPenOTs is already >99.97 %  $k_{\Delta}$ .<sup>11</sup> The least-squares line for the plot of log  $k_{\Delta}$  for neo-PenOTs at 75° vs. neophyl-OTs has a slope of 0.833 for the solvents EtOH, AcOH, HCOOH, and CF<sub>3</sub>COOH. The mean deviation for the fit of the points is 0.25 log unit.

It is interesting to examine the  $k_{\Delta}$  and  $k_{s}$  rate constants for the primary alkyl tosylates as regards their variation with structure. For  $k_{\Delta}$  the ROTs structure sequence is PhEt  $\Im$  *i*-Bu  $\Im$  neoPen > *n*-Pr, while for  $k_s$  the ROTs structure sequence is  $Et \simeq n-Pr > PhEt > i-Bu > neo-$ Pen.

Trifluoroacetic acid is certainly an effective solvent for bringing out  $k_{\Delta}$ . Even more effective is FSO<sub>3</sub>H, and in the following communication<sup>12</sup> we report the

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Figure 1. Trifluoroacetolysis of simple primary alkyl toluenesulfonates.

results of a study of solvolysis of the simple primary alkyl tosylates in this solvent.

> 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<sup>1</sup> Sir:

As reported in the preceding communication,<sup>2</sup> CF<sub>3</sub>-COOH is quite effective in increasing  $k_{\Delta}/k_s$  ratios in solvolysis of simple primary tosylates. Another such solvent is concentrated H<sub>2</sub>SO<sub>4</sub>, as is reported by Myhre in an accompanying communication.<sup>3a</sup> In this communication we report on the solvolysis of primary tosylates in FSO<sub>3</sub>H. This solvent, with its extremely low nucleophilicity and tremendously high ionizing power, is even more effective in promoting high  $k_{\Delta}/k_{s}$ ratios. In FSO<sub>3</sub>H, even *n*-PrOTs reacts completely by the anchimerically assisted  $k_{\Delta}$  route, as do *i*-BuOTs and neoPenOTs.

Solvolyses in FSO<sub>3</sub>H were followed directly by nmr<sup>4</sup> in nmr tubes<sup>5</sup> 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  $\alpha$ -H at  $\delta$  4.28 and the  $\gamma$ -H at  $\delta$  0.85 as *n*-PrOTs forms isopropyl product. The *p*-methyl and aromatic proton signals were used as standards. Good firstorder rate constants  $(k_t)$  were observed between 5 and 90% reaction, and the infinities were 100%. Added KFSO<sub>3</sub> reduces  $k_t$ ,  $k_t$  being *ca*. inversely proportional

<sup>(11)</sup> The acetolysis of neoPenOTs at 125° in the presence of 0.036 M NaOAc yields 0.03  $\pm$  0.007% neoPenOAc. However, all the evidence indicates that most of this small amount can be ascribed to the reaction with NaOAc.

<sup>(12)</sup> A. Diaz, I. L. Reich, and S. Winstein, J. Amer. Chem. Soc., 91, 5637 (1969).

<sup>(1)</sup> Research sponsored by the National Science Foundation.

<sup>(2)</sup> I. L. Reich, A. Diaz, and S. Winstein, J. Amer. Chem. Soc., 91, 5635 (1969).

<sup>(3) (</sup>a) P. C. Myhre and E. Evans, *ibid.*, 91, 5641 (1969); (b) P. C. (d) (d) 1. C. htylic and E. Zitang,  $i_{2}$ ,  $i_{3}$ ,  $i_{4}$ ,  $i_{5}$ , i

<sup>(5)</sup> 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.