

The Arrhenius plot was obtained by plotting both $\ln K_p$ and $\ln K_D$ against $1/T$ as shown in Figure 11. From these plots we obtained two apparent activation energies, E_p and E_D , of propagation and degradation, and their values were $E_p=148$ KJ/mol and $E_D=173$ KJ/mol, respectively. The apparent activation energy of determined by degradation rate is higher than that determined by the propagation rate. From this phenomenon, it can be seen that the degradation reaction is much more influenced by a temperature change than the propagation rate.

Concluding Remarks

The antimony catalyzed polycondensation on the formation of poly(ethylene 2,6-naphthalate) was investigated. The catalytic activities of antimony compounds were significantly influenced by the concentration of catalyst and the oxygen numbers of the antimony oxides as well as the metal species. Temperature was one of the most important factor to reduce the reaction time to reach the maximum value of the intrinsic viscosity of the formed polymer; the higher the temperature was, the faster the reaction rates were.

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Solvent Effects on Localized and Delocalized Cationic Charges in Solvolysis¹

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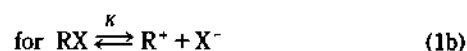
A measure of stabilities ($-\Delta H^{\circ}$) and resonance delocalization ($-\Delta q(C_a^+)$) for some carbocations has been estimated using the semiempirical AM1 method. The stability ($-\Delta H^{\circ}$) of carbocations can be correlated with the sensitivity (m) of localized cations to the solvent ionizing power scale Y, whereas the extent of resonance delocalization ($-\Delta q(C_a^+)$) can be correlated with the sensitivity (h) of delocalized cations to the solvent ionizing power scale I. It has been shown that two solvent ionizing power scales Y and I have in general opposite signs so that effects of electrostatic solvation are opposite for the localized and delocalized cationic charges. The use of two different solvent scales for a substrate with delocalizable cationic charge is not only prerequisite to the proper correlation of solvolysis rates but also is justified.

Introduction

Isolated carbocations, as those in the gas phase, are in general unstable unless the cationic charges are well delocalized; thus the instability of a carbocation in a given environment and at a given temperature is directly related to the degree to which the charge is localized. The unstable carbocations are stabilized either (i) by electrostatic solvation in solution or (ii) by delocalization of the cationic charge over relatively wide range as involved in resonance delocalization

of cationic charge into a benzene ring. The relative stability of a carbocation R^+ can be conveniently represented by the heat of formation (ΔH°) of the isolated ion pair² $R^+ + X^-$, as shown in eq (1a). By keeping

$$\Delta H^{\circ} = \Delta H_f(R^+) + \Delta H_f(X^-) - \Delta H_f(RX) \quad (1a)$$



the anion X^- constant, the relative stability of R^+ can be compared. An unstable carbocation is characterized by a la-

rge value of ΔH^\ddagger , which can be alternatively expressed as a small equilibrium constant K for the equilibrium shown in eq (1b) if entropy effects are neglected.³ This means that the equilibrium concentration of a more unstable carbocation is lower under the given environment and temperature, and hence when a more unstable carbocation is placed in a solvent the sensitivity or the susceptibility of the carbocation to the solvent ionizing power Y changes should be also lower. This is tantamount to a smaller value of m , which is the slope parameter of the Grunwald-Winstein equation¹ (eq. (2)) for a more unstable localized carbocation. In the original Grunwald-Winstein equation (eq. (2)) the rate constants k and k_0 ,

$$\log(k/k_0) = mY \quad (2)$$

for the solvolysis of *tert*-butyl chloride (for which m is 1.0) in a given solvent and in 80% ethanol, respectively are used to define solvent ionizing power Y .⁴ As a similarity model, the choice of *tert*-butyl chloride was rather fortunate; both the cation ($(\text{CH}_3)_3\text{C}^+$) and anion (Cl^-) have localized charges so that Y can represent the solvent effects on the localized ion pair, *i.e.*, the stabilization of the localized carbocation is well represented. Later studies have indicated that the solvolysis of *tert*-butyl chloride is nucleophilically assisted⁵ so that the Y scale does not depend only on the solvation stabilization of the localized ion pair. As an alternative model, 1-adamantyl chloride (Y_{Cl} scale) has been adopted.^{5a,6,7} The choice of 1-adamantyl system seems to be better since its cationic charge is more localized than that of *tert*-butyl system and the possibility of nucleophilic assistance can be precluded. The most important condition for the solvent parameter Y is that it should represent solely the solvent stabilization effect of localized charges, cations and as well as anions; the slope m should then reflect the sensitivity of localized charges to the solvent stabilization effect. The use of eq. (2) is adequate as long as the charges are localized. When, however, the cationic charge becomes resonance delocalized, the solvent stabilization effect on the delocalized charge can not be represented by the solvent parameter Y . For this purpose, an introduction of a new solvent ionizing power I for the delocalized cationic charge in the benzene ring was required, which is shown in eq. (3),⁸ where h is the sensitivity to the I scale, which was defined by in eq. (4). The second solvent parameter I in eq. (3)

$$\log(k/k_0) = mY + hI \quad (3)$$

$$I = \log(k/k_0)_{p\text{-MeOC}_6\text{H}_4\text{CH}_2\text{S}^+\text{Me}_2} - 1.3 \log(k/k_0)_{1\text{-AdS}^+\text{Me}_2} \quad (4)$$

thus represents the solvent stabilizing ability of the delocalized part of the cationic charge (into the benzene ring) and the susceptibility h should be proportionally related to the degree of resonance delocalization of the cationic charge into the ring; the greater the degree of charge delocalization, the more stable will become the carbocation and hence the larger will become the magnitude of h . In the present work, in order to provide firm theoretical bases for values of m and h in eq. (3), we carried out molecular orbital studies using the AM1 method.⁹

Calculations

Table 1. Solvent parameters Y , Y_{Cl} , Y_{OTs} and I for some solvents

Solvent	Y^a	Y_{Cl}^b	Y_{OTs}^c	I^d
100% EtOH	-2.03	-2.50	-1.96	0.20
80% EtOH	0.00	0.00	0.00	0.00
60% EtOH	1.12	1.38	0.92	-0.15
40% EtOH	2.20	2.75	1.97	-0.24
20% EtOH	3.05	4.09	3.32	-0.33
100% H ₂ O	3.49	4.57	4.10	-0.45
100% MeOH	-1.09	-1.20	-0.92	0.41
80% MeOH		0.67	0.47	0.14
60% MeOH		2.07	1.52	-0.02
40% MeOH		2.43	3.25	-0.13
20% MeOH		4.10	3.39	-0.26
95% Acetone			-2.95	-0.13
90% Acetone			-1.99	-0.17
80% Acetone		-0.80	-0.94	-0.23
70% Acetone		0.17	0.07	-0.29
60% Acetone		1.00	0.66	-0.28
40% Acetone		2.46	1.85	-0.35
20% Acetone		3.77	3.05	-0.40
90% Dioxane			-2.41	-0.12
80% Dioxane			-1.30	-0.13
97% TFE ⁹⁾		2.83	1.77	0.49
90% TFE			1.83	0.47
70% TFE		2.96	2.00	0.25
50% TFE		3.16	2.14	0.09
97% HFIP ⁹⁾		5.08	3.61	0.73

^a The solvent ionizing power scale Y with *tert*-butyl chloride.⁴

^b The solvent ionizing power scale Y with 1-adamantyl chloride.⁷

^c The solvent ionizing power scale Y with 1-adamantyl tosylate.⁷

^d The solvent ionizing power for delocalized cationic charge in the aromatic ring.^{8a} ¹2,2,2-trifluoroethanol. ¹1,1,1,3,3,3-hexafluoro-2-propanol.

We used the standard AM1 procedure⁹ as implemented in the MOPAC version 6 throughout in this work. Geometries of the reactants RCl and their cations R^+ were fully optimized with no assumption. The stabilities of carbocations were expressed with the ΔH^\ddagger values^{2a} (eqs. (1a) and (1b)) and the extent of resonance delocalization was estimated as the positive charge increment $\Delta q(\text{C}_\alpha^+)$,^{2a} which is defined as the difference in charge on C_α between the reactant RCl and carbocation R^+ , *i.e.*, $\Delta q(\text{C}_\alpha^+) = q(\text{R}^+) - q(\text{RCl})$. The $\Delta q(\text{C}_\alpha^+)$ will be smaller positive or will be more negative when the positive charge on the α -carbon of carbocation is resonance delocalized into a benzene ring to a greater extent.^{2a}

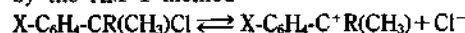
Results and Discussion

For comparison we have listed values of Y , Y_{OTs} and Y_{Cl} together with the I values^{8a} in Table 1. First of all, let us consider the three solvent ionizing power scales Y (defined by eq. (2)),⁴ Y_{Cl} (defined by using 1-adamantyl chloride)⁷ and Y_{OTs} (defined by using 1-adamantyl tosylate).⁷ Among the three scales, Y_{Cl} is numerically the largest, which is consis-

Table 2. Calculated reaction enthalpies (ΔH°) and charge increments (Δq) for the solvolysis of benzylic tosylates by the AM 1 method

Reactant	Reactant (R)		Product (P)		$\Delta\Delta H^{\circ}(\text{P-R})$	$\Delta q(q_{\text{R}^+} - q_{\text{R}})$	m^{th}	h^{th}
	$\Delta H(\text{R})$	$\Delta H(\text{C}^+)$	$\Delta H(\text{OTs}^-)^{\text{a}}$					
1. <i>tert</i> -butylbenzyl tosylate	-77.59	194.32			136.84	0.082	0.93	0.76
2. α - <i>tert</i> -butyl- <i>m</i> -chlorobenzyl tosylate	-84.82	191.42			141.17	0.091	0.91	0.59
3. α -trifluoromethyl- <i>p</i> -methylbenzyl tosylate	-223.62	65.94			154.49	-0.081	0.80	1.10
4. α -methyl- α -trifluoromethylbenzyl tosylate	-214.28	67.79			147.0	-0.032	0.85	0.86
5. α -(3,5-dichlorophenyl)- α -trifluoromethyl benzyl tosylate	-185.21	91.05			141.19	-0.064	0.88	1.46

^aCalculated enthalpies of formation are -135.07 in all cases.

Table 3. Calculated reaction enthalpies (ΔH°) and charge increments (Δq) for the solvolysis of cumyl chloride and derivatives by the AM 1 method

X	R	Reactant (R)		Product (P)		$\Delta\Delta H^{\circ}(\text{P-R})$	$\Delta q(q_{\text{R}^+} - q_{\text{R}})$	m^{th}	h^{th}
		$\Delta H(\text{R})$	$\Delta H(\text{C}^+)$	$\Delta H(\text{Cl}^-)^{\text{a}}$					
6	<i>o</i> -Me	Me	0.24	189.18		151.28	0.197	0.68	0.78
7	H	Me	1.94	194.67		155.07	0.224	0.71	0.58
8	<i>m</i> -Cl	Me	-5.02	191.54		158.90	0.235	0.66	0.35
9	<i>p</i> -CF ₃	Me	-154.05	49.13		165.52	0.257	0.61	0.50
10	H	Et	-3.08	188.95		154.37	0.219	0.75	0.70
11	H	<i>i</i> -Pr	-5.70	185.36		153.40	0.219	0.74	0.94
12	<i>m</i> -Cl	<i>i</i> -Pr	-12.69	182.17		157.20	0.230	0.71	0.85
13	H	<i>t</i> -Bu	-5.22	187.18		154.74	0.231	0.79	0.80
14	<i>m</i> -CH ₃	<i>t</i> -Bu	-12.76	178.53		153.63	0.221	0.86	1.11
15	3,4-di-Me	<i>t</i> -Bu	-19.83	168.91		151.08	0.208	0.82	1.33

^aCalculated enthalpies of formation are -37.66 in all cases.

tent with the truly localized nature of cationic (1-adamantyl cation) and anionic (chloride) charges of the model compound. In contrast, Y and Y_{OTs} are numerically smaller, *i.e.*, electrostatic solvation of localized charge is less efficient than Y_{Cl} since for Y there is nucleophilic assistance which will weaken the electrostatic solvation effect, and for Y_{OTs} , the delocalized tosylate anion, will also be weakly solvated electrostatically. The best solvent ionizing power scale is therefore Y_{Cl} , which reflects the strongest electrostatic solvation of localized charges.

Second, we note that the I and Y_{Cl} scales have either opposite signs or large numerical differences when they have the same sign. This is a reflection of opposite effects of a solvent on the delocalized and localized parts of cationic charge, *e.g.*, water is a strongly stabilizing solvent ($Y_{\text{Cl}} = +4.57$) for a localized cation but is a relatively strong destabilizing one ($I = -0.45$) for a delocalized cation. A large difference in the Y_{Cl} and I values with same signs reflects that although a solvent (*e.g.* 80% EtOH) is strongly stabilizing for a localized cation ($Y_{\text{Cl}} = +0.67$) it is only weakly stabilizing for a destabilized cation ($I = +0.14$). These comparisons demonstrate correctly that the effects of a solvent on the

localized and delocalized cations are significantly different so that the use of two separate solvent scales (I and Y_{Cl}) is entirely justified, eq. (3).⁸ The failure of using I scale, *i.e.*, eq. (3), to correlate the solvolysis rates of benzhydryl chloride resulted in a large scatter,¹⁰ especially for the fluorinated solvents. This is because the fluorinated solvents like $\text{CF}_3\text{CH}_2\text{OH}$ (TFE) and $(\text{CF}_3)_2\text{CHOH}$ (HFIP) have in general large positive I values (Table 1) and enhance solvolysis rates by strongly stabilizing ring delocalized cationic charges as in the benzhydryl cation. The neglect of hI in eq. (3) will result in the rate calculated by the mY term alone and a large positive deviation will be exhibited due to an additional unaccounted rate enhancement due to the hI term. It was difficult for Bunton *et al.*¹⁰ to interpret the large positive deviations of solvents with large I values like TFE and HFIP in the correlation of benzhydryl chloride solvolysis with the Y scale alone. It has since become apparent that their conclusion¹⁰ that "It is therefore probably not feasible to devise generally applicable kinetic solvent scales for $S_{\text{N}}1$ reactions" has been a rather pessimistic one.

Our AM1 results on ΔH° and Δq are summarized in Tables 2 and 3 for benzylic tosylates and substituted benzylic

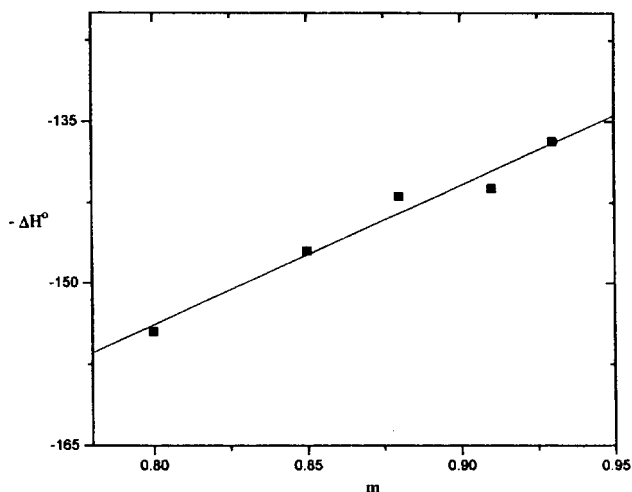


Figure 1. Plots of $-\Delta H^\circ$ vs. m for the solvolysis of benzylic tosylates.

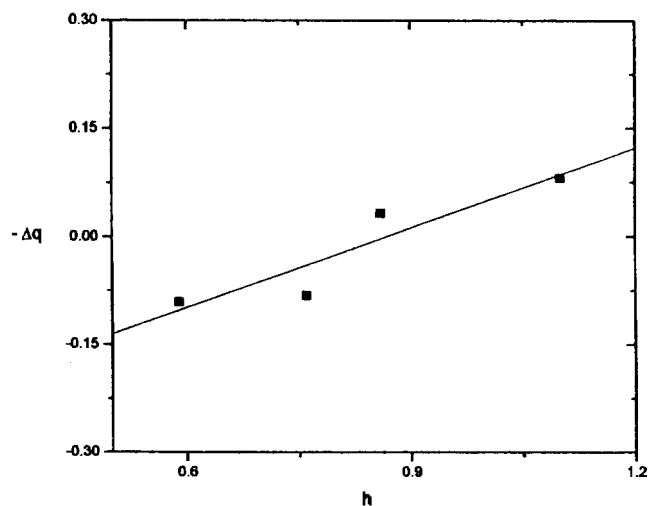


Figure 2. Plots of $-\Delta q$ vs. h for the solvolysis of benzylic tosylates.

chlorides series, respectively. As stated in the introduction, the reaction enthalpies, ΔH° , can be used as the relative cation stability scale within a series of compounds when the anionic part is kept constant. Since the stability ($-\Delta H^\circ$) or instability (ΔH°) of a cation depends primarily on the localized cationic charge, and since the lower the ΔH° , the more is the localized cation stabilized, we would expect a linear correlation between $-\Delta H^\circ$ and m , $\delta(-\Delta H^\circ) = a \cdot \delta m$. Such correlations are indeed obtained in Figure 1 for the data in Table 2 ($a=130.0$ with $r=0.98$ for 5 compounds) and for the data in Table 3 ($a=59.8$ with $r=0.92$ for 8 compounds, excluding $X=\text{OCH}_3$ and $m\text{-CH}_3$). Comparison of the two a values indicate that m reflects relatively large changes in the stability of the localized cationic charge for compounds 1-5 in Table 2 compared to that for compounds 6-15 in Table 3. This is because the carbocations of 3-5 are considerably destabilized, *i.e.*, have high ΔH° , due to a strong electron-withdrawing α -substituent, CF_3 ,^{3,11} in contrast to an electron-donating α -substituent present in compounds 6-15 which will

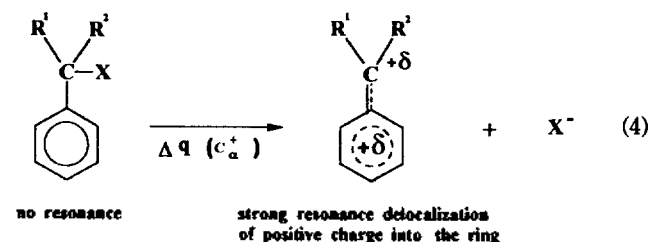
Table 4. The cross-interaction constants Θ for compounds 1-4

Compound	Θ	r^a	n^b
1	-0.08	0.996	15
2	-0.15	0.998	7
3	-0.45	0.990	7
4	-0.13	0.992	8

^aCorrelation coefficient. ^bNumber of data used

stabilize the localized cationic charge leading to lower ΔH° values.^{2a}

On the other hand, the parameter h is related approximately to $\Delta q(\text{C}_\alpha^+)$, $\delta(-\Delta q) = \beta \cdot \delta h$ a smaller positive or a larger negative value of which reflects a greater resonance delocalization of positive charge, eq. (4). For the compounds



1-5, the value of β was 3.4 with $r=0.82$, a rather poor correlation. But if we exclude the benzhydryl compound 5, which has two rings to delocalize positive charge in contrast to one for others 1-4, we get a plot in Figure 2 with $\beta=2.3$ and $r=0.92$, a more satisfactory correlation. For the compounds in Table 3, the resonance delocalization effect ($\Delta q(\text{C}_\alpha^+)$) was found to correlate with h in separate groups with the same R^1 and R^2 groups. There was no general correlation between $\Delta q(\text{C}_\alpha^+)$ and h for all the compounds including all different series of R^1 and R^2 . Moreover, due to electron donating nature of the two α -substituents, R^1 and R^2 , resonance delocalization of cationic charge into the ring was relatively small so that very little differences in Δq values were obtained. This could be a reason for the irregular correlation between Δq and h for the compounds in Table 3. However, albeit there is no precise correlation, there is a general trend of low Δq for high h .

We can conclude that the scale Y reflects the solvent ionizing or stabilizing power for a localized carbocation whereas the scale I reflects the solvent stabilizing power for a resonance delocalized cationic charge into a benzene ring. Because a large destabilizing α -substituent like $\text{R}=\text{CF}_3$ results in a strong localization of cationic charge leading to a strong destabilization of the carbocation with a large ΔH° value,¹¹ the m value is small. However such an α -substituent causes a strong resonance delocalization of the cationic charge into the ring^{2a,3,11,12} so that h is relatively high. This shows that the two values m and h are complementary, *i.e.*, if one is low (e.g. m) the other (h) is high. This can be attributed to the opposite signs of Y and I found in Table 1; a solvent which stabilizes the localized charge, $\delta Y > 0$, will have destabilizing effect on the resonance delocalized charge, $\delta I < 0$, or have much weaker stabilizing effect on the delocalized charge $\delta I \cong 0$. The fact that the two solvent scales, Y and

I, have opposite effects is reflected in a negative cross-interaction coefficient Θ ,¹³ defined by eqs 5.

$$\log\left(\frac{k}{k_0}\right) = mY + hI + \Theta \cdot YI \quad (5a)$$

$$\Theta = \frac{\partial m}{\partial I} = -\frac{\partial h}{\partial Y} \quad (<0) \quad (5b)$$

We have subjected the solvolysis rate data to multiple regression using eq. (5a) for compounds 1-4 and found the negative Θ values listed in Table 4. The negative Θ value reflects that a solvent which stabilizes the delocalized charge ($\delta I > 0$) reduces the sensitivity of Y on the localized charge ($\delta Y < 0$), and conversely a solvent which is strongly ionizing for the localized charge ($\delta Y > 0$), reduces the sensitivity of the delocalized charge to the scale I ($\delta h < 0$).

In view of the distinctly different effects of solvent ionizing power on the localized and delocalized cationic charges, correlation of solvolysis rates with two different solvent scales, Y for a localized charge and I for a delocalized charge, is not only required but also justified. Any attempt to correlate rates of solvolysis with one scale, e.g. with Y alone, will introduce large deviations for the substrate in which resonance delocalization of positive charge into the ring is possible.^{10,14}

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