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FAILURE OF THE LINEAR CORRELATION OF Log*k* WITH Y_{AdCl} IN THE SOLVOLYSIS OF TERTIARY BENZYLIC CHLORIDES. THE ESTABLISHMENT OF A NEW *Y* SCALE BASED ON 2-ARYL-2-CHLOROADAMANTANES

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Abstract: A new *Y* scale based on 2-aryl-2-chloroadamantanes (**2**) has been developed for the correlation of solvolysis rates of benzylic chlorides, in which the solvation on the delocalized transition state is significant.

The Winstein-Grunwald equation, $\log(k/k_o) = mY$, defines the first scale of empirical solvent ionizing power(Y) based on the solvolytic rate constants of *t*-butyl chloride.[1] Later studies exhibited that 1- or 2-substituted adamantanes were better references for examinining the intervention of solvent participation in a solvolytic reaction,[2] and different *Y* scales were necessary for substrates containing different leaving groups.[3,4] For example, Y_{AdCl} for chlorides was derived from 1-chloroadamantane.[3] On the other hand, the solvolysis of 2-aryl-2-chloropropanes(**1**) has long been considered to proceed *via* a rate-determining carbocationic transition state, and to be the primary standard reaction for defining the σ^+ constants[5] in the Hammett type correlation analysis.[6] To our knowledge, however, no study has ever been reported on the solvent effect on the solvolysis of **1** in terms of *Y*. Consequently, we undertook to study the solvolysis of some representative tertiary chlorides in a variety of solvents, and found the failure of using Y_{AdCl} scale to correlate the reactivity of tertiary benzylic chlorides, in which the delocalization of the cationic reaction center in the transition state was significant. A *Y* scale based on other reference is thus developed.

2-Aryl-2-chloropropanes(**1a**, Ar = C_6H_5; **1b**, Ar = 3'-ClC_6H_5), 2-aryl-2-chloroadamantanes(**2a**, Ar = 4'-$CH_3C_6H_4$; **2b**, Ar = 4'-FC_6H_4; **2c**, Ar = C_6H_5; **2d**, Ar = 3'-ClC_6H_4; **2e**, Ar = 3'-$CF_3C_6H_4$; **2f**, Ar = 4'-$CF_3C_6H_3$), 2-chloro-2,3,3-trimethylbutane(**3**), and 2-chloro-3,3-dimethyl-2-phenylbutane (**4**) were prepared and the first order solvolytic rate constants were measured by means of the conductimetric method. Pertinent data are listed in **Table I.** The correlation analyses of the logarithms of the rate constants against Y_{AdCl} values were carried out. Fairly good linear relationships were observed in the case of **3** (m = 0.743 and r = 0.993) and of **4**(m = 0.908 and r = 0.988), but not **1** or **2** (**Figure 1a**). The small rate retardation observed

Table I. Y_{BnCl} Values and pertinent solvolytic rate constants for chlorides

Solvent	Y_{BnCl}	*k*, s^{-1} (25^{o}C)				
		1b	**2c**	**2d**	**3**	**4**
100E	-1.608	6.68x10^{-6}	1.64x10^{-3}	2.59x10^{-5}		
90E	-0.645	6.38x10^{-5}	2.24x10^{-2}	2.38x10^{-4}		6.24x10^{-6} [a]
80E	0.000	2.60x10^{-4}	1.53x10^{-1} [a]	1.05x10^{-3}	1.10x10^{-5}	1.01x10^{-5}
70E	0.571	8.80x10^{-4}	5.91x10^{-1} [a]	3.91x10^{-3}	4.45x10^{-5}	2.06x10^{-5}
60E	1.072		1.76x10^{0} [a]	1.24x10^{-2}	1.38x10^{-4}	7.52x10^{-5}
90A	-2.276	1.94x10^{-6}	4.28x10^{-4}	5.56x10^{-6}		
80A	-1.085	2.52x10^{-5}	7.09x10^{-3}	8.64x10^{-5}		
70A	-0.259	1.60x10^{-4}	4.90x10^{-2}	5.79x10^{-4}		8.12x10^{-6}
60A	0.518	8.64x10^{-4}	5.17x10^{-1} [a]	3.46x10^{-3}	7.04x10^{-5}	2.77x10^{-5}
50A	1.232		1.89x10^{0} [a]	1.79x10^{-2}		1.47x10^{-4}
40A					1.47x10^{-3}	6.73x10^{-4}
100M	-0.253	8.00x10^{-5}	5.05x10^{-2}	5.86x10^{-4}	2.06x10^{-6}	
90M	0.585		2.88x10^{-1} [a]	4.04x10^{-3}		
60M	2.960			9.57x10^{-1} [a]	6.80x10^{-4}	2.83x10^{-4}
TFE	3.550	1.82x10^{-2}	2.79x10^{2} [b]	3.72x10^{0} [b]	1.06x10^{-3}	2.76x10^{-3}
70T	3.601		3.13x10^{2} [b]	4.19x10^{0} [b]	1.86x10^{-3}	3.48x10^{-3}
50T					3.34x10^{-3}	4.56x10^{-3}
80T-20E	2.420			2.76x10^{-1} [a]		
40T-60E	0.180		1.48x10^{-1} [a]	1.59x10^{-3}		

[a] Extrapolated from data at other temperatures. [b] Extrapolated from the linear logarithm plot with *k*s of **2f**.

for **3** in trifluoroethanol-water system could be attributed to the lack of nucleophilic solvent assistance,[7] similar to the cases of *t*-butyl halides.[3] Although the benzylic carbon in **1** may still be liable to the back-side solvent attack, it is unlikely in the highly congested **2** because the 2-methyl analogue displays a linear log*k* - *mY* correlation.[8] More plausible explanations should then be considered.

The difference between **1**, **2** and **3**, **4** suggests that the resonance contribution of the α-aryl group in the transition state plays an important role. The Hammett-Brown treatment of the rate data for **2** in various solvents showed excellent correlations with ρ values of -4.57 to -4.74, in agreement with the reported value -4.83[9] in 90% acetone. The resonance effect in the solvolysis of **2** is thus as important as in the case of **1**. On the contrary, the small rate ratios for **3** and **4**, k_{Ph}/k_{Me} = 0.39-2.6, indicate the insignificance of resonance stabilization by the phenyl ring in the solvolysis of **4**.[10] Obviously, there is a close relationship between the effectiveness of resonance contribution from the α-aryl group and the applicability of the generally accepted Y_{AdX} scales.

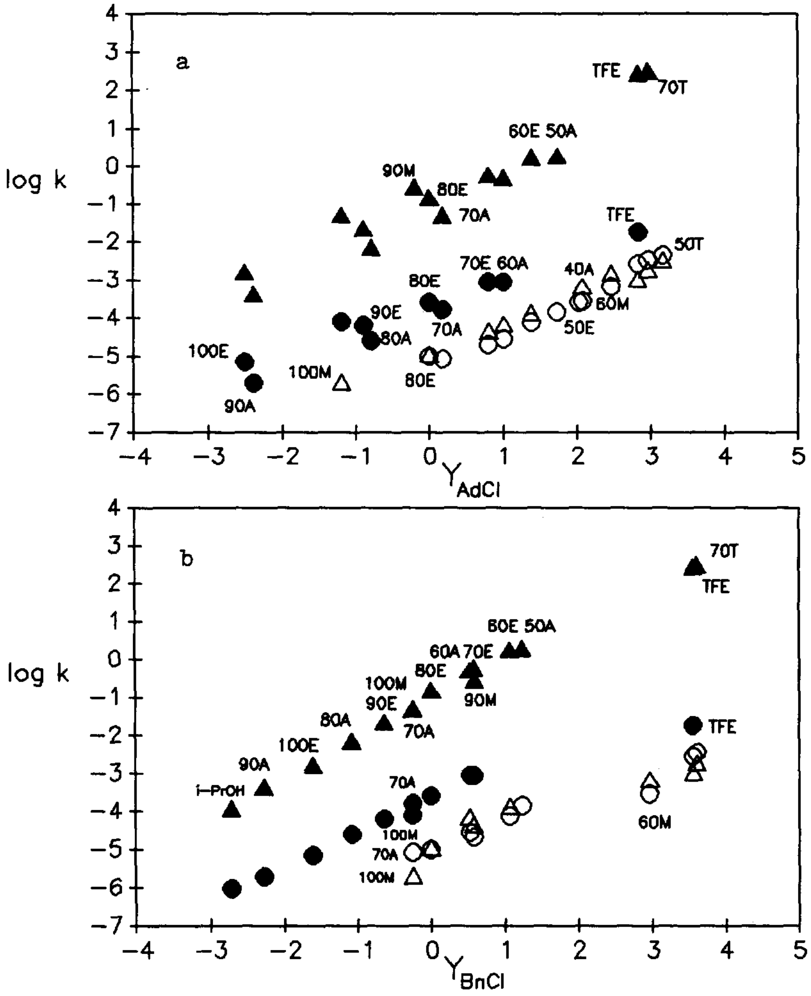

Figure 1. Correlations of logarithms of rate constants for chlorides 1b(●), 2c(▲), 3(△), and 4(○). (a) against Y_{AdCl}. (b) against Y_{BnCl}.

For 1-adamantyl and tertiary aliphatic derivatives the partial positive charge developed in the transition state is localized, but for **1** and **2** it is delocalized. The extent of solvent interaction is likely to be different. Accordingly, a new *Y* scale applicable to **1** and **2**, and other similar substrates, seems to be a necessity.

Excellent linear correlations between log*k*s were realized for any two chlorides in **2a**-**2f**. The best inter-correlation, correlation coefficient > 0.995, could be found if **2d** was employed as the reference (**Figure 1b**, *m* = 1.016 and r = 0.998 for **2c**). In addition, linear log*k*(**1**) - log*k*(**2d**) plots were also observed. Thus, similar to the cases for defining Y_{AdX},[4] we are able to establish a new *Y* scale, Y_{BnCl}(**Table I**), from the solvolytic rate constants of 2-chloro-2-(3'-chlorophenyl)adamantane (**2d**) to correlate the log*k*s for the tertiary benzylic chlorides.

The solvent effect on the solvolysis of benzylic chlorides is not in parallel with that of 1-chloroadamantane. The Y_{BnCl} value is greater than the corresponding Y_{AdCl} value[3] in $MeOH-H_2O$, $TFE-H_2O$, and some $EtOH-H_2O$ (100E-80E), but is smaller in acetone-water and other $EtOH-H_2O$ (70E and 60E) mixtures. Hence, both the electrophilicity and the nucleophilicity of the solvents[11] seem to have significant effects on the solvation in the transition state. The slight deviation of the data point corresponding to k_{TFE} for **1b** in **Figure 1b** again exhibited the importance of solvent intervention.[8] Moreover, neither **3** nor **4** gave linear plot with Y_{BnCl}. Clearly, this new Y scale, rather than Y_{AdCl}, is the choice to correlate the solvolytic reactivity of benzylic chlorides, in which the transition state involves the delocalization of the positive charge at carbinyl carbon to the aryl group. The observation of decreasing m values in mY_{BnCl} plots with increasing electron-attracting ability of the substituent on the aryl ring, *e.g.*, m = 1.016 for **2c** and m = 0.852 for **2f**, also indicates the relevance of charge delocalizations in this concern.

Studies on new Y sacles for other benzylic substrates, such as bromides, *p*-nitrobenzoates and tosylates, and on the solvent participation in the solvolysis of benzylic substrates by using these Y scales are in progress.

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