

Solvolysis of 9-Fluorenyl Bromide and Tosylate. Nucleophilic Solvent Intervention and Insignificance of Antiaromaticity

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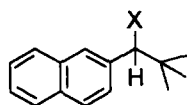
Abstract: Grunwald-Winstein type correlation analysis on the solvolysis of 9-fluorenyl bromide and tosylate suggests extensive charge delocalization throughout the whole system at cationic transition states in both cases, and significant nucleophilic solvent intervention for the bromide..

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The behavior of 9-fluorenyl or substituted 9-fluorenyl cation has been an attractive subject of recent studies.¹⁻³ Direct observation of the destabilized α -carbomethoxy-9-fluorenyl cation by laser flash photolysis was reported.² From the measured pK_R of the corresponding alcohol and the *ab initio* calculation the 9-fluorenyl carbocation was suggested to be not antiaromatic,¹ whereas the antiaromatic fluorenyl cation character was noticed from the solvolysis of 9-(trifluoromethyl)fluorenyl tosylate.³ Our recent studies on the Grunwald-Winstein type correlation analysis (eq 1)⁴ of solvolytic reactivities for benzylic substrates indicated an important contribution of solvation of the delocalized cationic transition state to solvent ionizing power Y ,⁵ and the dependence of solvation on the extent of charge delocalization as shown from the different solvolytic behaviors of α -*tert*-butyl-(2-naphthyl)methyl bromide (1)⁶ and tosylate (2)⁷ in comparison with benzylic analogues, respectively. Therefore, it is desirable to solve the problem by employing eq 1 with appropriate Y scale to correlate solvent effect on reactivities for elucidating the transition state structure, the extent of charge delocalization, of solvolysis. We now wish to report the results of solvolysis of 9-fluorenyl bromide (3) and

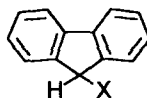
$$\log(k/k_0) = mY \quad (\text{eq 1})$$

tosylate (4) which conclude the existence of an extensively delocalized cationic transition state in both cases, indicating the insignificance of antiaromaticity as has been suggested,¹ and the presence of significant nucleophilic solvent intervention for the bromide.



1 : X = Br

2 : X = OTs



3 : X = Br

4 : X = OTs

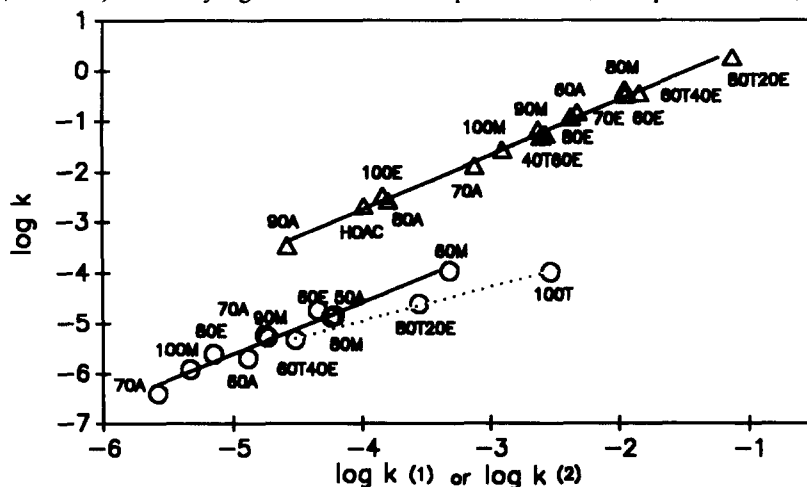
9-Fluorenyl bromide (3)⁸ and tosylate (4)⁹ were prepared by using conventional methods from 9-fluorenyl Methanolysis of 3,¹⁰ acetolysis¹¹ and hydrolysis¹² of 4 in aqueous acetone were considered to proceed via S_N1 mechanisms. In the present study, first order rate constants of solvolyses were measured by conductimetry at

Table 1. Pertinent Rate Constants for 3 and 4

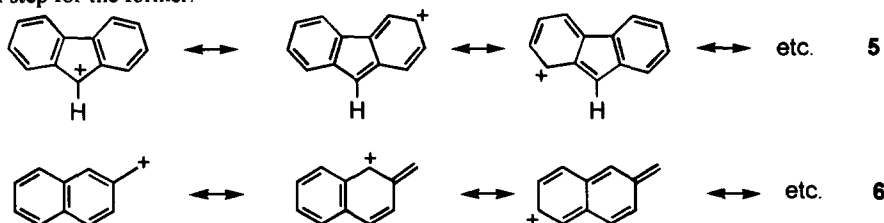
solvent ^a	k , 1/s ^b		k_{OT}/k_{Br} , $\times 10^4$	solvent ^a	k , 1/s ^b		k_{OT}/k_{Br} , $\times 10^4$
	bromide 3	tosylate 4			bromide 3	tosylate 4	
100E		3.34×10^{-3}		100M	1.22×10^{-6c}	2.71×10^{-2}	2.22
80E	2.45×10^{-6c}	6.71×10^{-2}	2.74	90M	5.23×10^{-6c}	0.119 ^c	2.28
70E	5.87×10^{-6c}	0.146	2.49	80M	1.46×10^{-5c}	0.334 ^c	2.29
60E	1.83×10^{-5c}	0.414 ^c	2.26	60M	1.08×10^{-4}		
90A		3.42×10^{-4}		100T	1.05×10^{-4}		
80A		2.66×10^{-3}		80T20E	2.45×10^{-5}	1.82 ^c	7.43
70A	4.00×10^{-7c}	1.31×10^{-2}	3.28	60T40E	4.79×10^{-6c}	0.354 ^c	7.39
60A	2.00×10^{-6c}	4.87×10^{-2}	2.44	40T60E		5.46×10^{-2}	
50A	1.32×10^{-5c}			HOAc		2.07×10^{-3d}	

^aAbbreviation of solvents: A: acetone; E: ethanol; M: methanol; T: 2,2,2-trifluoroethanol. The numbers denote the percentage of the specific solvent in the mixture, but those for water were omitted. ^bAverage of duplicate or more runs ($\pm 2\%$) at 25 °C. ^cFrom Arrhenius plots of data at other temperatures. ^dRef. 11.

least in duplicate. Sufficiently wide ranges of solvents were covered in both cases. The error was $\pm 2\%$ and the pertinent data were listed in Table 1. The tosylate/bromide rate ratios are in the order of 10^4 , similar to those found for 1-adamantyl analogues.^{13,14} No good linear relationship with Y_X ¹⁵ or Y_{BnX} ⁵ using eq 1 could be obtained in either case. However, excellent linear correlation ($R = 0.997$, $m = 1.09$) was observed if $\log k(4)$ s were plotted against $\log k(3)$ s for α -*tert*-butyl-(2-naphthyl)methyl tosylate 2, although poor correlation ($R = 0.950$, $m = 0.793$) was found again for $\log k(3)$ s versus $\log k(1)$ s. (Figure 1) In the case of 3, a splitting of the line ($R = 0.979$, $m = 1.03$) defined by $\log k$ measured in nucleophilic solvents, *i.e.* aqueous acetone, ethanol and

**Figure 1.** Correlations of logarithms of rate constants for 3 (o) against $\log k(1)$ and for 4 (Δ) against $\log k(2)$

methanol, from that ($R = 0.999$, $m = 0.673$) defined by $\log k$ measured in the less nucleophilic trifluoroethanol-ethanol systems was noticed. The large difference, 0.36, in m values for **3** with respect to $\log k(1)$ indicated profound nucleophilic solvent intervention as was found, for example, in the solvolysis of 2-aryl-2-propyl *p*-nitrobenzoates.¹⁶ Obviously, the extent of partial positive charge delocalization in the solvolytic transition state for 9-fluorenyl substrates **3** and **4** resembles to that for 2-naphthylmethyl derivatives **1** and **2**, respectively. In other words, the similar delocalization of positive charge throughout both rings in the 9-fluorenyl system (**5**) and in the aromatic 2-naphthylmethyl system (**6**) reveals aromatic, but not antiaromatic, character for the former. It could be further supported by the observation of excellent linear correlation between $\log ks$ for **1** and for benzhydryl bromide.⁶ The planar structure in **5** would be susceptible to nucleophilic attack by solvent at C-9 especially in the case where a relatively poor leaving group, the bromide ion, is involved. The low reactivity of **3** as compared with benzhydryl bromide (about $10^4 : 1$) is likely due to the larger amount of energy needed in the ionization step for the former.¹⁷



Moreover, the dual-parameter Grunwald-Winstein equation including nucleophilic term (eq 2)¹⁸ was applied to analyze the solvolytic behavior of **3**. Among different N scales available N_T ¹⁹ was the one suggested

$$\log(k/k_o) = mY + IN \quad (\text{eq 2})$$

for general use, and was thus employed in the correlation by using eq 2. The logarithms of ks for **1**, were used in place of Y . An improved linear correlation ($R = 0.989$, $m = 1.08$) with quite large contribution of N_T ($l = 0.288$) was found. Significant nucleophilic solvent intervention could be concluded again.

Recently a scale of aromatic ring parameter, l , and modified equations (eq 3 and 4) were proposed to accommodate the dispersion involved in Grunwald-Winstein treatment of rate data for benzylic substrates using Y_X values.^{20,21} However, it was pointed out that based on several pieces of evidence the utility of this term would be limited and less preferable than the use of Y_{BnX} in the understanding of benzylic solvolyses.²² In addition, limited number of data points would make the interpretation of multiparameter eq 4 less reliable. Nevertheless, the proposal of using eq 3 and 4 was also tested by the kinetic data for the solvolysis of **3** and **4**. The results in **Table 2** showed relatively poor linear correlation and demonstrated the failure of the application of both equations to correlate the solvolytic reactivities of **3** or **4**.

$$\log(k/k_o) = mY + hl \quad (\text{eq 3})$$

$$\log(k/k_o) = mY + IN + hl \quad (\text{eq 4})$$

Table 2. Correlation Analyses of log *k* for **3** and **4** Using Equations 3 and 4

substrate	parameters	<i>n</i>	<i>m</i>	<i>h</i>	<i>l</i>	<i>R</i>
3	Y_{Br}, I	13	0.616	0.818		0.889
	Y_{Br}, I, N_T	13	0.894	1.36	0.334	0.933
4	Y_{OTs}, I	14	0.903	1.42		0.983
	Y_{OTs}, I, N_T	14	0.969	1.51	0.241	0.988

In conclusion, the cationic transition states for the solvolysis of 9-fluorenyl bromide and tosylate are found to be extensively delocalized, *i.e.* not antiaromatic, and to involve significant nucleophilic solvent intervention in the case of **3**, contrary to those suggested in literatures.^{3, 10, 12}

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