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Variation of Coplanarity between Aryl Ring and Cationic Center at Transition State. Agreement of Results of Solvolytic Study with *ab initio* Calculations

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Abstract: *Ab initio calculations indicated in 2-aryl-3,3-dimethyl-2-butyl cations the aryl ring and the cationic center were not in the same plane, and the coplanarity would be improved by introducing an electron-donating substituent, in agreement with results of previous study of solvolysis. The heats of isodesmic reaction (Eq. 3) showed linear correlation with gas phase basicities and with logarithms of solvolytic rate constants.*
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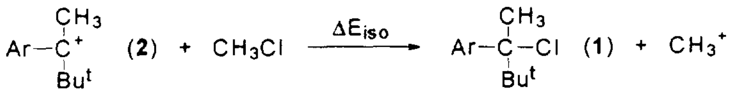
Solvolyses of 2-aryl-3,3-dimethyl-2-butyl chlorides (**1**) have drawn much attention of recent studies.[1,2] The substituent effect on the rates in 80% acetone[2] and on the gas-phase basicities of α-t-butylstyrenes[3] were found to correlate with the Yukawa-Tsuno equation (*Eq. 1*),[4] and to give similar r values. Correlation analysis of solvolytic reactivities of **1** with Y_{BnCl}[5] scales using Grunwald-Winstein equation (*Eq. 2*)[6] suggested small deviation of the cationic transition state from the condition of effective delocalization to the aryl ring in the case of 2-phenyl compound (**1f**), but no such deviation for those containing electron-donating group, such as 2-(4-methylphenyl) derivatives (**1d**).[1] Now we would like to report the results of *ab initio* calculations which indicated

$$\log(k/k_o) = \rho[\sigma^o + r(\sigma^+ - \sigma^o)] \qquad (1)$$

$$\log(k/k_o) = mY_{BnCl} \qquad (2)$$

linear correlation between the heats of isodesmic reactions (*Eq. 3*) with gas phase basicities and with logarithms of solvolytic rate constants. The variation of the coplanarity for 2-aryl-2,3-dimethyl-2-butyl cations with substituents was in agreement with the results of previous solvolytic study.[1]

The geometries of **1a**-**1k** and the corresponding cations were optimized within the Hartree-



$$\mathrm{Ar{-}\overset{CH_3}{\underset{Bu^t}{C^+}}}\ \mathbf{(2)} + \mathrm{CH_3Cl} \xrightarrow{\Delta E_{iso}} \mathrm{Ar{-}\overset{CH_3}{\underset{Bu^t}{C}}{-}Cl}\ \mathbf{(1)} + \mathrm{CH_3^+} \qquad (3)$$

Ar = 4-$CH_3OC_6H_4$	**1a,2a**;	Ar = 3-$CH_3C_6H_4$	**1e,2e**;	Ar = 3-FC_6H_4	**1i,2i**
= 4-$CH_3SC_6H_4$	**1b,2b**;	= C_6H_5	**1f,2f**;	= 3-$CF_3C_6H_4$	**1j,2j**
= 4-CH_3O-3-ClC_6H_3	**1c,2c**;	= 4-FC_6H_4	**1g,2g**;	= 4-$CF_3C_6H_4$	**1k,2k**
= 4-$CH_3C_6H_4$	**1d,2d**;	= 3-ClC_6H_4	**1h,2h**		

Fock approximation using a 3-21G$^{(*)}$ or a larger 6-31G* basis set. The heats of isodesmic reactions (*Eq. 3*), ΔE_{iso}, were calculated at the RHF/6-31G*//3-21G$^{(*)}$ level.[7] All calculations were performed using SPARTAN version 4.0 or GAUSSIAN-92 program. The results of calculation, the literature data of solvolytic rate constants in 80% acetone at 45°C (k)[2] and the gas phase basicity (ΔGB)[3] were listed in **Table 1**. Figure 1 showed linear correlations between ΔE_{iso} and log k (R = 0.987)[8] and between ΔE_{iso} and ΔGB (R = 0.980).[9] The linearity would be even better if the data point for 4-methylthiophenyl derivative was omitted.[8,9]

Such linear correlations suggested that the applicability of the calculated properties for gaseous cations to the cationic transition state of solution chemistry for the tertiary benzylic system, although inconsistency between theoretical (semiempirical AM1) calculations and experimental results had been observed in the case of secondary α-*t*-butylbenzylic system.[10,11] On the other hand, the parameter r in the Yukawa-Tsuno equation (*Eq. 1*) had been considered to be related to sterically

Table 1. Heats of isodesmic reactions, solvolytic rate constants, and gas phase basicities

Substrate	ΔE_{iso}, kcal/mole[a]	k, /s[b]	ΔGB, kcal/mole[c]
1a	95.60	2.927×10^{-2}	8.6
1b	90.13	2.242×10^{-3}	8.1
1c	90.14	5.942×10^{-4}	5.5
1d	89.51	1.969×10^{-4}	3.6
1e	86.73	2.332×10^{-5}	2.0
1f	84.81	1.323×10^{-5}	0.0
1g	84.02	1.859×10^{-5}	-0.7
1h	79.33	3.931×10^{-7}	-4.3
1i	79.23	6.016×10^{-7}	-4.7
1j	78.22	9.720×10^{-8}	-6.0
1k	76.38	8.376×10^{-8}	-7.2

[a] The present study. [b] Ref. 2. [c] Ref. 3.

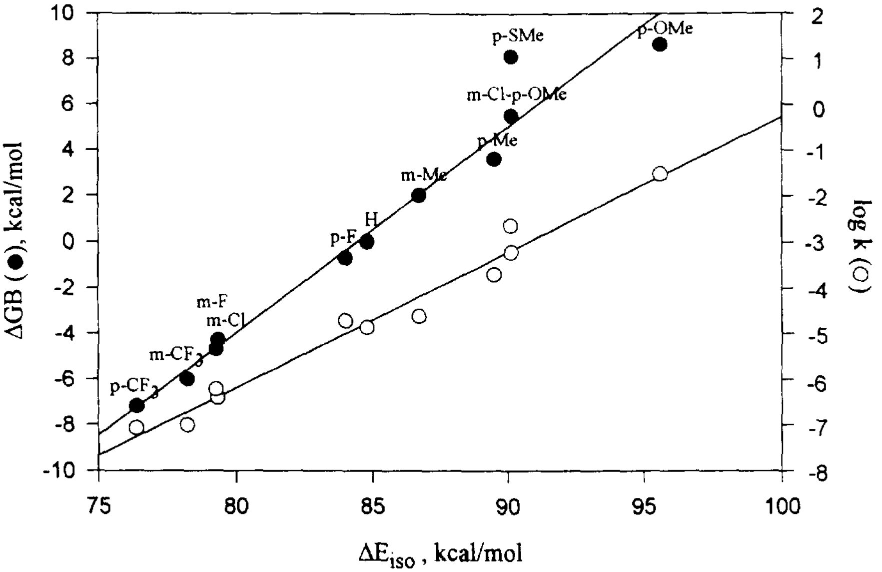


Figure 1. Correlations of log k and ΔGB for **1a** -- **1k** against ΔE$_{iso}$.

twisting out of planarity of the α-benzene π system in carbocations by an equation, *Eq. 4*,[3,12,13] and a twisted angle of 24.5° was derived for the solvolysis of 1.[2] Therefore, the optimized structure of

$$r/r_{max} = \cos^2\theta \tag{4}$$

carbocations **2** were calculated at both the RHF/3-21G$^{(*)}$ and the RHF/6-31G* levels. The results were given in **Table 2**.

It is interesting to note that the twisted angle is not constant, but varies with the nature of the substituent. Although the calculated angle between the plane of cationic center and the benzene ring,

Table 2. Calculated angles of twisting out of coplanarity between the aryl ring and the sp^2 plane of carbocations.

Carbocation	twisted angle, degree from RHF/3-21G$^{(*)}$ (from RHF/6-31G*)	Carbocation	twisted angle, degree from RHF/3-21$^{(*)}$ (from RHF/6-31*)
2a	14.0 (14.5)	**2g**	21.7
2b	16.2	**2h**	25.7
2d	20.3	**2i**	26.4
2e	24.4	**2j**	25.3
2f	24.3 (23.8)	**2k**	28.7(26.5)

24.3° using a 3-21G$^{(*)}$ basis set and 23.8° using a 6-31G* basis set for **2f**, was in agreement with literature value, 24° by calculation and 24.5° from rate data for the parent system,[2] a smaller angle with the more electron-donating substituent was realized. For example, the angle was reduced to 14.0° or 14.5° in the case of **2a** (with 4-methoxy group).[14] In other words, despite the surprisingly good agreement found in the unsubstituted system, the variation of the twisted angle in the carbocations **2** cast doubt on the soundness of the proposed *Eq. 4*. It is then likely to be a result of coincidence. Moreover, the smaller angle of twisting indicated better charge delocalization within the benzylic moiety. In the previous study on the solvolysis of 2-chloro-3,3-dimethyl-2-phenylbutane (**1f**) and the 2-(4-methylphenyl) analogue (**1d**), we observed a small deviation from linear relationship in the log k - mY_{BnCl} regression ananlysis for **1f** but no deviation for **1d**.[1] Steric inhibition of resonance and thus the effective delocalization in the solvolytic transition state of **1d** due to the presence of α-*t*-butyl group, and the suppression of such a destablization by the 4-methyl substituent were suggested to account for the observation.[1] The present result of *ab initio* calculation is in line with the solvolysis outcome, which reveals the advantage of using Y_{BnX} scale in the correlation analysis of solvent effects on solvolytic reactivities. Further work in this aspect is in progress.

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