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NEIGHBORING GROUP PARTICIPATION IN SOLVOLYSIS. III.

k_Δ SOLVOLYSIS AS THE MAIN PATH IN TRIFLUOROACETOLYSIS OF 2-ARYLETHYL NOSYLATES WITH ELECTRON-WITHDRAWING SUBSTITUENTS[1]

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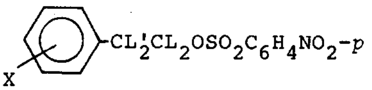
In recent years solvolysis of 2-arylethyl arenesulfonates has been successfully discussed based on the idea that the reaction proceeds *via* two discrete and competing paths designated as k_Δ and k_s.[2-5] While electron-donating substituents accelerate the reaction mainly or almost exclusively by the anchimerically assisted pathway (k_Δ), solvolysis of 2-arylethyl arenesulfonates having strongly electron-withdrawing substituents has been revealed to proceed mainly by the solvent-assisted pathway (k_s).

Recently, trifluoroacetic acid with its very low nucleophilicity and relatively high ionizing power has become an important solvolyzing solvent which gives rise to k_Δ/k_s ratios much higher than formic acid.[6,7] Consequently, it is interesting to investigate the behavior of trifluoroacetolysis of 2-arylethyl arenesulfonates having strongly electron-withdrawing substituents on the 2-aryl group and to determine the per cent fraction of the anchimerically assisted path in the total solvolytic reaction (Fk_Δ/k_t). Thompson and Cram reported that trifluoroacetolysis of 3-(*p*-nitrophenyl)-2-butyl tosylate was mainly k_Δ,[8] but the evidences obtained from the stereochemistry of the trifluoroacetates isolated as the minor products are, in our opinion, indirect and only qualitative. We now report the unambiguous and quantitative evidences supporting that trifluoroacetolysis of 2-(*m*-bromophenyl)ethyl and even 2-(*p*-nitrophenyl)ethyl *p*-nitrobenzenesulfonates (I and II , respectively) proceeds mainly *via* the k_Δ pathway.



I : X=*m*-Br, L=L'=H   II : X=*p*-NO_2, L=L'=H
I_α: X=*m*-Br, L=D, L'=H II_α : X=*p*-NO_2, L=D, L'=H
I_β: X=*m*-Br, L=H, L'=D II_β : X=*p*-NO_2, L=H, L'=D

The rate of trifluoroacetolysis of I and II was determined by the method described by Bentley and Dewar[9] with a slight modification. The reactions exhibited good first-order behavior through 70% of reaction in all cases (r>0.999). Acetolysis of them was also carried out titrimetrically for comparison. The results are summarized in Table I.

Striking differences are obvious between these two solvolyses; while the acetolysis rates of I and II are almost equal, the trifluoroacetolysis rate of I is about 100 times greater than that of II. The rate of trifluoroacetolysis of unsubstituted 2-phenylethyl nosylate is, in turn, about 100 times greater than that of I.[1] The facts suggest that some factor other than inductive one is operative in trifluoroacetolysis of these substrates.

In order to obtain further informations about the mechanism of the reaction, deuterium isotope effects were measured for the labeled esters, I_α, I_β, II_α, and II_β. The rates for the labeled compounds were determined at the early stage of reaction (0-20%) to avoid the complication caused by the scrambling of deuterium in the starting esters. The results are shown in Table II. The large isotope effects at the α-position and the small one around unity at the β-position were observed for trifluoroacetolysis of I. These are the characteristics of k_Δ solvolysis and are in contrast with the behaviors of k_s solvolysis,[10,11] namely acetolysis of I and II. Trifluoroacetolysis of II also showed the larger effects at the α than that at the β, but the differences are not so obvious as that of trifluoroacetolysis of I.

Finally, the dissection of k_t into k_s and Fk_Δ was accomplished using the labeled esters I_β and II_β. The rate of ion-pair return, $(1-F)k_\Delta$, was measured by isolating the unreacted esters to determine the per cent scrambling by nmr spectroscopy. The linearily of the rate plots was also good in both

Table I. Solvolysis Rates of 2-Arylethyl Nosylates

Solvent	Substrate	Temp, °C	$10^5 k_t$, sec^{-1}	$\Delta H^‡$, kcal/mol	$\Delta S^‡$, eu
AcOH (0.05 *M*, I or II)	I	100.0	2.65±0.01	22.4	-19.9
		110.0	5.93±0.02		
		115.0	8.85±0.02		
	II	100.0	2.62±0.02	22.4	-19.9
		115.0	8.73±0.04		
CF_3CO_2H (0.02 *M*, I or II)	I	70.0	1.94±0.02	21.9	-17
		80.0	4.88±0.04		
		90.0	12.0±0.1		
		100.0	27.7 (Calcd)		
	II	100.0	0.237 (Calcd)		
		110.0	0.558±0.007	23.9	-21
		120.0	1.31±0.01		
		130.0	2.80±0.03		
CF_3CO_2H (0.02 *M*, I or II; 0.04 *M*, CF_3CO_2Na)	I	70.0	3.88±0.06	21.1	-18
		85.0	14.8±0.4		
	II	110.0	1.03±0.01	23.0	-22
		120.0	2.24±0.02		
		130.0	4.88±0.04		

Table II. Deuterium Isotope Effects in Solvolysis of 2-Arylethyl Nosylates[a]

k^H/k^D	AcOH	CF_3CO_2H, unbuffered	CF_3CO_2H, buffered
I/I_α; I/I_β	1.041; 1.052 (100.0°C)	1.19; 1.01 (70.0°C)	1.24; 0.99 (70.0°C)
II/II_α; II/II_β	1.044; 1.061 (100.0°C)	1.14; 1.08 (110.0°C)	1.11; 1.09 (110.0°C)

a) The standard deviations are ±0.005-0.007 in AcOH and ±0.02-0.04 in CF_3CO_2H.

Table III. Partitioning of Rate Constants for Trifluoroacetolysis of 2-Arylethyl Nosylates

Substrate	Exptl value	Calcd by t=∞ data	Calcd by t=0 data	Av value
I (0.05 *M*, I_β; unbuffered; 70.0°C)				
k_t (sec^{-1})	$2.05\pm0.03\times10^{-5}$			
$(1-F)k_\Delta$ (sec^{-1})	$6.85\pm0.07\times10^{-5}$			
F		0.215	0.218	0.216
k_Δ (sec^{-1})		8.73×10^{-5}	8.76×10^{-5}	8.75×10^{-5}
k_s (sec^{-1})		0.180×10^{-5}	0.143×10^{-5}	0.162×10^{-5}
$(Fk_\Delta/k_t)\times100$		91	93	92
II (0.05 *M*, II_β; unbuffered; 110.0°C)				
k_t (sec^{-1})	$0.544\pm0.008\times10^{-5}$			
$(1-F)k_\Delta$ (sec^{-1})	$0.837\pm0.015\times10^{-5}$			
F		0.299	0.252	0.276
k_Δ (sec^{-1})		1.19×10^{-5}	1.12×10^{-5}	1.16×10^{-5}
k_s (sec^{-1})		0.188×10^{-5}	0.262×10^{-5}	0.225×10^{-5}
$(Fk_\Delta/k_t)\times100$		65	52	59

cases. The per cent rearrangement in the products for each compounds was determined for the initial stage of reaction (time=0) by extrapolation and for the final stage of reaction (time=∞) by direct observation. According to Coke *et al.*,[3] the former corresponds to Fk_Δ/k_s and the latter to k_Δ/k_s, when the secondary deuterium isotope effects are ignored. The results of the calculations are summarized in Table III. Control experiments showed the absence of scrambling in the products under the reaction conditions.

In the case of I, the per cent rearrangement of the product was almost complete throughout the reaction, so that the good agreement between the time=0 and time=∞ calculations was observed. Neglect of the secondary deuterium isotope effects apparently does not cause serious errors in this case. In trifluoroacetolysis of II, however, the per cent rearrangement varied considerably through the reaction and the two calculations gave some differences. As we can not at present decide which approach may give the correct results, the average of them is regarded as the most reliable one. The same treatment of the buffered trifluoroacetolysis shows that Fk_Δ/k_t is *ca.* 90% for I and *ca.* 20% for II. In acetic acid it is 0% in both cases.

As a conclusion, the results described above clearly verify that trifluoroacetolysis of 2-(*m*-bromophenyl)ethyl nosylate proceeds *via* k_Δ almost exclusively (92%), and that even 2-(*p*-nitrophenyl)ethyl nosylate solvolyzes mainly *via* the k_Δ pathway (*ca.* 60%).

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