The study on the resonance demand in benzylic solvolyses

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IN BENZYLIC SOLVOLYSES

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Contents

The linear free energy relationship is an extremely useful tool in the exploration of reaction mechanisms in a wide variety of situations.[1]   In particular the Yukawa-Tsuno (LArSR) Eq. (1-1)[2] is one of the most useful tool to predict characters of transition state whose reaction center is affected by benzene π-system, and was widely applied to a lot of substrates with success.[3-4]

$$\log (k/k_0) = \rho (\sigma^0 + r \, \Delta\bar{\sigma}_R^+). \qquad\qquad (1\text{-}1)$$

This equation is characterized by empirically obtained resonance demand parameter r which indicates the degree of resonance interaction between the reaction center and benzene π-system.   The r value has been found to change widely with the reactions; r = 1.00 for solvolysis of α-cumyl chloride by definition, r = 1.15 for the secondary α-methylbenzyl system,[3d] and r = 1.30 for the primary benzyl system.[3c]   In addition, r values of 1.39 and 1.51 were found for highly deactivated carbocationic solvolyses of α-methyl-α-trifluoromethylbenzyl   system[3b]   and α-trifluoromethylbenzyl system,[3a] respectively.   The r value increases in proportion to instability of cation.   Thus the r value should be a measure of the resonance demand reflecting the stability of cationic transition state and provides very important information to evaluate the nature of the transition state.

Substituent effect on the solvolysis of α-methylbenzyl chlorides gave the r value of 1.15 which is referred to the higher

resonance demand of this secondary system than the σ^+ reference system. However, the incursion of solvent participation is suggested for this borderline solvolysis.[5] If this is the case, solvent participation might become important as the substituent becomes more electron attracting and give a monotonically concave σ^+ correlation. It has thus often been claimed in the literature that the higher r value observed in such a case will be meaningless.[6] The solvolysis of α-(t-butyl)benzyl tosylates where there is little possibility of solvent participation can be an alternative reference for secondary S_N1 solvolysis system. Nevertheless, this system may not generate a coplanar cation with benzene π-system in the transition state due to bulkiness of the t-Bu group at α position.[3e] The intrinsic resonance demand of secondary benzylic systems has not been determined yet. In order to prove the origin of the r values relating to the inherent stabilities of a series of the benzylic cation, the r value which reflects the fully conjugated secondary system is needed. Thus the substituent effect on the solvolysis of 2,2-dimethylindan-1-yl chlorides,[3g] where the vacant p-orbital developed at the benzylic position is fixed in preferred conformation to overlap with the benzene π-system, was analyzed by LArSR Eq. (1-1). The neopentyl skeleton of this system will solvolyze via S_N1 mechanism. Moreover, this system will attain a full resonance stabilization in the transition state because of the fused five membered ring, and then provide an standard r value anticipated for the inherent secondary benzylic solvolysis system.

Results of substituent effect analysis of 2,2-dimethylindan-1-yl chloride at 25°C are shown below.

$$\log (k/k_0) = -6.121\,\sigma^+$$
$$(n=11, \ R=0.999, \ SD=\pm0.16) \qquad\qquad (1-2)$$

$$\log (k/k_0) = -5.80\,(\sigma^0 + 1.11\Delta\bar{\sigma}_R^+)$$
$$(n=11, \ R=0.999, \ SD=\pm0.12) \qquad\qquad (1-3)$$

The LArSR plot was shown in Fig. 1-1. Comparison of $\rho^+\sigma^+$ and LArSR correlations clearly shows that the LArSR equation can describe the present reaction more precisely than the Brown $\rho^+\sigma^+$ treatment; the SD value are 1.5 times larger than those of the LArSR correlation.

Both the large negative ρ value and the enhanced r value larger than unity suggest that this solvolysis proceeds through a highly charged transition state of a rate-determing k_C-ionization leading to a carbocation intermediate. Furthermore this linear relationship should be free of either nucleophilic solvent assistance or neighboring methyl participation. Thus the r value of 1.11 may be referred to as the reference value characteristic of open secondary benzylic carbenium ion which is essentially coplanar and capable of exerting essentially maximum conjugative stabilization interaction with the benzene π system.

It has been noted that most systems favored by the LArSR treatment are secondary substrates in nucleophilic solvents and such systems may also be subject to nucleophilic solvent
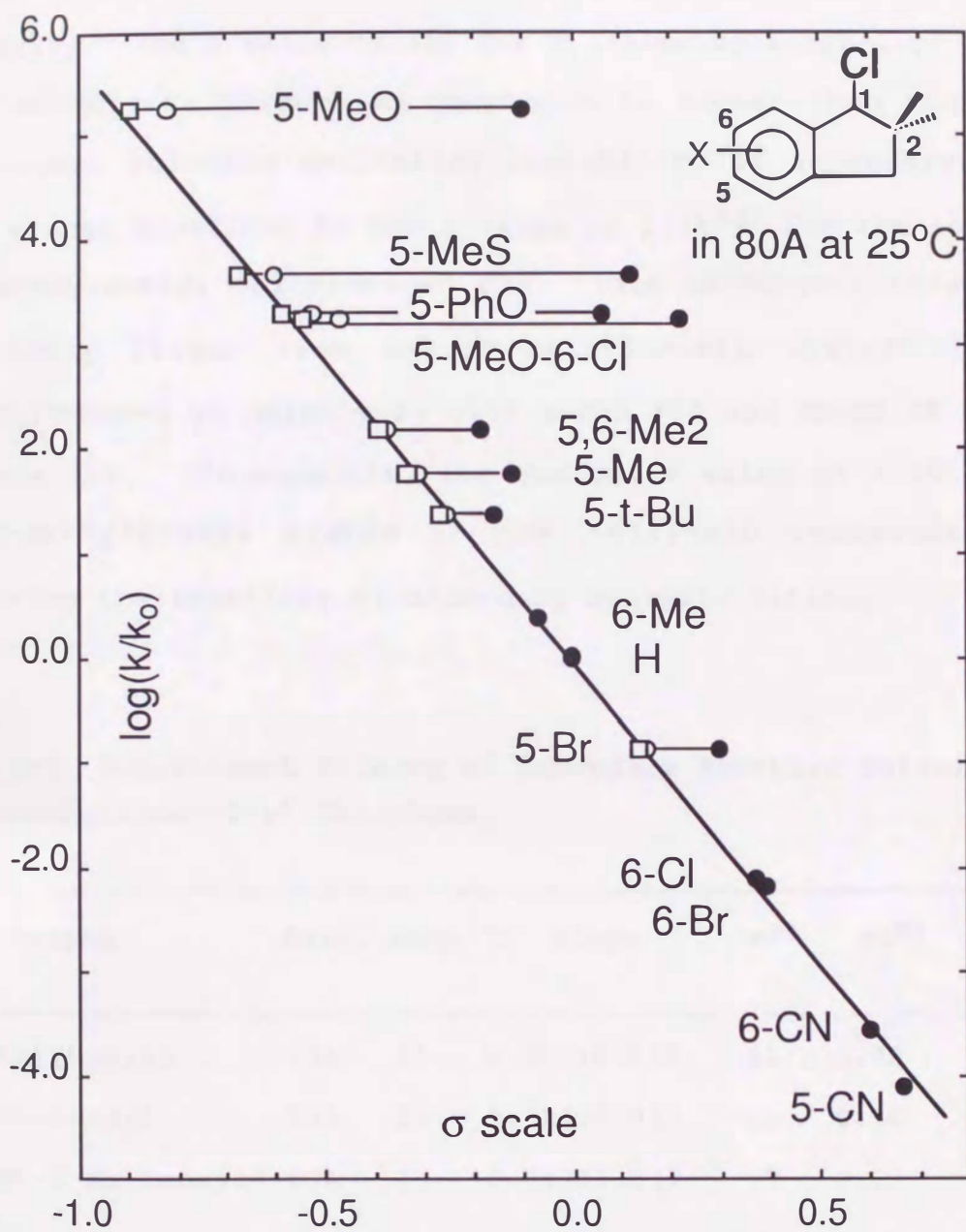
Fig. 1-1. LArSR plot for the solvolysis of
2,2-dimethylindan-1-yl chlorides in 80A at
25°C; open circle σ^+, closed σ^0, and squares $\bar{\sigma}$
for r=1.11.

participation,[5] and that the high r value of 1.15 for α-methylbenzyl chloride is an artifact arising from such mechanistic complexity. The r value (1.11) for 2,2-dimethylindan-1-yl chloride which solvolyzes through k_C mechanism is higher than that (1.00) for α-cumyl chloride reflecting instability of secondary system. It is almost identical to the r value of 1.15[3d] for the solvolysis of α-methylbenzyl chlorides in 80A. This solvolysis indeed shows a strictly linear free energy relationship against the 2,2-dimethylindan-1-yl solvolysis with a R=0.994 and SD=±0.08 as shown in Table 1-1. Consequently, the exalted r value of 1.15 obtained for α-methylbenzyl system is the intrinsic resonance demand reflecting the stability of secondary benzylic cations.

Table 1-1. Substituent Effects of Secondary Benzylic Solvolyses vs. 2,2-Dimethylindan-1-yl Chlorides.

System	Solv.	temp/°C	Slope	n[a]	SD[b]	R[c]
α-methylbenzyl	80A	45	0.907±0.010	11	0.08	0.9994
α-t-Bu-benzyl	80A	25	0.929±0.011	12	0.10	0.9993
α-t-Bu-2-Me-benzyl	80A	25	0.917±0.037	7	0.22	0.9960
α-t-Bu-2,2-Me$_2$-benzyl	80A	25	0.814±0.024	4	0.09	0.9992

a) Number of substituents involved. b) Standard deviation. c) Correlation coefficient.

The r value should be related most closely to the degree of π-overlapping between the aryl-π-orbital and benzylic-p-orbital in the incipient carbocation as shown in Fig. 1-2. In the case where the dihedral angle made by benzylic p-orbital and benzene π-system is 0°, the system acquires a full resonance stabilization to provide the maximum r value. Then for the congested system where both p-orbitals can not maintain coplanarity owing to steric hindrance, the efficiency of resonance effect decreases compared with that of the coplanar system, resulting in the decrease of r value. Therefore the examination of the dependence of r value upon the dihedral angle of both p-orbitals will provide the convincing evidence for the real origin of the empirical resonance demand parameter r in the LArSR Eq. (1-1).
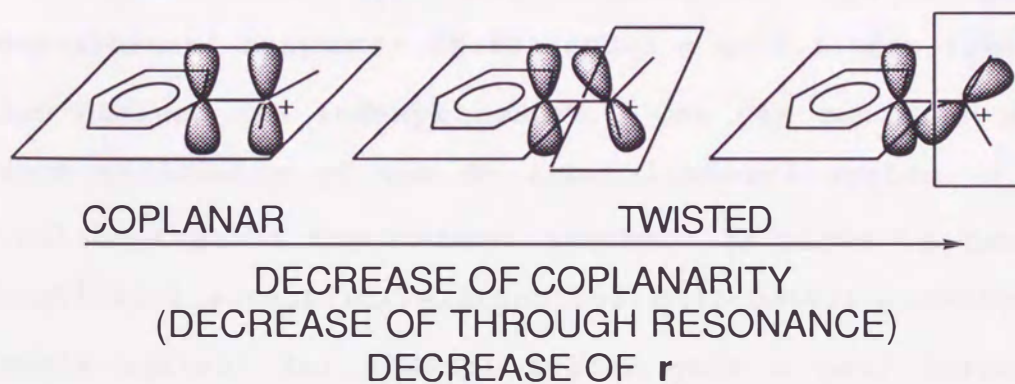

COPLANAR   TWISTED

DECREASE OF COPLANARITY
(DECREASE OF THROUGH RESONANCE)
DECREASE OF **r**

Fig. 1-2. Coplanarity and the resonance effect.

From this point of view, the benzylic k_C solvolyses where the incipient carbenium center p-orbitals are sterically twisted out of the coplanarity with the aryl ring have been studied. In the substituent effect on the solvolyses of secondary α-(t-butyl)benzyl tosylates[3e] and their o-methyl analogues, o-methyl and o,o-dimethyl substituted series,[3f] r value of 1.09, 1.01, and 1.02 were reported by using Eq. (1-1). No significant loss of resonance for these systems compared with coplanar 2,2-dimethyl-1-indanyl system has been observed. Increased steric congestion around the carbenium ion center does not appear to be effective enough to cause a significant loss of the coplanarity in the transition state.

The comparison of substituent effects of secondary congested systems with that of 2,2-dimethylindan-1-yl chlorides are summarized in Table 1-2. The direct comparison of logarithms of rate constants for two systems will provide the information on the relative degree of the resonance interaction. The solvolysis of α-(t-butyl)benzyl tosylates in 80A shows a good linear free energy relation against the indanyl system. One can conclude that the resonance efficiency of the α-(t-butyl)benzyl system is almost identical to that of the indanyl system. As shown in Table 1-2, the substituent effect correlation for α-(t-butyl)-2-methylbenzyl solvolysis against for indanyl system gave a poor correlation, suggesting the loss of resonance in the transition state of α-(t-butyl)-2-methylbenzyl system. The same tendency can be seen for α-(t-butyl)-2,2-dimethylbenzyl system. Consequently, it can be

said that qualitative loss of resonance interaction for these systems exist.

The r value of 1.11 is regarded as a reference r_{max} value, i.e., an intrinsic r value characteristic of the coplanar sec. benzylic carbocation. The efficiency of resonance interaction can be accounted for in terms of $\cos^2\theta$ where θ is the dihedral angle of twisting out of coplanarity.[7] The ratio of the r value for a given solvolysis relative to the r_{max} may reflect the efficiency of the resonance effect of that system and the r value for a twisted benzylic system can be given by Eq. (1-4),

$$r = r_{max} \cos^2\theta. \hspace{3cm} (1-4)$$

The decrease of r values of o-methyl and o,o-dimethyl α-(t-butyl)benzyl systems from r_{max} of 1.11 should be attributed to a loss of the resonance interaction between the carbocation center and the benzene π-system in the solvolysis transition state caused by the steric hindrance. Thus the torsional angle θ_{obs} at the transition state can be calculated to be 8° for α-(t-butyl)benzyl, and 17° for both o-methyl and o,o-dimethyl solvolysis based on Eq. (1-4). Torsional angles of these congested secondary systems increase in proportion to the bulkiness around the reaction center, although these twisting angles are not very serious compared with those of tertiary systems reported.[3h] The stabilization by the extended π-delocalization should be the most predominant driving force to promote ionization in the ordinary benzylic solvolysis. The transition state should be able to attain the maximum

stabilization to overcome the large steric strain required for the most preferred conformation. For tertiary solvolysis systems, r=0.91 for α-t-butyl-α-methylbenzyl chlorides and r=0.26 for α,α-di-t-butylbenzyl OPNBs were observed against r=1.00 of α-cumyl chlorides which is considered to be coplanar. Torsional angles of 17° α-t-butyl-α-methylbenzyl and 59° for α,α-di-t-butylbenzyl systems were estimated based on Eq. (1-4). Larger steric effect can be seen for tertiary systems than that for secondary systems.

Substituent effects on the gas-phase stabilities of benzylic cations can be described in terms of the LArSR equation (1-5) excellently,[2] similarly as seen in solvolysis.

$$\delta\Delta G^0 = \rho \ (\ \sigma^0 + r\Delta\overline{\sigma}_R^+ \ ) \tag{1-5}$$

where r is the parameter measuring the degree of resonance interaction between benzene π-system and cationic center. In continuous studies on gas phase benzylic cations in this laboratory, the r value 1.00 for α-cumyl[4f] and α-ethyl-α-methylbenzyl,[4e] 1.14 for α-phenylethyl,[4d] 1.29 for benzyl,[4c] 1.41 for α-methyl-α-trifluoromethylbenzyl,[4b] and 1.54 for α-trifluoromethylbenzyl[4a] cations are obtained by Eq. (1-5). It has been demonstrated that the r values of substituent effects on the gas phase stabilities are in complete agreement with those in the corresponding solvolyses for these systems.[4a] This result leads to the

important concept for k_c benzylic solvolysis; the structure of transition state should be similar to that of cation. However this phenomenon has not been confirmed for both secondary and tertiary hindered resonance systems. In order to confirm the identity of r values between in solution and in gas phase, substituent effect analysis on gas phase stabilities for congested system must be done. Intrinsic stability of cation in the gas phase can be easily measured using ICR (ion cyclotron resonance) method. The substituent effect on gas phase stabilities concerning the r value for twisted benzylic carbocation system has not yet been examined. The substituent effect on gas phase stabilities of α-t-butyl-α-methylbenzyl cations (**14**) is chosen for this purpose as a sterically hindered carbocation. The twisted structure of the cation **14** may be produced by the bulkiness of two α-groups, and therefore a reduced r value may be expected similarly for this solvolysis.

The gas phase stabilities of α-t-butyl-α-methylbenzyl cations (**14**) were determined by the equilibrium constants for the proton transfer reaction of the corresponding 2-aryl-3,3-dimethyl-1-butene with suitable reference cations of known stability by means of a pulsed ion cyclotron resonance mass spectrometer at 343K as described in detail in experimental chapter. As shown in Fig. 1-3, an application of the LArSR Eq. (1-5) to **14** provides an r of
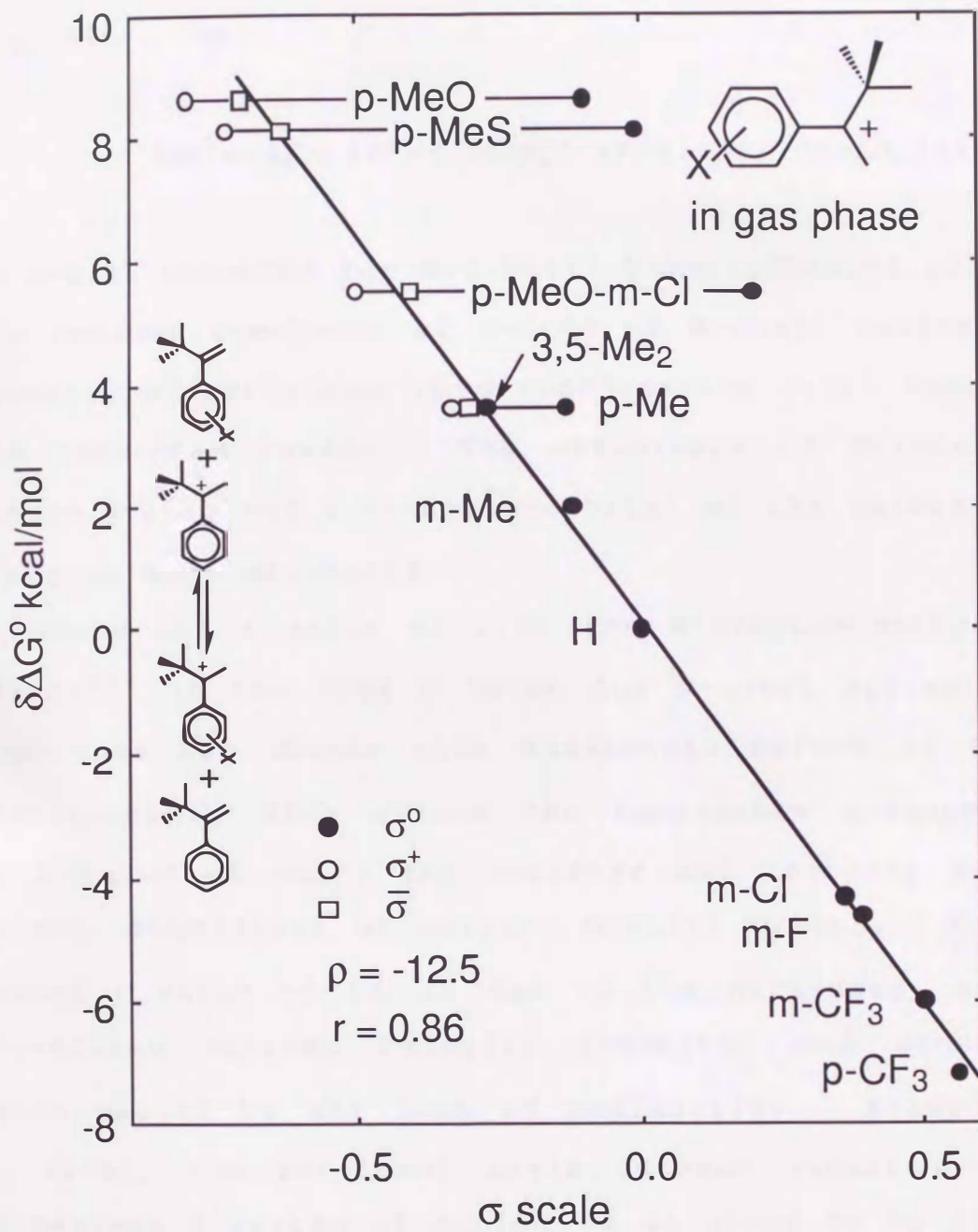
Fig. 1-3. LArSR plot for the gas phase
stabilities of α-t-butyl-α-methylbenzyl cations.

0.86 lower than the unity for α-cumyl cation, whereas a ρ of -12.5 is comparable to that for α-cumyl cation (-13.0).[4f]

$$\delta\Delta G^0 = -12.5 \, (\sigma^0 + 0.86\Delta\bar{\sigma}_R^+) \quad (R=0.999, \ SD=\pm 0.28) \quad (1-6)$$

The r=0.86 obtained for α-t-butyl-α-methylbenzyl cation is only reduced one-tenth of r=1.00 of α-cumyl cation. The resonance effect close to σ^+-conjugation still remains in this congested cation. The efficiency of π-interaction between π-ring and a vacant p-orbital of the carbenium ion is not so much decreased.

Since the r value of 1.01 for α-ethyl-α-methylbenzyl cations[4e] is the same r value for α-cumyl system, the r value does not change with electronic effect of α-alkyl substituents. This allows the reasonable assumption of the r value of unity for coplanar and tertiary benzylic cations, regardless of varying α-alkyl groups. Thus the reduced r value of **14** is due to the decreased resonance interaction between benzylic p-orbital and benzene π-system caused by the loss of coplanarity. According to Eq. (1-4), the torsional angle between vacant p-orbital and benzene π-system of cation **14** is given to be 22°. Ab initio calculation supports this result; optimized structure of carbocation **14** using a 6-31G* basis set with Hartree-Fock level gives the dihedral angle between vacant

benzylic p-orbital and benzene π-system 24° as described later.

The gas phase stability of unsubstituted α-t-butyl-α-methylbenzyl cation is found to be lower by 1.1 kcal mol^{-1} than the corresponding α-cumyl cation; this may be attributed to polar effect or increased internal strain due to replacing the α-methyl group by bulky t-butyl group, or the loss of resonance stabilization by reduced overlapping of both p and π-orbitals due to congestion bulkiness around the cation center in **14**. The LArSR r values were plotted against relative stabilities of parent substrate (ring substituent = H) for α-substituted benzylic cations in Fig. 1-4. Only α-tert-butyl-α-methylbenzyl system (**14**) shows a different behavior; the parent cation is more destabilized than α-cumyl system although **14** has reduced r value. The plot for **14** deviates clearly from the line which is linearly correlated with plots of other systems. Consequently good relation between the r value and the intrinsic stability discriminates hindered resonance system such as **14**. In turn, it is concluded that this linear relationship is generally retained for benzylic system as far as the benzene π-orbital and a vacant p-orbital lie on the same plane. That is, the intrinsic stability of the parent benzylic carbocation is a factor which govern the resonance demand.
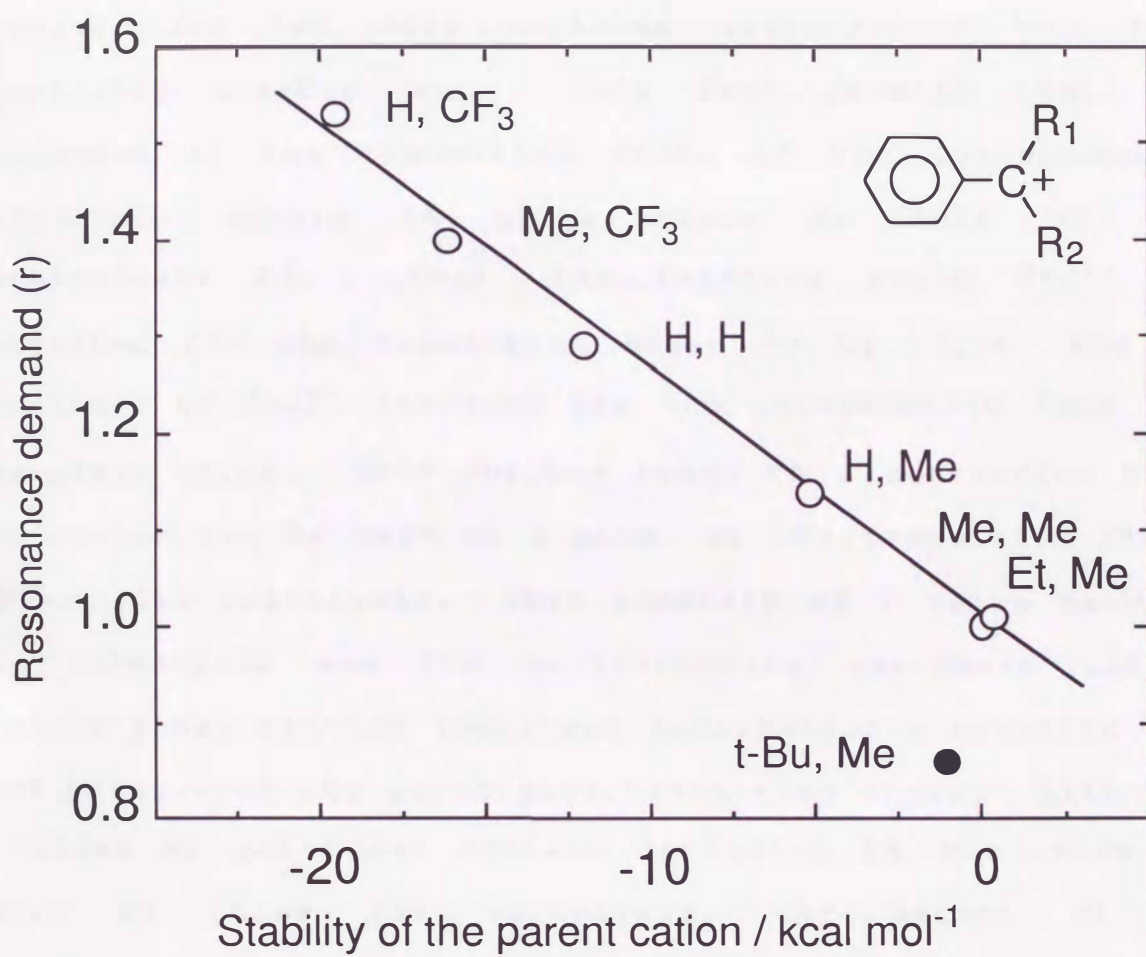
Fig. 1-4. Linear relationship between r value and stabilities of the unsubstituted member of each series. A closed circle denotes the twisted system.

The r value of 0.86 for gas-phase stabilities of carbocation **14** is in complete agreement with that of 0.91 obtained from the recent result of the solvolysis of α-t-butyl-α-methylbenzyl chlorides.[3i] The agreement of r values between solvolysis and gas phase stability has been observed for not only coplanar carbocations but also sterically twisted one. This fact reveals that the structure of the transition state of the corresponding solvolysis should be quite close to that of the intermediate **14**. Thus, the twisting angle $\theta=21°$ is estimated for the transition state by Eq. (1-4) and is identical to $\theta=22°$ assigned for the intermediate from the gas-phase value. This further leads to a conclusion that the cation can be used as a model of the transition state of benzylic solvolysis. This identity of r value between the solvolysis and the corresponding gas-phase cation stability may provide important information concerning the real picture of the solvolysis transition state. Although ρ values of gas phase cations including **14** are twice as large as those for solvolysis, the degree of π-delocalization of the charge into the aryl ring relative to the inductive/field stabilization will remain essentially the same in the gas phase as in solution. The solvation of cation lowers the response to substituent perturbation, essentially without the change in intramolecular charge-delocalization. Furthermore, the charge delocalization or structure in the S_N1 transition

state in the benzylic solvolysis should also be quite close to those of the carbocation intermediate, so that one can use the cation as a model of transition state of S_N1 solvolysis. This suggests that the benzylic cations are very important species to interpret the r value theoretically.

In organic chemistry, the "resonance theory" which is derived from valence bond theory is of course important concept to predict reactivity. This theory estimates changes of physical constants (stabilization energy, bond length, charge density, bond order, and so on) qualitatively, which is affected by resonance. Thus the existence of good correlation between the r values and physical quantities of benzylic cations which is calculated by molecular orbital theory provides the real origin of the r value.

From this point of view, the geometries of benzylic cations were optimized by ab initio MO methods with some kinds of basis sets. The ab initio LCAO-MO method[8] was used for the study of α-substituted benzyl cations. Structural formulas of calculated cations were shown in Fig. 1-5 (**1-10**) and Fig. 1-6 (**11-20**). The numbers of atom and the dihedral angle θ correspond to those in Fig. 1-7. All calculations were performed on the IBM RS/6000 computer with GAUSSIAN-92 suite of programs.[9] Geometries were optimized completely by the gradient procedure[10] at the C_1 symmetry. The closed-shell restricted Hartree-Fock level with STO-3G, 3-21G, and 6-31G* basis sets was applied to find stationary points on the potential energy surface (PES). At RHF/6-31G* level all optimized structures were checked by analysis of harmonic
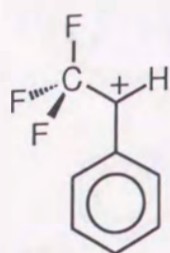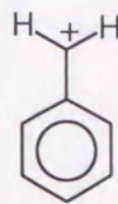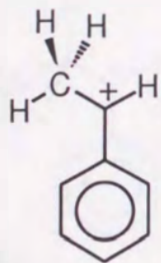
1a
α-trifluoro-
methylbenzyl
cation.

1b
α-trifluoro-
methylbenzyl
cation.
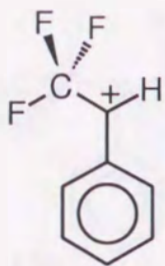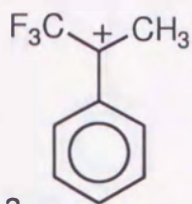
2
α-trifluoro-
methyl-α-
methylbenzyl
cation.

3
benzyl
cation.

4a
α-methyl-
benzyl cation.
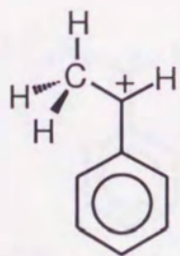
4b
α-methyl-
benzyl cation.
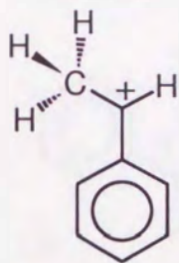
4c
α-methyl-
benzyl cation.
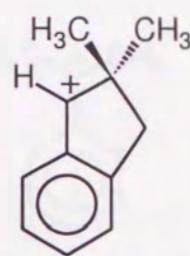
5
2,2-dimethyl-
1-indanyl
cation.
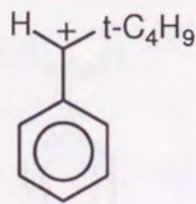
6
α-tert-butyl
benzyl cation.
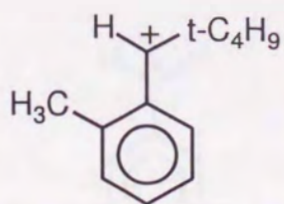
7
α-tert-butyl-
o-methyl
benzyl cation.
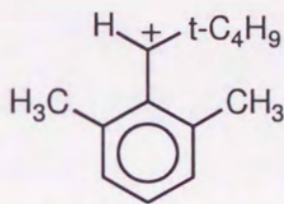
8
α-tert-butyl-
o,o-dimethyl
benzyl cation.
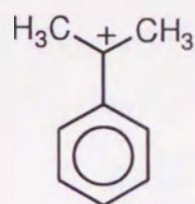
9
α,α-dimethyl-
benzyl cation.
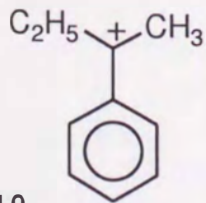
10
α-ethyl-
α-methyl
benzyl cation.
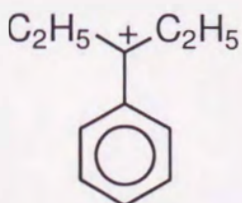
11
α,α-diethyl-
benzyl cation.
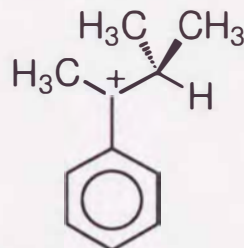
12a
α-isopropyl-
α-methylbenzyl
cation.
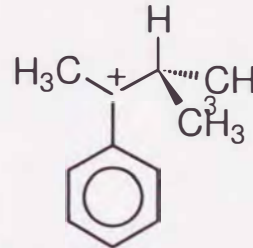
12b
α-isopropyl-
α-methylbenzyl
cation.

Fig. 1-5. Calculated benzylic cations (**1**-**12**).

13a
α,α-diiso-
propylbenzyl
cation.

13b
α,α-diiso-
propylbenzyl
cation.

13c
α,α-diiso-
propylbenzyl
cation.

14
α-tert-butyl-
α-methylbenzyl
cation.

15
α-tert-butyl-
α-isopropyl-
benzyl cation.

16
α,α-di-tert-
butylbenzyl
cation.

17
4-methyl-
benzobicyclo
[2.2.2]octen-
1-yl cation

18
α,α-dimethyl-
benzyl cation
(90° fixed).

19
α-methyl-
benzyl cation
(90° fixed).

20
benzyl cation
(90° fixed).
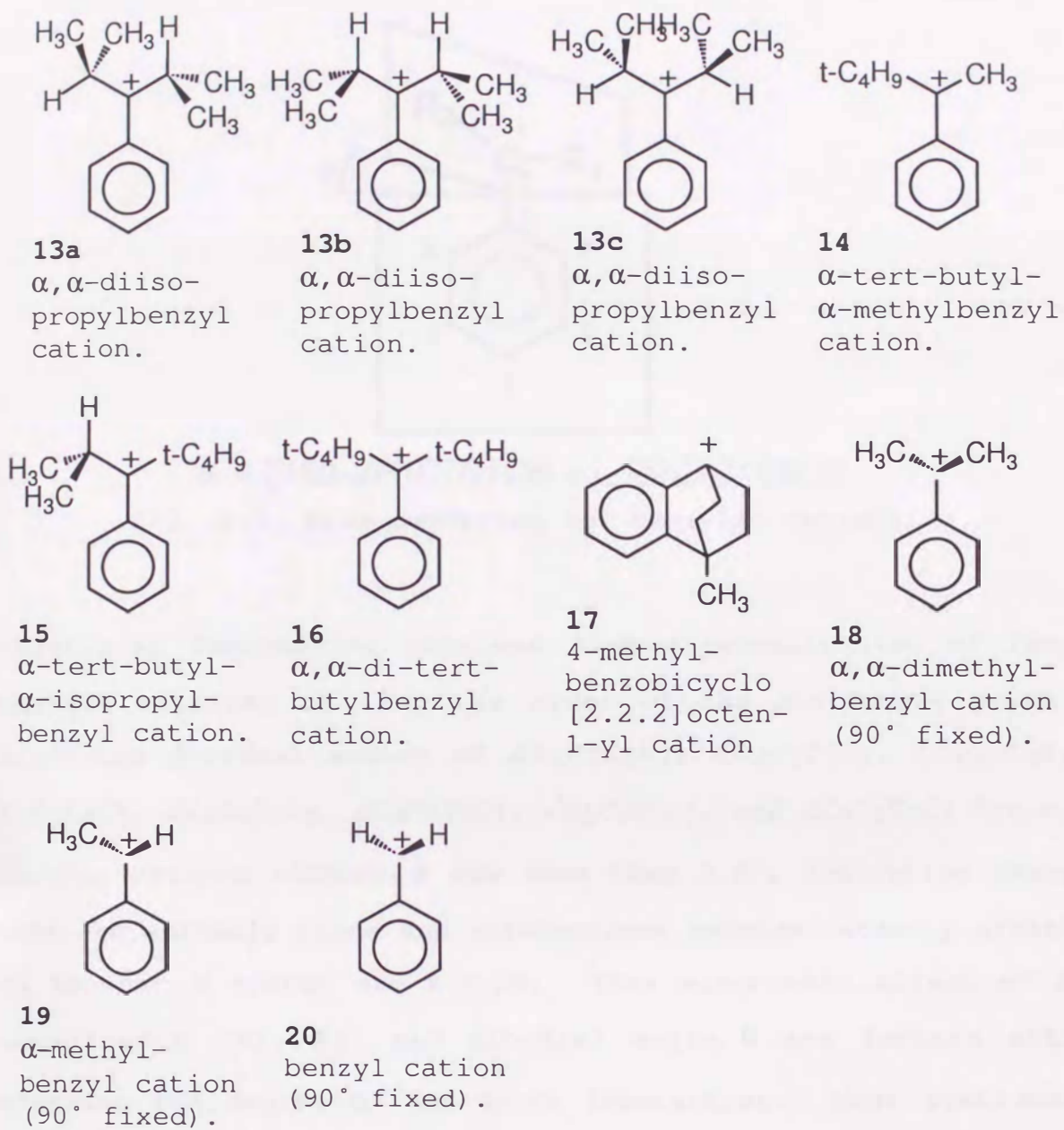
Fig. 1-6. Calculated benzylic cations (**13-20**).

-18-
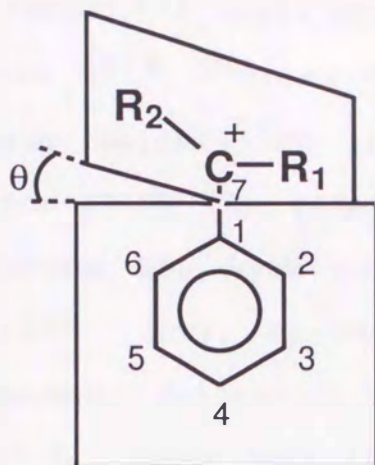
$$\theta = (|180 - \angle R1C7C1C6| + |\angle R2C7C1C6|)/2.$$

Fig. 1-7. Atom numbering for benzylic cations.

vibrational frequencies obtained from diagonalization of force constant matrices to find the order of the stationary points. Calculated dihedral angles of $\angle R_1C_7C_1R_2$, $\angle C_2C_1C_7C_6$, $\angle C_1C_2C_3C_4$, $\angle C_2C_3C_4C_5$, $\angle C_3C_4C_5C_6$, $\angle C_4C_5C_6C_1$, $\angle C_5C_6C_1C_2$, and $\angle C_6C_1C_2C_3$ for all benzylic cations without **8** are less than 3.0°, indicating phenyl rings are actually plane and interactions between vacant p orbital and benzene π system are π-type. Thus electronic effect of α-substituents (R_1, R_2) and dihedral angle θ are factors which determine the degree of resonance interaction. Most stationary conformations without **4b**, **4c**, **18**, **19**, and **20** have only positive vibrational frequencies so that these species are minimum structures at the RHF/6-31G* PES.

The energy difference between these 90° fixed cations (**18-20**) and corresponding coplanar cations can be approximated as the rotational barriers around C_1-C_7 axis. In practice the perpendicular conformation is energetically maximum in all the

-19-

rotamers for benzyl cation,[11] while steric effect may exists for the coplanar structure of **9** ($\theta=5°$). Moreover, the normal mode analysis in frequency calculation indicates that **18-20** are transition states concerning the rotation of C_1-C_7 axis. The barrier to the rotation has been used as a measure of the "resonance energy".[12] Thus, we can estimate the resonance energies for these species. Rotational barrier for each cation was summarized in Table 1-2. Basis sets and electron correlation do not affect the barriers seriously. At our final level (MP2/6-31G*//RHF/6-31G*) which does not include ZPE correlation, barriers (resonance energy) are 49.3 kcal/mol for benzyl cation, 33.8 kcal/mol for α-methylbenzyl cation, and 20.7 kcal/mol for α,α-dimethylbenzyl cation. Previously Houk et al. reported the rotational barrier of benzyl cation (45.4 kcal/mol) at HF/3-21G level which agrees with this result. One methyl substitution to the benzylic position lowers the rotational barrier by 15 kcal/mol, which can be attributed to the resonance interaction. The primary benzyl cation (**3**) is required larger degree of conjugation in order to stabilize the total energy. On the other hand, tertiary α,α-dimethylbenzyl cation (**9**) is stabilized by the inductive effect of α-methyl group, so that the requirement of resonance stabilization is small. It is worthy to note that the r value in Yukawa-Tsuno equation runs parallel with rotational barriers of corresponding benzylic cations. This is instructive, because the r value can be connected to the resonance energy for these structurally similar species.

Table 1-2. Rotational barrier[a] (kcal mol^{-1}) of benzylic cation.

species	RHF/ STO-3G	RHF/ 3-21G	RHF/ 6-31G*	MP2/6-31G*// RHF/6-31G*[b]
benzyl cation				
	47.086	45.390	45.887	49.302
α-methylbenzyl cation				
	34.548	31.840	32.440	33.771
α,α-dimethylbenzyl cation				
	22.011	19.045	19.685	20.740

a) Rotational barriers were estimated by the total energy difference between coplanar and 90° fixed structure; E(**18**)-E(**9**) for α,α-dimethylbenzyl cation, E(**19**)-E(**4a**) for α-methylbenzyl cation, and E(**20**)-E(**3**) for benzyl cation. b) ZPE are not included.

For benzylic cations, bond length of C_1-C_7 and average bond length of C_1-C_2 and C_6-C_1, C_2-C_3 and C_5-C_6, and C_3-C_4 and C_4-C_5 should be affected by the degree of resonance interaction between benzylic p orbital and benzene π system. The "resonance theory" predict the elongation of C_1-C_2 and C_3-C_4, and shortening of C_1-C_7 and C_2-C_3 as increases the conjugation. As shown in Fig. 1-8, these bond lengths at RHF/6-31G* are plotted against r values. For cations **7** and **8**, C_1-C_7 and C_1-C_2 are correlated poorly. This may be attributed to the steric interaction between o-Me and α-alkyl group. In cases of cations **5** and **17**, C_1-C_7 fail below the

Fig. 1-8. Bond length vs r values in Yukawa-Tsuno
equation for benzylic cations. Numbers correspond
those for species in Figures 1-5 and 1-6.

correlated line due to the steric strain of the ring structure. Although C_1–C_7 of 90° fixed cations (**18**, **19**, and **20**) also failed slightly, satisfactory correlation exists as a whole. This plot is not basis set dependent.

When r=0, bond length of C_1–C_7 comes to 1.52Å which is almost same as normal carbon–carbon single bond length (1.54Å in ethane). The C_1–C_7 become shorter in proportion to increase of the r value. When r=1.51 (**1**), C_1–C_7 is 1.35Å which is almost same as normal carbon–carbon double bond length (1.33Å in ethylene). When r=0, bond lengths of C_1–C_2, C_2–C_3, and C_3–C_4 are 1.39Å which are the same as carbon–carbon bond length of benzene. As the r value increases, C_1–C_2 and C_3–C_4 increase but C_2–C_3 decrease. C_1–C_2 varies twice as large as C_3–C_4. These tendency agree with the prediction of the resonance theory. Contributions of five resonance structures shown in Fig. 1-9 elucidate partial alternation of single and double bonds in the benzene ring. Thus this plot is evidence that the r value is the parameter indicating the degree of the resonance interaction.
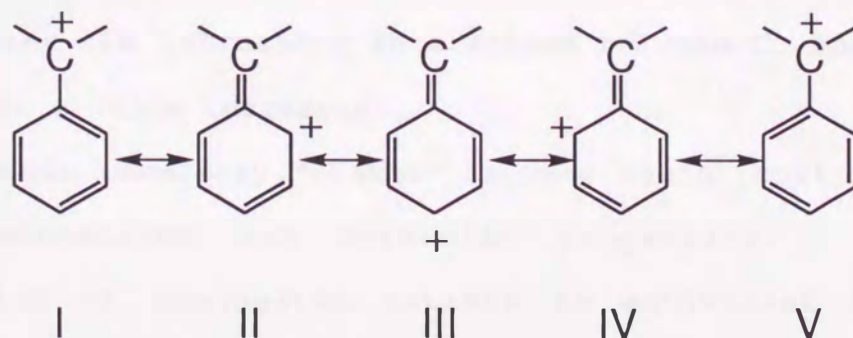
Fig. 1-9. Resonance structures of bezylic cations.

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As shown in Fig. 1-9, contributions of II, III, and IV become larger according to increase of resonance interaction between benzylic p orbital and benzene π system. This should be detected as a change of Wieberg bond order[13] of C_1-C_7 and average bond orders of C_1-C_2 and C_6-C_1, C_2-C_3 and C_5-C_6, and C_3-C_4 and C_4-C_5. The plots of bond order against the r value are shown in Fig. 1-10. In case of C_1-C_7, bond order converge to 1.0 when r=0, reflecting the importance of unconjugated structure (I and V). The index increases in proportion to the r value, indicating the increasing contribution of structures II, III, and IV. C_1-C_7 connects the cationic center and aromatic moiety. Thus this way of change reveals that the r value shows the degree of overlapping between benzylic p orbital and benzene π orbital. Bond orders of C_1-C_2, C_2-C_3, and C_3-C_4 also change reflecting the importance of contribution of each structure (I-V) in Fig. 1-9. When r=0, the Wieberg indices take 1.4, which is an intermediate value between single and double bond. As the r increases, bond order of C_2-C_3 increases but C_1-C_2 and C_3-C_4 decrease. All the behavior is consistent to the prediction of resonance theory. Consequently this indicates the increasing interaction between C_7 and aromatic moiety as the r value increases.

In organic chemistry "charge" is very useful tool to predict reaction mechanisms and molecular properties. Resonance stabilization of conjugated cations is equivalent to charge delocalization. Thus the charge distribution should be related to the r value, if the r value in the Yukawa-Tsuno Eq. (1-1) is a parameter indicating resonance degree. Unfortunately charge is not
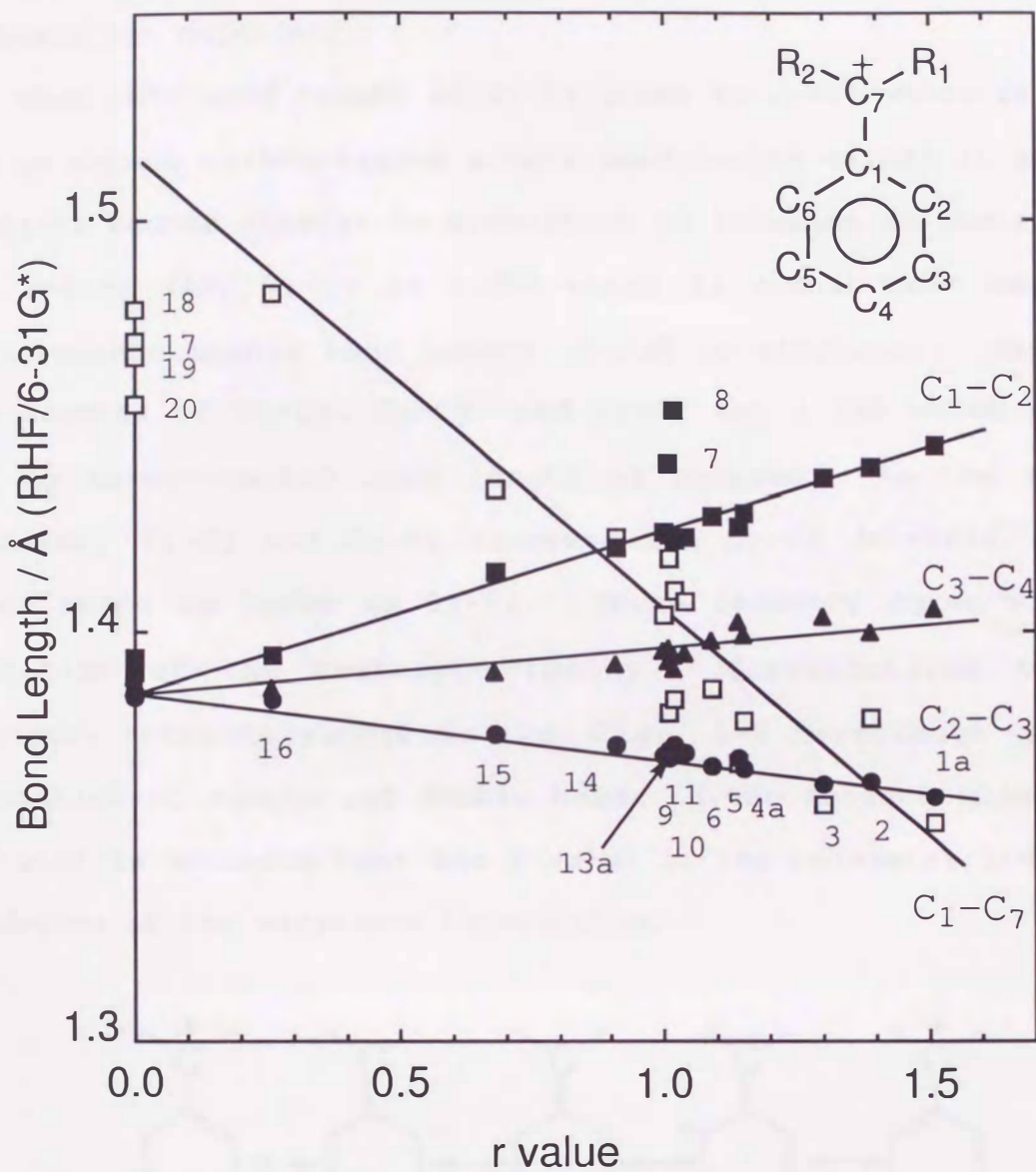
-24-
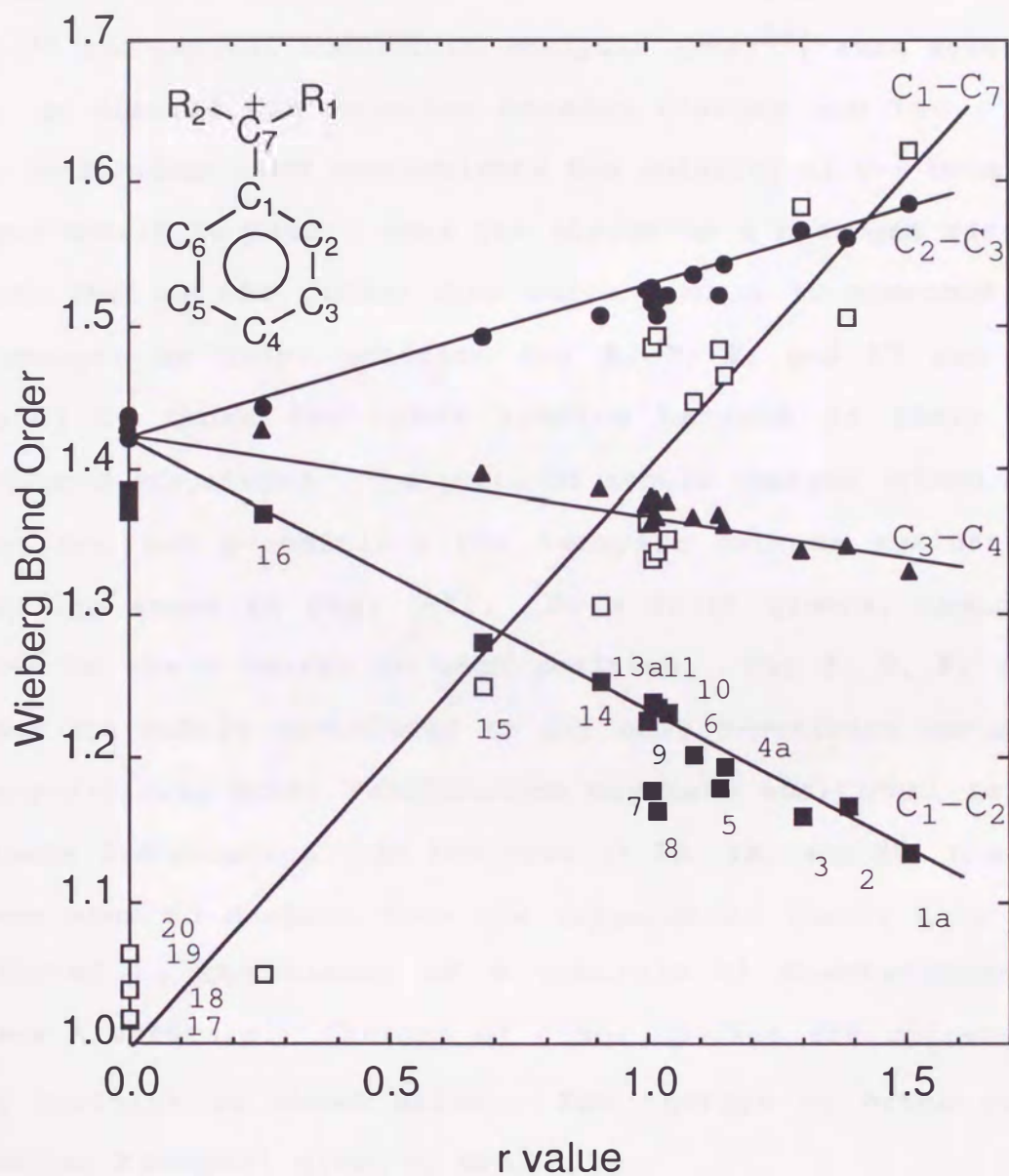
Fig. 1-10. Wieberg bond orders from NBO analtsis
(RHF/6-31G*) vs r values in Yukawa-Tsuno equation
for benzylic cations. Numbers correspond those
for species in Figs. 1-5 and 1-6.

quantum mechanically observable though it is easy to understand intuitively. Several arbitrary method have been proposed to estimate atomic charges.[14] The Mulliken population analysis (MPA)[15] and natural population analysis (NPA)[16] were selected in order to discuss the relation between charges and the r value. These methodology seem overestimate the polarity of C–H bond, group charges should be used. Thus the charge on a hydrogen was summed up into that on the carbon atom which connect to hydrogen atoms. The charges on ortho position for **5, 7, 8,** and **17** can not be compared to those for other species because of their carbon substituted structures. The plots of atomic charges (given by MPA) on o–, m–, and p-positions for benzylic cations against the r values are shown in Fig. 1-11. At a first glance, charges are related to the r values in each position. For **5, 7, 8,** and **17,** charges are poorly correlated to not only o-position but also p- and m-positions; ortho substitution may have additional influence to charge distribution. In the case of **18, 19,** and **20,** the atomic charges seem to deviate from the correlation lines; this may be attributed to the mixing of σ orbitals of α-substituents to benzene π orbitals. Charges of other species are correlated in every position as shown below. For charges on ortho position (hereafter P(ortho)) given by MPA,

$$P(ortho) = 0.125\ r + 0.016,\ (R=0.987\ SD=\pm0.0070).\quad (1-7)$$

For charges on meta position (P(meta)),
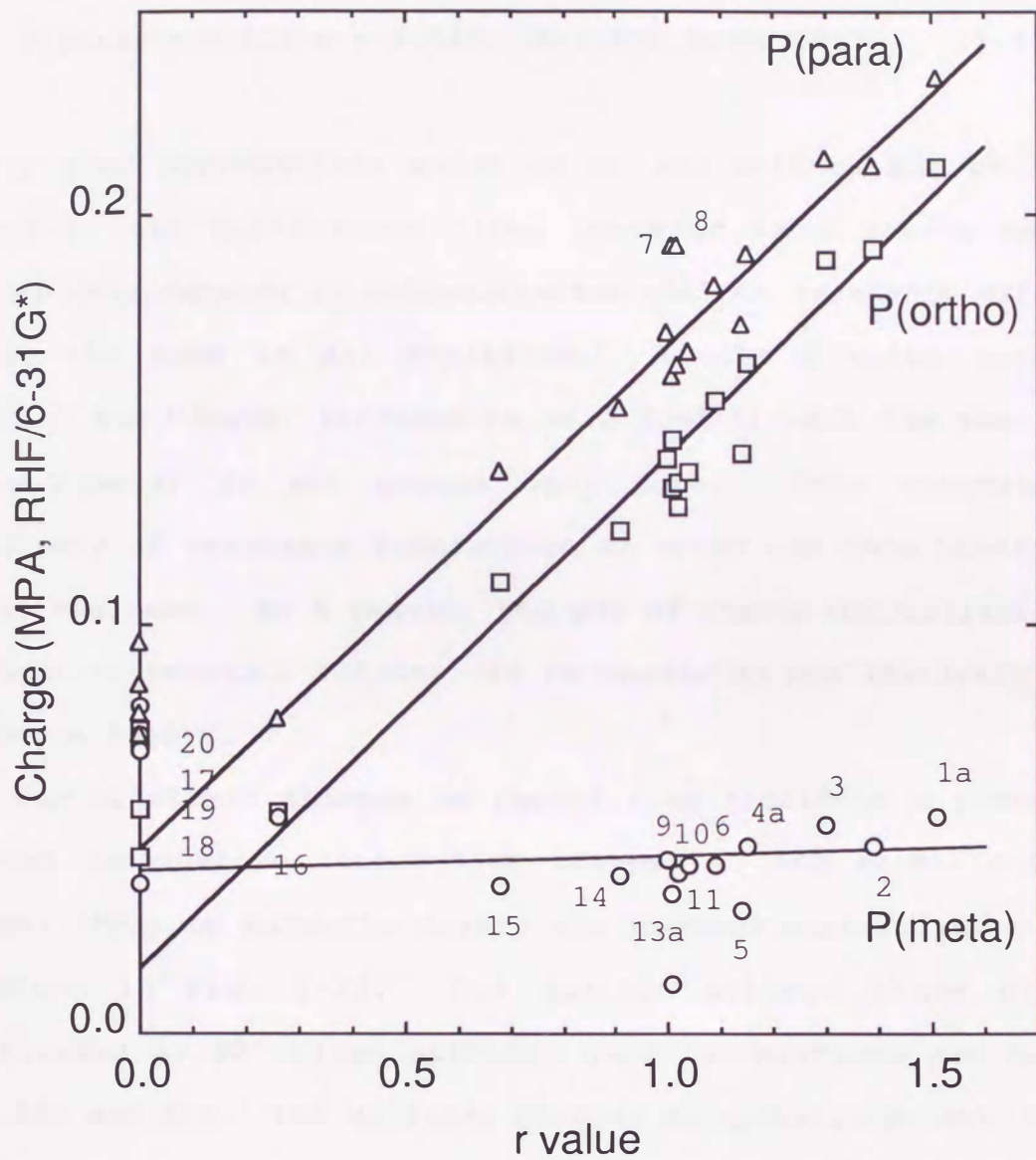
Fig. 1-11. Mulliken population (summed into
heavy atom) on ortho (P(ortho)), meta (P(meta)),
and para (P(para)) position of phenyl ring (RHF/
6-31G*) vs r values in Yukawa-Tsuno equation for
benzylic cations. Numbers correspond to those
for species in Figs. 1-5 and 1-6.

$$P(meta) = 0.003 \ r + 0.040, \quad (R=0.176 \ SD=\pm0.0066). \quad (1-8)$$

For charges on para position ($P(para)$),

$$P(para) = 0.123 \ r + 0.045, \quad (R=0.991 \ SD=\pm0.0057). \quad (1-9)$$

Fairly good correlations exist on o- and p-lines but on m-line. When $r=0$, all correlation lines converge in a narrow range of 0.015-0.045; degrees of delocalization without resonance effect are nearly the same in all positions. As the r value increases, $P(ortho)$ and $P(para)$ increase to +0.2 ($r=1.5$) with the same slope, while $P(meta)$ do not change very much. This suggests that efficiency of resonance interaction on ortho and para position are nearly the same. As a result, the way of charge delocalization for conjugative benzylic cations can be predicted qualitatively by the resonance theory.

Sum of atomic charges on phenyl ring should be a probe which measure conjugative interaction between C_7 and aromatic moiety. Charges (MPA) on aromatic moiety was plotted against the r values as shown in Fig. 1-12. For species without those of ortho substituted or 90° fixed species, good correlations are found in both MPA and NPA. For Mulliken charges on aromatic moiety ($P(Ar)$),

$$P(Ar) = 0.425 \ r + 0.051, \quad (R=0.966 \ SD=\pm0.039). \quad (1-10)$$
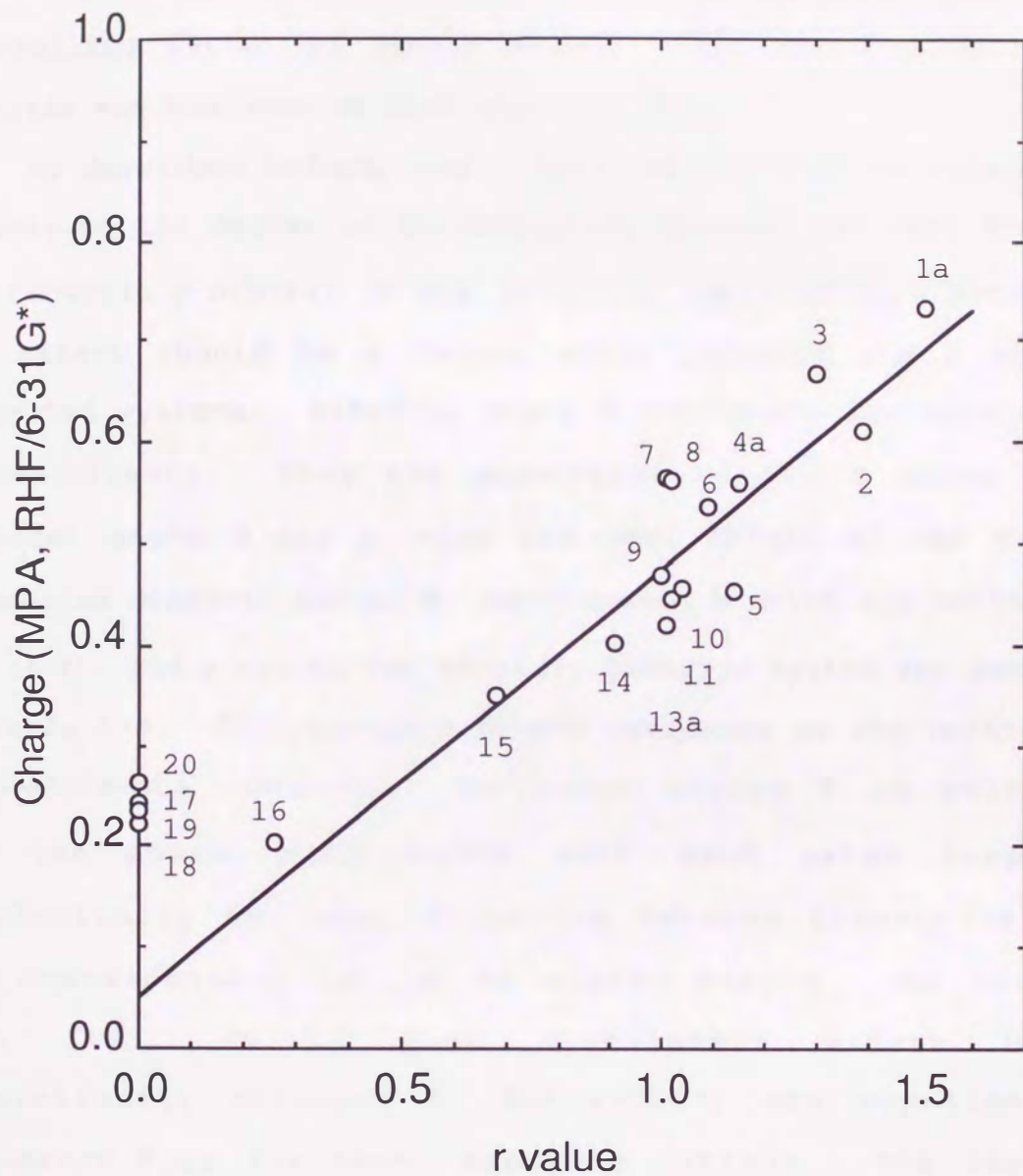
Fig. 1-12. Sum of Mulliken population on phenyl ring (RHF/6-31G*) vs r values in Yukawa-Tsuno equation for benzylic cations. Numbers correspond to those for species in Figs. 1-5 and 1-6.

Charges on aromatic moiety increase in proportion to the r values. This suggests that delocalization to the phenyl ring is the controlling factor of the r value. The result given by NPA analysis was the same as that given by MPA.

As described before, the r value should also be related most closely to the degree of π-overlapping between the aryl π-orbital and benzylic p-orbital in the incipient carbocation. Accordingly the effect should be a factor which controls the r value of congested systems. Dihedral angle θ represents the bulkiness of α-substituents. Thus the dependence of the r value on the dihedral angle θ may provide the real origin of the r value. Calculated dihedral angles θ, experimental θ which are estimated by Eq. (1-4), and r values for tertiary benzylic system are summarized in Table 1-3. The resonance demand decreases as the bulkiness of α-substituents increases. Torsional angles θ in solvolysis and gas phase study agree with each other supporting intrinsically the same structure between transition state and corresponding cation as argued before. As shown in Fig. 1-13, fairly good correlation exists between theoretically obtained θ (RHF/6-31G*) and experimentally estimated θ_{sol} for tert. benzylic cations. The important thing in the MO calculation is whether the level of theory and basis set are satisfactory to describe the phenomena or not. Especially interatomic orbital interaction becomes important in the congested systems. One may suggest that electron correlation must be considered for

Table 1-3. Calculated torsion angles (in unit of θ[a])) between alkyl groups and benzene ring for some tertiary benzylic cations and the comparison with the experimental data.

species	RHF/ STO-3G	RHF/ 3-21G	RHF/ 6-31G*	MP2/ 6-31G*// RHF/ 6-31G*[b]	r_{sol}[c]	θ_{sol}[d]	r_{gas}[e]	θ_{gas}[f]
9	0	5	5	4.3	1.00	0	1.00[k]	0
10	2	2	3		1.04[g]	0	1.01[l]	0
11	1	1	0		1.02[h]	0		
13a	10	11	10		1.01[g]	0		
14	20	24	24	23.8	0.91[i]	17	0.87[m]	21
15	31	37	33		0.68[h]	34		
16	55	77	76	71.0	0.26[j]	59		
17	90	90	90		0	90		

a) θ is the angle of the α-C-C bond with respect to the aromatic plane. Also see Fig. 1-9. b) Given by 6-31G*+MP2. See text. c) r value given in Yukawa-Tsuno substituent effect analysis for the solvolysis of each system. d) $r_{sol}/r_{solmax} = \cos^2\theta_{sol}$. e) r value given in Yukawa-Tsuno substituent effect analysis for the gas phase stabilities of each system. f) $r_{gas}/r_{gasmax} = \cos^2\theta_{gas}$. g) Ref. 3h. h) Unpublished results in this laboratory. i) Ref. 3i. j) Ref. 3j. k) Ref. 4f. l) Ref. 4e. m) Ref. 4g.
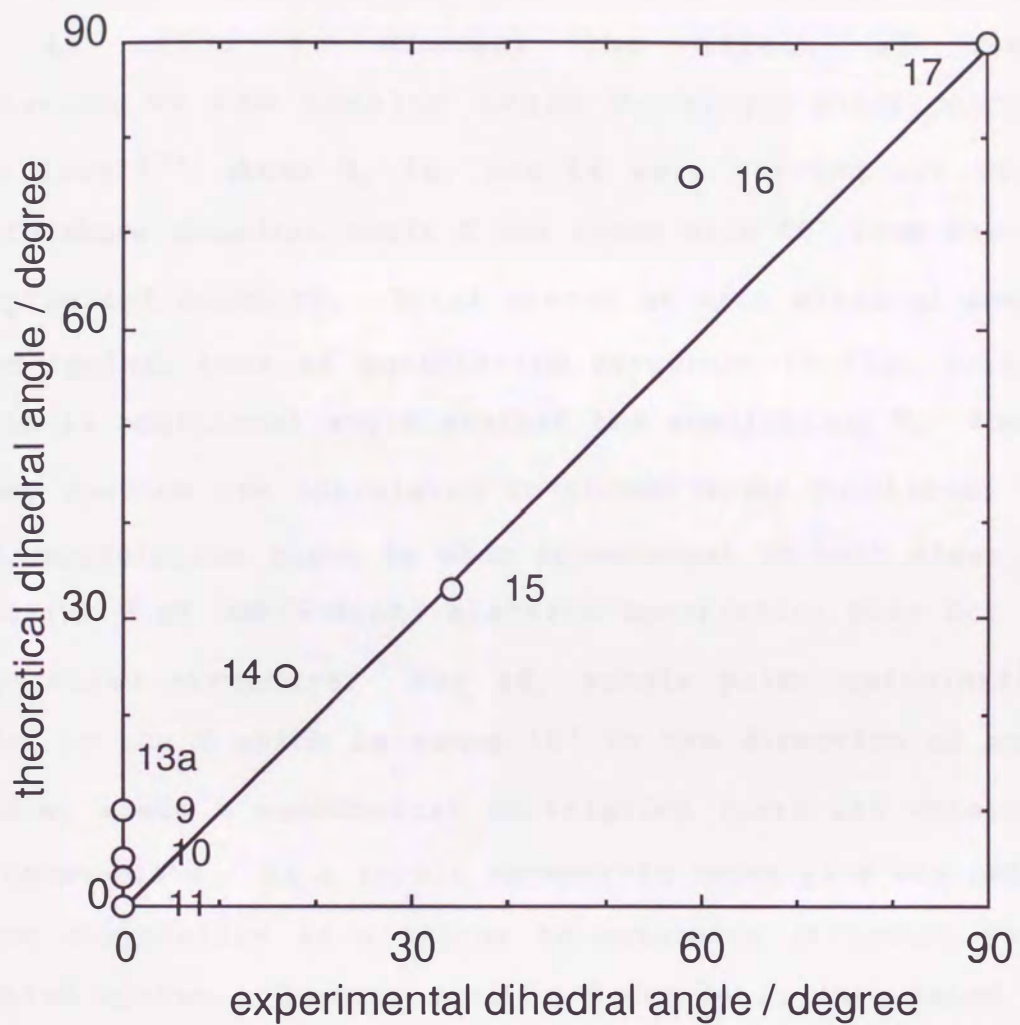
Fig. 1-13. Calculated dihedral angle θ (refer to Figure 1-7) at RHF/6-31G* vs. torsion angle θ estimated by $r/r_{max}=cos^2\theta$, where r is the resonance demand in Yukawa-Tsuno equation obtained from solvolysis of the corresponding precursors. Numbers correspond to those for species in Figs. 1-5 and 1-6.

such species. Unfortunately geometry optimization at MP2 or larger level of theories can not be performed for these bulky systems because of the limitation of the hardware. Thus, in order to discuss the effect of electron correlation on the torsion angle θ, single point calculation at MP2 level[17] about **9**, **14**, and **16** were carried out with the geometry whose dihedral angle θ was swung with ±5° from the RHF/6-31G* optimized geometry. Total energy at each dihedral angle are plotted against that of equilibrium structure in Fig. 1-14. The abscissa is additional angle against the equilibrium θ. The plots of every species are correlated in second order functions. For **9** and **14**, correlation curve is also symmetrical to both sides of the equilibrium θ at RHF/6-31G*; electron correlation does not affect the optimized structure. For **16**, single point calculation was extended to the θ which is swung 10° to the direction of coplanar structure, since a monotonical correlation curve was obtained for these three plots. As a result asymmetric curve plot was obtained; electron correlation is a factor to determine structure for this conjugated system. However minimum θ for **16** is calculated 71° in the assumption of second order correlation. That is electron correlation effect decreases θ in only 5°. Consequently electron correlation is not so important for these tertiary benzylic cations. Force constants are estimated in the assumption that the potential of the rotation is obeyed in the second order function. 7.35 kcal/mol, 28.5 kcal/mol, and 17.0 kcal/mol are estimated for **9**, **14**, and **16** successively. Rigid structure for the rotation were
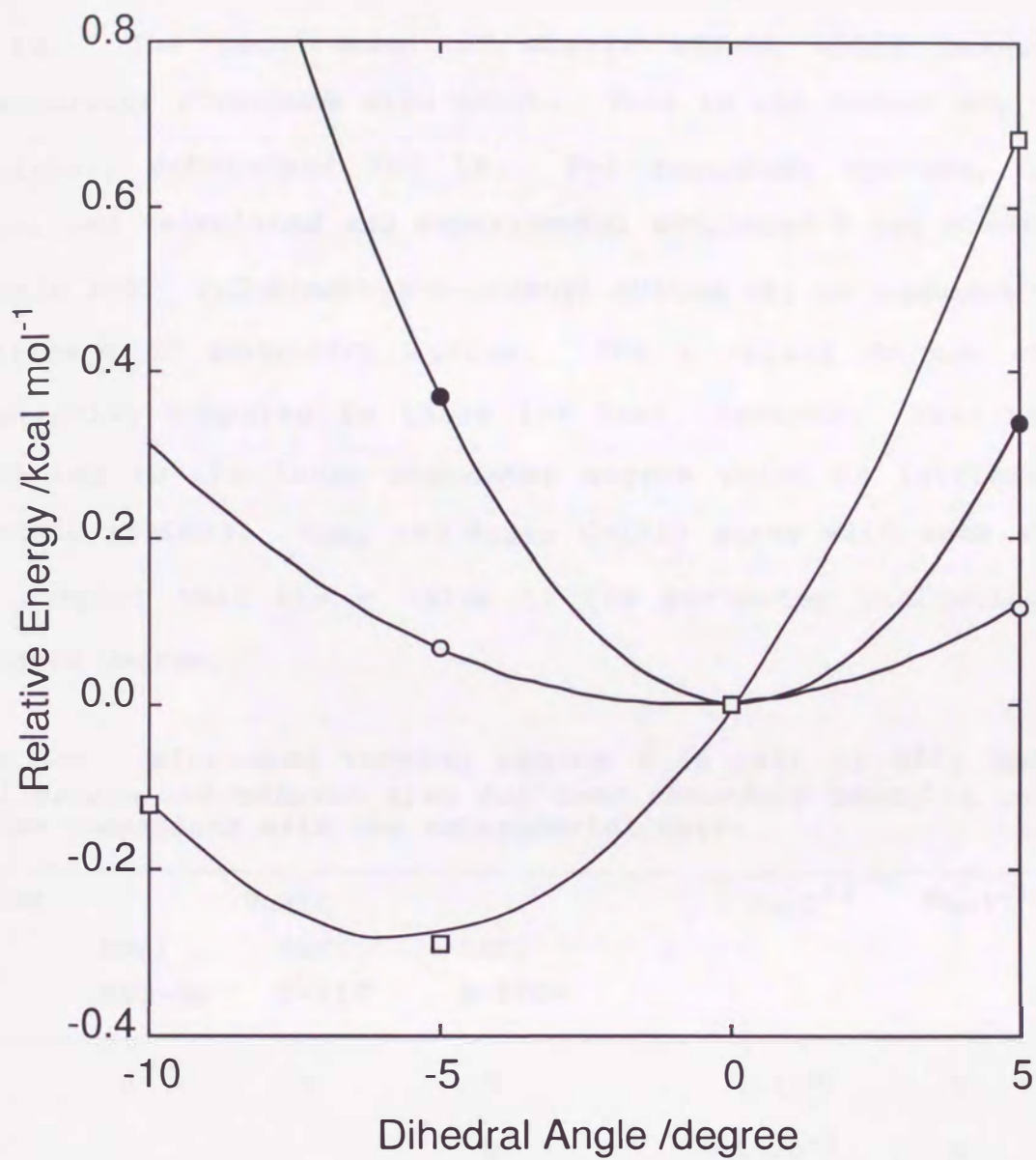
Fig. 1-14. Fixed dihedral angle vs. energy for α,α-dimethylbenzyl (open circle), α-t-buthyl-α-methylbenzyl (closed circle), and α,α-di-t-butylbenzyl (open square) cations.

given for congested cations. The requirement of resonance stabilization which forces the structure coplanar is still large for **14**. The requirement of steric effect which makes the perpendicular structure also exist. This is the reason why the θ is rigidly determined for **14**. For secondary systems, the r values, and calculated and experimental estimated θ are summarized in Table 1-4. 2,2-Dimethyl-1-indanyl system (**5**) is supposed to be a standard of secondary system. The r values do not change dramatically compared to those for tert. systems. This may be attributed to the large resonance degree which is intrinsic to secondary systems. θ_{obs} and θ_{calc} fairly agree with each other. This support that the r value is the parameter indicating the resonance degree.

Table 1-4. Calculated torsion angles (in unit of θ[a])) between alkyl groups and benzene ring for some secondary benzylic cations and the comparison with the experimental data.

species	θ_{calc}			r_{sol}[b]	θ_{sol}[c]
	RHF/ STO-3G	RHF/ 3-21G	RHF/ 6-31G*		
5	0	0	0	1.11[d]	0
4 a			0	1.15[e]	0
6	0	0	0	1.09[f]	8
7	0	0	0	1.01[g]	17
8	16	25	22	1.02[g]	17

a) θ is the angle of the α-C-C bond with respect to the aromatic plane. Also see Fig. 1-9. b) r value given in Yukawa-Tsuno substituent effect analysis for the solvolysis of each system. c) $r_{sol}/r_{solmax} = \cos^2\theta_{sol}$. d) Ref. 3g. e) Ref. 3d. f) Ref. 3e. g) Ref. 3f.

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Chapter 2　　　　Substituent Effect on the Solvolysis of

2,2-Dimethylindan-1-yl Chlorides[1]

　　　The LArSR (Yukawa-Tsuno) equation (2-1)[2] is widely applied to substituent effect analysis of many benzylic solvolyses.

$$\log (k/k_0) = \rho (\sigma^0 + r \, \overline{\Delta\sigma_R^+}), \qquad (2\text{-}1)$$

where r (resonance demand) is the parameter measuring the degree of resonance interaction between the reaction center and benzene π-system.　The r value changes widely with the reactions; r = 1.00 for solvolysis of α-cumyl chloride by definition, r = 1.15 for the secondary α-methylbenzyl system (1),[3] and r = 1.30 for the primary benzyl system.[4]　In addition, r values of 1.39 and 1.51 were given for highly deactivated carbocationic solvolyses of α-methyl-α-trifluoromethylbenzyl[5] and α-trifluoromethylbenzyl systems,[5b] respectively.　The r value increases in proportion to instability of cationic reaction center.　Thus the r value is a measure of the resonance demand reflecting the stability of cationic transition state and provides very important information to evaluate the nature of the transition state.

　　　Substituent effect on the solvolysis of α-methylbenzyl chlorides (1) gave the r value of 1.15 which is referred to the higher resonance demand of this secondary system than the σ^+ reference system.　However, the incursion of solvent participation is suggested in this borderline solvolysis.[6]　If this is the case, solvent participation might become important as the substituent

becomes more electron attracting and give a monotonically concave σ^+ correlation. It has thus been claimed in the literature that the higher r value observed in such a case will be meaningless.[7] The alternative secondary S_N1 solvolysis system of $\alpha-(t-$ Butyl)benzyl tosylates (**2**) where there is little possibility of solvent participation may not generate a coplanar cation with the benzene π-system in the transition state due to bulkiness of the $t-$ Bu group at α position.[8] In order to prove the origin of the r values relating to the inherent stabilities of a series of the benzylic cations, the r value which reflects the fully conjugated secondary system is needed. That is, the system which has a different r value from that of this standard system should give important informations on the physical meaning of the r value. Thus the substituent effect on the solvolysis of 2,2-dimethylindan-1-yl chlorides (**3**),[1] where the vacant p-orbital developed at the benzylic position is fixed in the preferred conformation overlapping with the benzene π-system, was analyzed by LArSR Eq. (2-1) in this chapter. The neopentyl skeleton of **3** will be expected to solvolyze via S_N1 mechanism. Moreover, this system will attain a full resonance stabilization in the transition state due to the fused five membered ring, and then provide an standard r
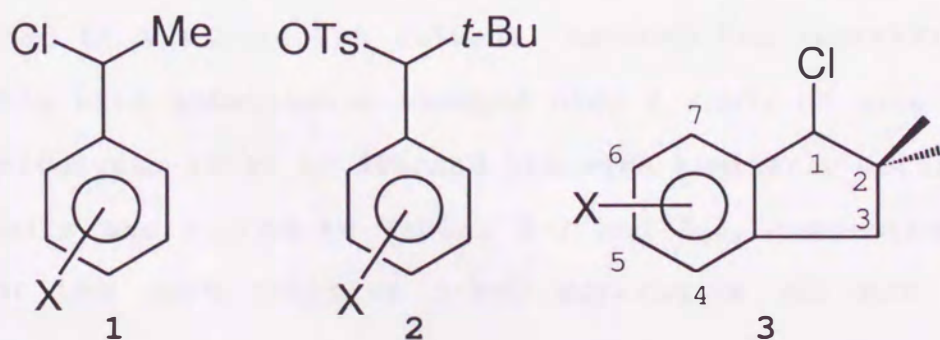
value anticipated for the inherent secondary benzylic solvolysis system.

Results

A series of 5- or 6-substituted 2,2-dimethylindan-1-yl chlorides were prepared by dimethylation and reduction of the corresponding indanones, and subsequent chlorination. Substituted indan-1-ones were prepared by the Friedel-Crafts ring-closure of substituted 3-chloropropiophenones, or by the Friedel-Crafts ring closure of aryl propionic acids.

The solvolysis rates of 2,2-dimethylindan-1-yl chlorides in 80% (v/v) aqueous acetone (80A) were determined conductometrically at the initial chloride concentrations of $10^{-4}-10^{-5}$ mol dm^{-3}. The rate constants are summarized in Table 2-1 together with the activation parameters.

The rate data of slow solvolyzing 6-Cl and 6-Br derivatives, and those of fast 5-MeS, 5-PhO, and 5-MeO-6-Cl ones were extrapolated from rate data at other temperatures by means of the Arrhenius equation.

The rate constants for all derivatives were unable to be determined in a single 80A solvent, because the reactivity varies remarkably with substituent changes over a range of nine powers of ten. Solvolysis rates in 90A and 50A were similarly determined and the results are listed in Tables 2-2 and 2-3, respectively. The rate for the most reactive 5-MeO derivative was not precisely

Table 2-1. Solvolysis Rates of 2.2-Dimethylindan-1-yl Chlorides in 80% aq Acetone.

Subst.	Temp./°C	$10^5 k/s^{-1}$	$\Delta H^{\ddagger}_{25°C}$ kcal mol^{-1}	$\Delta S^{\ddagger}_{25°C}$ e.u.
p-MeO	25	324000[b]		
p-MeS	-20	41.90		
	0	532.5		
	10	1705		
	25	8140[a]	17.0	-6.6
p-PhO	-20	12.65		
	0	198.8		
	10	652.7		
	25	3540[a]	18.2	-4.3
p-MeO-m-Cl	-25	4.855		
	-15	22.31		
	0	177.4		
	15	973.7		
	25	3080[a]	18.3	-4.1
3.4-Me2	-15	1.397		
	0	12.42		
	15	82.96		
	25	254.9	19.3	-5.5
p-Me	0	4.675		
	15	32.27		
	25	102.7	19.4	-7.1
p-t-Bu	25	41.91	18.9	-10.6
	45	331.1		

Table 2-1. Continued.

Subst.	Temp./°C	$10^5 k/s^{-1}$	$\Delta H^{\ddagger}_{25°C}$ kcal mol^{-1}	$\Delta S^{\ddagger}_{25°C}$ e.u.
m–Me	15	1.323		
	25	4.312	20.6	−9.2
	45	43.23		
H	25	1.744	21.1	−9.4
	45	17.50		
m–MeO	25	3.596	20.8	−9.0
	45	34.90		
p–Br	25	0.2326	22.2	−9.9
	45	2.666		
	55	7.759		
m–Cl	25	0.0133[a]	23.5	−11.2
	45	0.1692		
	55	0.5575		
	75	4.535		
m–Br	25	0.0116[a]	23.5	−11.5
	45	0.1493		
	55	0.4734		
	75	3.977		
m–CN	25	0.000482[c]		
p–CN	25	0.000139[c]		

a) Extrapolated from rate data at other temperatures. b) Calculated from linear logarithmic rate relation between 80A and 90A at 25°C. c) Calculated from linear logarithmic rate relation between 80A and 50A at 25°C.

Table 2-2. Solvolysis Rates of 2.2-Dimethylindan-1-yl Chlorides in 90% aq Acetone.

Subst.	Temp./°C	$10^5 k/s^{-1}$	$\Delta H^{\ddagger}_{25°C}$ kcal mol^{-1}	$\Delta S^{\ddagger}_{25°C}$ e.u.
p-MeO	-25	63.35		
	-15	215.1		
	0	1264		
	25	15100[a]	15.6	-10.1
p-MeS	0	30.94		
	25	421.5	16.3	-14.7
p-PhO	0	12.72		
	25	188.3	16.9	-14.5
p-MeO-m-Cl	-15	1.461		
	0	10.46		
	15	58.66		
	25	162.3	17.4	-12.8
3.4-Me2	0	0.8336		
	15	5.324		
	25	16.07	18.3	-14.5
	45	115.4		
p-Me	15	1.970		
	25	6.118	18.7	-15.2
	45	47.14		
p-t-Bu	25	2.763	19.6	-13.5
	45	23.63		
m-Me	25	0.315[a]	20.3	-15.7
	45	2.881		
	55	7.873		
H	25	0.109[a]	20.4	-17.5
	35	0.3414		
	45	1.012		
	75	17.51		
m-MeO	25	0.2778	21.1	-13.3
	45	2.769		

a) Extrapolated from rate data at other temperatures.

Table 2-3. Solvolysis Rates of 2.2-Dimethylindan-1-yl Chlorides in 50% aq Acetone.

Subst.	Temp./°C	$10^5 k/s^{-1}$	$\Delta H^{\ddagger} 25°C$ kcal mol^{-1}	$\Delta S^{\ddagger} 25°C$ e.u.
m-Me	−15	6.536		
	0	57.16		
	25	1044	18.8	−4.6
H	−15	2.260		
	0	21.07		
	25	403.2	19.2	−5.1
m-MeO	0	28.55		
	25	575.3	18.8	−5.6
p-Br	25	45.12	19.9	−7.1
	45	396.9		
m-Cl	25	2.341	21.3	−8.2
	45	23.96		
m-Br	25	2.007	21.4	−8.4
	45	20.63		
m-CN	25	0.0693[a]	23.0	−9.7
	45	0.8059		
	55	2.817		
	75	20.39		
p-CN	25	0.0186[a]	23.5	−10.6
	45	0.2385		
	75	6.331		

a)Extrapolated from rate data at other temperatures.

followed in 80A by the present method even at low temperatures. The rate data of this derivative in 80A at 25°C was estimated from the rate in 90A at 25°C, using a linear logarithmic rates relation (R = 0.9997, SD = ±0.030, and n = 8) between 90A (25°C) and 80A (25°C),

$$\log(k/k_H)_{80A}(25°C) = 1.034 \log(k/k_H)_{90A}(25°C) - 0.049.$$

On the other hand, the rates of strongly deactivated 6-CN and 5-CN derivatives were too slow in 80A to be obtained directly by the present conductometric measurement. The rate data for these derivatives in 80A at 25°C were estimated from the rates in 50A at 25°C, using a linear logarithmic rates relation (R = 0.9999, SD = ±0.013, and n = 5) between 50A (25°C) and 80A (25°C),

$$\log(k/k_H)_{80A}(25°C) = 0.9469 \log(k/k_H)_{50A}(25°C) + 0.006.$$

The rate data estimated for these derivatives were also included in Table 2-1. As shown in Tables 2-1, 2-2, and 2-3, the 6-MeO derivative reacts consistently faster than unsubstituted derivative for all solvents, and is different from the normal behavior expected by the standard σ_m value of 0.050. Ohkata et al. also observed a similar rate acceleration for m-MeO derivatives in solvolysis of spiro[cyclopropane-1,2'-indan]-1'-yl[9] and 3,4-benzotricyclo[4.3.1.0^{1,6}]dec-3-en-2-yl p-nitrobenzoates.[10] The m-MeO group behaves actually as a slightly electron-donating group and this seems to be characteristic of these congested indanyl

systems.   Thus substituent effect analysis for the present indanyl system was treated excluding 6-MeO derivative.

The LArSR Eq. (2-1) was applied to the rate constants in 80A at 25°C by the least-squares method.   The substituent parameters employed in this analysis are listed in Table 2-4, and are employed for the analysis of substituent effects of α-(t-butyl)benzyl systems.[8]   The 5- and 6-positions of 2,2-dimethyl-1-indanyl system correspond to p- and m-positions, respectively.   Results of substituent effect analysis of 2,2-dimethylindan-1-yl chloride at 25°C are shown in Table 2-5.   For a comparison, the Brown $\rho^+\sigma^+$ Eq. (2-2),

$$\log \ (\ k/k_0\ ) \ = \ \rho^+\sigma^+, \qquad\qquad (2-2)$$

has also been applied, and the result was included in Table 2-5. The LArSR plots are shown in Fig. 2-1.

Discussion

Comparison of $\rho^+\sigma^+$ and LArSR correlations in Table 2-5 clearly shows that the LArSR equation describes the present reaction more precisely than the Brown $\rho^+\sigma^+$ treatment; the SD value is 1.5 times larger in $\rho^+\sigma^+$ than in the LArSR correlation.

Both the large negative ρ value and the enhanced r value larger than unity suggest that this solvolysis proceeds through a highly positive charged transition state of a rate-determing k_c-ionization leading to a carbocation intermediate.   Furthermore this

Table 2-4. Substituent Constants.

Subst.[a)	σ^o	$\Delta\bar{\sigma}_R^+$
p-MeO	-0.100	-0.720
p-MeS	0.120	-0.720
p-PhO	0.063	-0.590
p-MeO-m-Cl	0.220	-0.690
p,m-Me$_2$	-0.183	-0.187
p-Me	-0.124	-0.187
p-t-Bu	-0.155	-0.100
m-Me	-0.069	0.000
H	0.000	0.000
p-Br	0.296	-0.146
m-Cl	0.373	0.000
m-Br	0.391	0.000
m-CN	0.600	0.000
p-CN	0.670	0.000

a) p- and m-positions correspond 5- and 6-positions for 2,2-dimethyl-1-indanyl system.

Table 2-5. Results of Substituent Effect Analysis of 2,2-Dimethylindan-1-yl Chlorides (**3**).

Correlation	ρ	r	n[a)	SD[b)	R[c)
$\rho^+\sigma^+$	-6.121±0.095	(1.00)	14	0.16	0.9985
LArSR	-5.798±0.127	1.11	14	0.12	0.9992

a) Number of substituents involved. b) Standard deviation. c) Correlation coefficient.
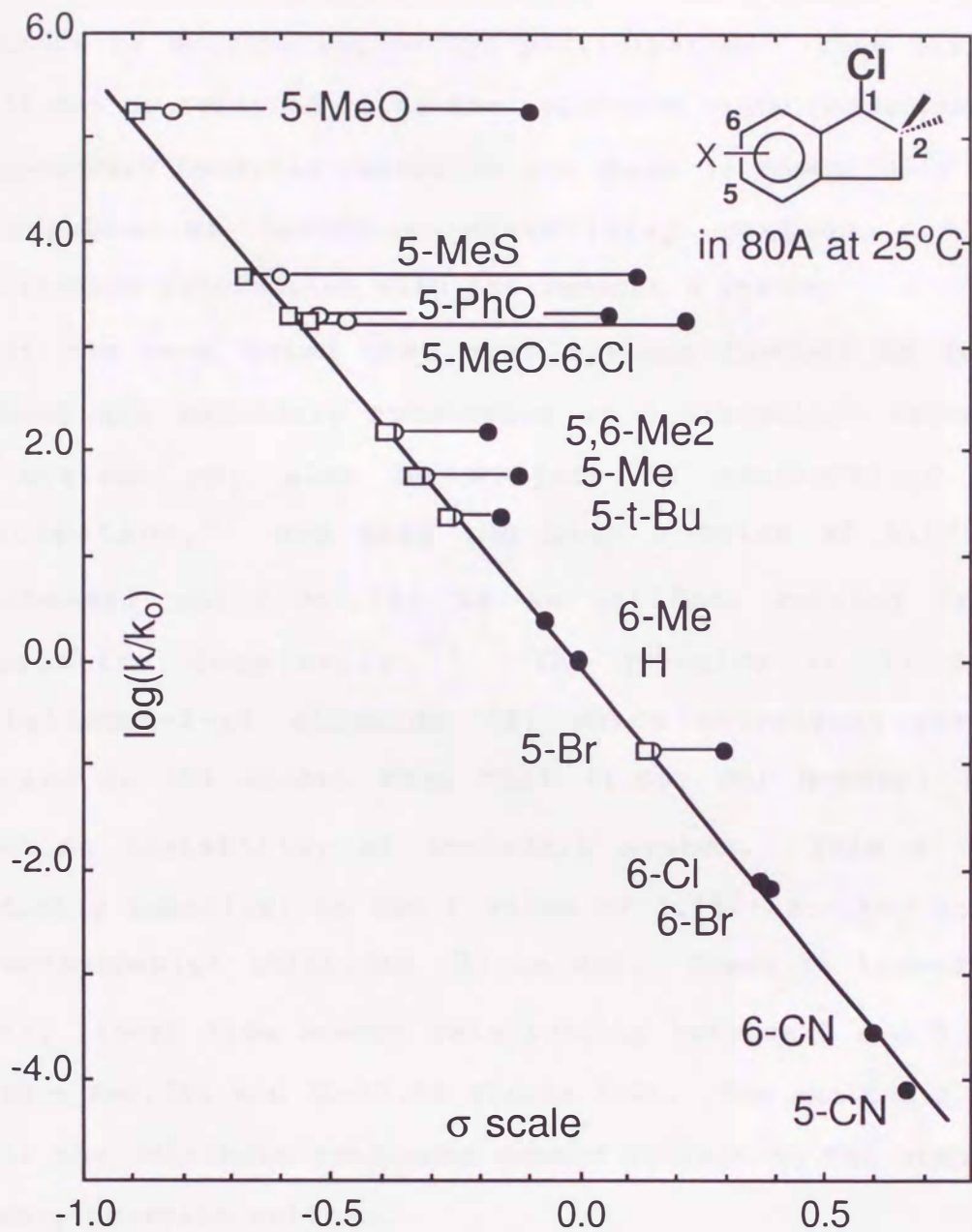
Fig. 2-1. LArSR plot for the solvolysis of 2,2-dimethylindan-1-yl chlorides in 80A at 25°C; open circle σ^+, closed σ^0, and squares $\bar{\sigma}$ for r=1.11.

precise linear relationship excludes either nucleophilic solvent assistance or neighboring methyl participation. Thus the r value of 1.11 may be referred to as the reference value characteristic of open secondary benzylic carbenium ion which is essentially coplanar and capable of exerting essentially maximum conjugative stabilization interaction with the benzene π system.

It has been noted that most systems favored by the LArSR treatment are secondary substrates in nucleophilic solvents and such systems may also be subject to nucleophilic solvent participation,[6] and that the high r value of 1.15 for α-methylbenzyl chloride (**1**) is an artifact arising from such mechanistic complexity.[7] The r value (1.11) for 2,2-dimethylindan-1-yl chloride (**3**) which solvolyzes through k_C mechanism is 10% higher than that (1.00) for α-cumyl chloride reflecting instability of secondary system. This r value is essentially identical to the r value of 1.15[3] for the solvolysis of α-methylbenzyl chlorides (**1**) in 80A. There is indeed shows a strictly linear free energy relationship between **1** and **3** (Fig. 2-2) with a R=0.994 and SD=±0.08 (Table 2-6). The exalted r value of 1.15 is the intrinsic resonance demand reflecting the stability of secondary benzylic cations.

The r value should be related most closely to the degree of π-overlapping between the aryl-π-orbital and benzylic-p-orbital in the incipient carbocation. In the case where the dihedral angle between benzylic p-orbital and benzene π-system is 0°, the system acquires a full resonance stabilization to provide the maximum r value. Then for the congested system where both p-orbitals can not
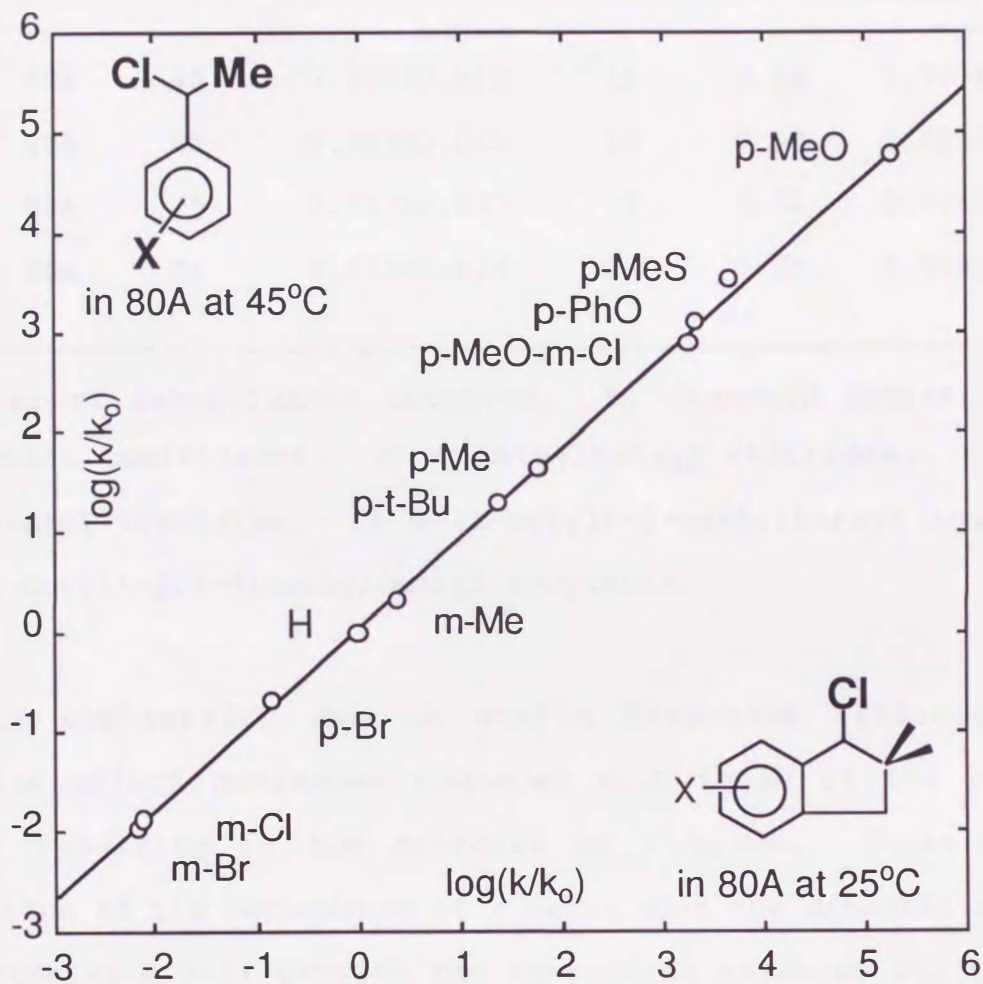
Fig. 2-2. Logk-logk plot between solvolysis
of α-methylbenzyl chlorides at 45°C and 2,2-
dimethylindan-1-yl chlorides at 25°C in 80A.

Table 2-6. Substituent Effects of Secondary Benzylic Solvolyses vs. 2,2-Dimethylindan-1-yl Chlorides (**3**).

System	Solv.	temp/°C	Slope	n[a]	SD[b]	R[c]
1[d]	80A	45	0.907±0.010	11	0.08	0.9994
2[e]	80A	25	0.929±0.011	12	0.10	0.9993
4[f]	80A	25	0.917±0.037	7	0.22	0.9960
5[g]	80A	25	0.814±0.024	4	0.09	0.9992

a) Number of substituents involved. b) Standard deviation. c) Correlation coefficient. d) α-methylbenzyl chlorides. e) α-(t-butyl)benzyl tosylates. f) α-(t-butyl)-2-methylbenzyl tosylates. e) α-(t-butyl)-2,2-dimethylbenzyl tosylates.

maintain coplanarity due to steric hindrance, efficiency of resonance effect decreases compared with those of the coplanar system, resulting in the decrease of r value. Therefore the examination of the dependence of r value upon the dihedral angle of both p-orbitals will provide the convincing evidence for the real origin of the empirical resonance demand parameter r in the LArSR Eq. (2-1).

In the substituent effect on the solvolyses of secondary α-(t-butyl)benzyl tosylates (**2**)[8] and their o-methyl analogues, 2-methyl (**4**)[11] and 2,6-dimethyl substituted series (**5**),[11] r value of 1.09 for **2**, 1.01 for **4**, and 1.02 for **5** were reported by an application of Eq. (2-1). Solvolysis rates for these systems are available for the parallel studies in this laboratory as shown in
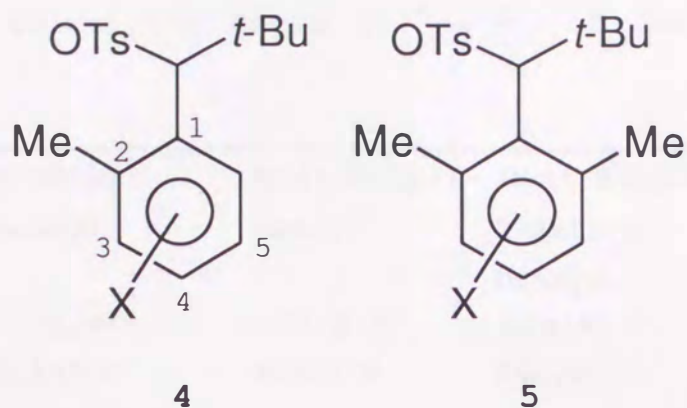
Table 2-7. No significant loss of resonance for the latter two systems compared with parent system **2** has been observed. Increased steric congestion around the carbenium ion center for **4** and **5** systems does not appear to be effective enough to cause a significant loss of the coplanarity in the transition state. However this conclusion is based on the assumption of the coplanarity for **2** solvolysis, and there is no information concerning the steric hindrance of **2**.

The comparison of substituent effects of congested secondary systems with that of 2,2-dimethylindan-1-yl chlorides (**3**) are summarized in Table 2-6. The direct comparison of logarithm of rate constants for two systems will provide the exact information on the relative extent of resonance interaction. The solvolysis of α-(t-butyl)benzyl tosylates (**2**) in 80A shows a good linear free energy relationship against that of **3**. One can conclude that the resonance efficiency of **2** is almost identical to that of **3**. In Fig. 2-3, log(k/k_H) values for the α-(t-butyl)-2-methylbenzyl solvolysis (**4**) are plotted against those for **3**. Deviations of

Table 2-7. Solvolysis Rates ($10^5/s^{-1}$) of Secondary Benzylic System.

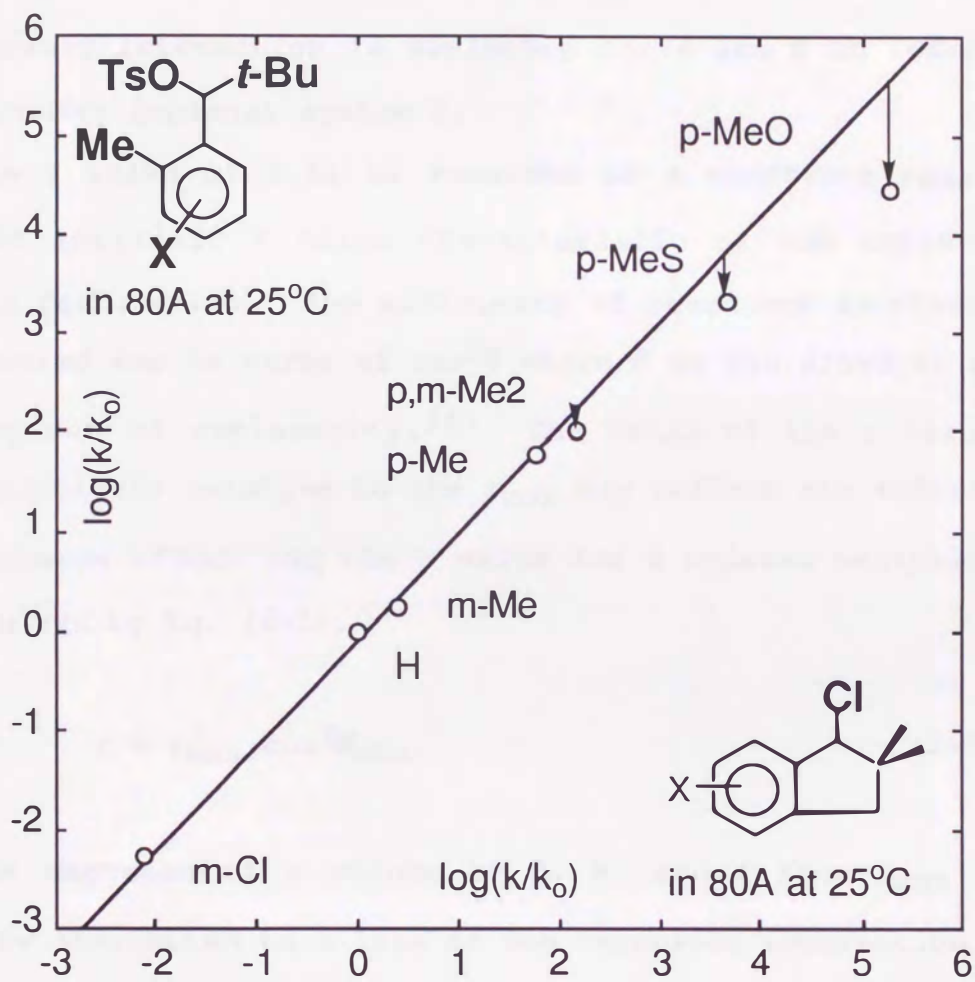| Subst.	α-methyl benzyl Cl(**1**)[a] 80A45°C	α-(*t*-Butyl)-benzyl OTs(**2**)[b] 80A25°C	α-(*t*-Butyl)-2-methyl-benzyl OTs(**4**)[c] 80A25°C	α-(*t*-Butyl)-2,6-dimethyl-benzyl OTs(**5**)[c] 80A25°C
p-MeO	42000	94600	197000	3753
p-MeS	2430	5592	14900	257.0
p-PhO	894	1760		
p-MeO-m-Cl	545	1180		
p.m-Me2		186.7	717.9	
p-Me	31.0	95.07	425.7	7.256
p-t-Bu	14.4	39.16		
m-Me	1.46	2.862	12.29	
H	0.729	1.420	7.048	0.1967
m-MeO		0.6096		
p-Br	0.151	0.252		
m-Cl	0.00969	0.00691	0.03589	
m-Br	0.00826	0.00659		
m-CN		0.000720		
p-CN		0.000242		

a) Ref. 3. b) Ref. 8. c) Ref. 11.

Fig. 2-3. Logk-logk plot between solvolyses of
α-(t-butyl)-2-methylbenzyl tosylates at 45°C and
2,2-dimethylindan-1-yl chlorides at 25°C in 80A.

para π-donors are systematic; the stronger the para π-donor substituent shows the larger the deviation, suggesting the loss of resonance effects in the transition state of **4**. The same tendency with **4** exists for **5**. It can be said qualitatively that the loss of resonance interaction is evaluated for **4** and **5** in reference to the secondary coplanar system **3**.

The r value of 1.11 is regarded as a reference r_{max} value, i.e., an intrinsic r value characteristic of the coplanar sec. benzylic carbocation. The efficiency of resonance interaction can be accounted for in terms of $\cos^2\theta$ where θ is the dihedral angle of twisting out of coplanarity.[14] The ratio of the r value for a given solvolysis relative to the r_{max} may reflect the efficiency of its resonance effect and the r value for a twisted benzylic system can be given by Eq. (2-3),

$$r = r_{max} \cos^2\theta_{obs}. \hspace{2cm} (2-3)$$

The decrease of r values of **2**, **4**, and **5** from r_{max} of 1.11 should be attributed to a loss of the resonance interaction between the carbocation center and the benzene π-system in the solvolysis transition state caused by the steric hindrance. Thus the torsional angle θ_{obs} at the transition state can be calculated to be 8° for α-(t-butyl)benzyl, and 17° for both o-methyl (**4**) and o,o-dimethyl (**5**) solvolysis based on Eq. (2-3). Torsional angles of these congested secondary systems (**2**, **4**, and **5**) increase in proportion to the bulkiness of the alkyl groups around the reaction center, although these twisting angles are not significant compared

with those in the tertiary systems reported.[1] Particularly surprising is that the through-conjugation interaction with the benzylic reaction center is not decreased seriously even in the solvolysis of **5**. The stabilization by the extended π-delocalization should be the most predominant driving force to promote ionization in the ordinary benzylic solvolyses. Support for this view is provided by the fact that the free energy of the rotation of the phenyl-Cα bond of benzylic carbenium ions under the stable ion condition is found to be 10 - 20 kcal/mol, and the rotation barrier to be 4 - 5 kcal/mol higher for the p-MeO derivative than for the unsubstituted one.[15] This strong π-delocalization interaction with the Cα-cation p-orbital should be the cause of attaining coplanar transition state, to overwhelm the steric repulsion interaction between o-methyl and α-t-Bu groups in the systems **4** or **5**. All these solvolyses have been found to have a degree of steric deceleration associated with steric congestion; nevertheless the effect does not significantly prevent the aryl group from exerting its maximum resonance effect on stabilizing the incipient carbenium ion. The transition state should be able to attain the maximum stabilization to overcome the large steric strain required for the most preferred conformation.

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Chapter 3   Substituent Effect on Gas Phase Stabilities
            of α-*t*-Butyl-α-methylbenzyl Cations[1]

    Substituent effects on the gas-phase stabilities of
benzylic cations can be described excellently in terms of
the LArSR equation (3-1),[2] similar to that in solvolysis.

$$\delta\Delta G^0 = \rho\ (\ \sigma^0 + r\Delta\bar{\sigma}_R^+\ ) \tag{3-1}$$

where r is the parameter measuring the degree of resonance
interaction between benzene π-system and cationic center.
In continuing studies on gas phase benzylic cations in
this laboratory, the r value 1.00 for α-cumyl[3] and α-
ethyl-α-methylbenzyl,[4] 1.14 for α-phenylethyl,[5] 1.29 for
benzyl,[6] 1.41 for α-methyl-α-trifluoromethylbenzyl,[7] and
1.54 for α-trifluoromethylbenzyl[8] cations are obtained by
Eq. (3-1).   It has been demonstrated that the r values of
substituent effects on gas phase stabilities for these
benzylic systems are in complete agreement with those of
corresponding solvolyses.[8]   This result leads to the
important concept for the k_C benzylic solvolysis; the
structure of transition state should be similar to that of
cation.

    In chapter 2, a r value of 1.11 was obtained for
solvolysis of 2,2-dimethylindan-1-yl chlorides[9] and is
clearly larger than that of α-cumyl system (r=1.00).   This
exalted r value reflects the instability of secondary

benzylic cation compared to r=1.00 for the stable tertiary benzylic cation, and is the maximum r value referable to that for planar secondary benzylic cations. Therefore the reduced r values from 1.11 were observed for congested α-(t-Butyl)-2-methylbenzyl (r=1.01), and α-(t-Butyl)-2,6-dimethylbenzyl (r=1.02) system and were ascribed to the steric hindrance of resonance due to sterically congested reaction center.[10] The same phenomenon was observed in tertiary systems; r=0.91[11] for α-t-Butyl-α-methylbenzyl system and r=0.26[12] for highly congested α,α-di-(t-butyl)benzyl system, compared to that for α-cumyl system (r=1.00).

In order to confirm the identity of the r value between in solution and in gas phase, substituent effect analysis on gas phase stabilities for congested system should be examined. Intrinsic stability of cation in gas phase can be easily measured using ICR (ion cyclotron resonance) method. The substituent effects on gas phase stabilities of twisted benzylic carbocation systems have not been performed yet.

The substituent effect on gas phase stabilities of α-t-butyl-α-methylbenzyl cations (**1**) is chosen for this purpose, as a sterically hindered carbocation. The twisted structure of the cation **1** is due to the bulkiness of methyl and t-butyl groups at α-position, and therefore a reduced r value may be expected similarly from the

observed identity of r values between the solvolysis and the gas phase coplanar carbocation.

Results and Discussion

2-Aryl-3,3-dimethyl-1-butenes were synthesized by the nucleophilic addition of aryllithium derived from substituted bromobenzene and n-butyllithium to pinacolone, and subsequent dehydration with Al_2O_3 as a catalyst. The gas phase stabilities of α-t-butyl-α-methylbenzyl cations (**1**) were determined by the equilibrium constants for the proton transfer reaction (3-2) of the corresponding 2-aryl-3,3-dimethyl-1-butene with suitable reference cations of known stability by means of a pulsed ion cyclotron resonance mass spectrometer at 343K as described in detail in chapter 5.

$$\text{(3-2)}$$

(**1**)
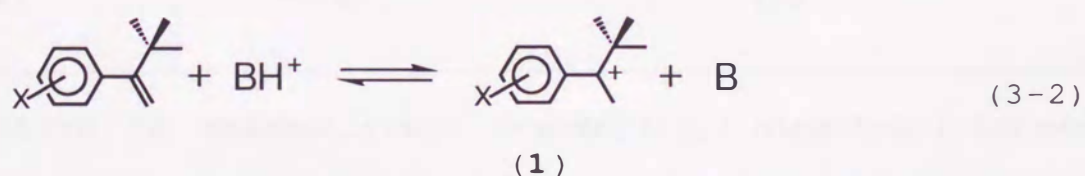
Relative basicities of substituted carbocations **1** to the unsubstituted one which corresponds to the free energy changes of the reaction (3-3) are listed in Table 3-1.
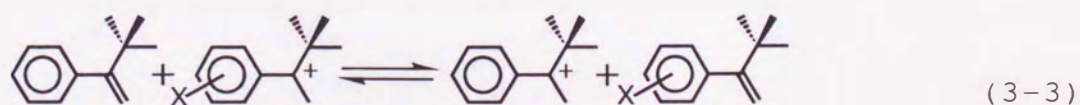
$$\text{(3-3)}$$

Table 3-1. Relative Gas Phase Basicities of 2-Aryl-3,3-dimethyl-
1-butenes and 2-Aryl-1-propenes.

| Substituent | $\Delta\Delta GB$ / kcal mol^{-1} | |
	2-Aryl-3,3-dimethyl-1-butenes[a]	2-Aryl-1-propenes[b]
p-MeO	8.6	10.5
p-MeS	8.1	10.0
p-MeO-m-Cl	5.5	6.7
p-Me	3.6	4.1
3,5-Me$_2$	3.6	3.5
m-Me	2.0	1.8
H	0.0 (198.0)[c]	0.0 (199.1)[c]
m-Cl	-4.3	-4.7
m-F	-4.7	-5.1
m-CF$_3$	-6.0	-6.3
p-CF$_3$	-7.2	-7.2

[a] Relative to unsubstituted 2-phenyl-3,3-dimethyl-1-butene.
Positive value has larger basicity compared to parent substrate.
[b] Relative to unsubstituted 2-phenyl-1-propene. [c] Absolute GB
value relative to ammonia of 201.5 kcal/mol.

The relative stabilities of carbocations **1** are plotted against the corresponding values of α-cumyl cations (**2**) in Fig. 3-1.[3] This plot is regarded as a gas-phase σ^+-plot, since the gas-phase stabilities of **2** are described excellently by the ordinary σ^+ derived from the reactivities in the solution.[3]

$$\delta\Delta G^0_{cumyl} = 14.0\,\sigma^+ + 0.4 \quad (R=0.993,\ SD=\pm0.82) \qquad (3-4)$$

There exists a good linear relationship between for the whole range of substituents.

$$\delta\Delta G^0 = 0.88\,\delta\Delta G^0_{cumyl} - 0.22 \quad (R=0.997,\ SD=\pm0.47) \qquad (3-5)$$

However, there seems to exist an excellent linear relationship with a slope of unity for meta substituents and p-π-acceptor group,

$$\delta\Delta G^0 = 0.98\,\delta\Delta G^0_{cumyl} + 0.17 \quad (R=0.999,\ SD=\pm0.20) \qquad (3-6)$$

and all para π-donor substituents deviate systematically and significantly downward from this correlation line, indicating inadequacy of the σ^+-constant to this system as shown in Fig. 3-1. The line of a unit slope for meta substituents and para π-acceptor suggests that the stabilization of the cation by these substituents must be identical for both systems except for the small difference

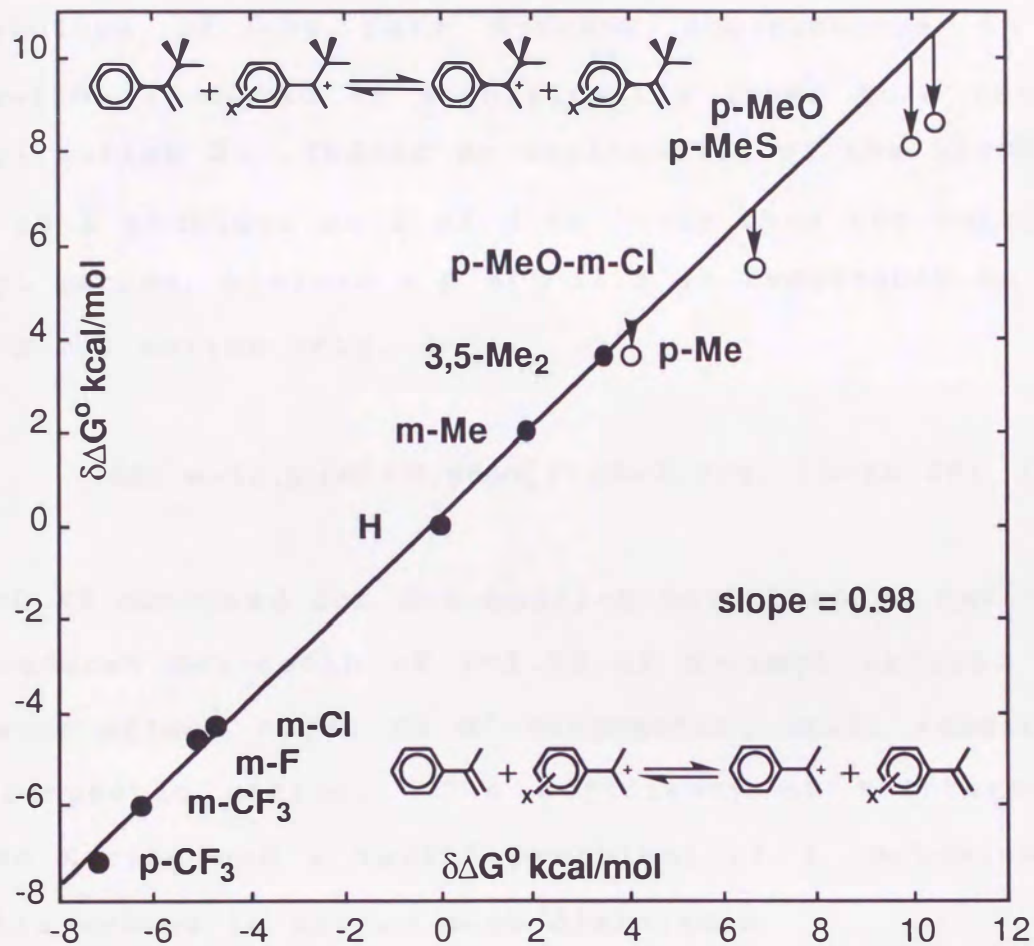Fig. 3-1. Plots of gas phase stabilities of α-
t-butyl-α-methylbenzyl against the corresponding
α-cumyl cations.

in absolute carbocation stability by 1.1 kcal/mol. Downward deviations of para π-donors are observed so systematic that the stronger π-donor substituents show the larger deviations. In consequence, the resonance contribution of the para π-donor substituents in the carbocation **1** should be significantly lower than that in α-cumyl cation **2**. Indeed an application of the LArSR Eq. (3-1) to **1** provides an r of 0.86 lower than the unity for α-cumyl cation, whereas a ρ of -12.5 is comparable to that for α-cumyl cation (Fig. 3-2).

$$\delta\Delta G^0 = -12.5 \, (\sigma^0 + 0.86\Delta\bar{\sigma}_R^+) \quad (R=0.999, \ SD=\pm0.28) \quad (3-7)$$

The r=0.86 obtained for α-t-butyl-α-methylbenzyl cation is only reduced one-tenth of r=1.00 of α-cumyl cation. The resonance effect close to σ^+-conjugation still remains in this congested cation. The efficiency of π-interaction between π-ring and a vacant p-orbital of a carbenium ion for this system is not so much diminished.

Since the r value of 1.01 for α-ethyl-α-methylbenzyl cations[4] is practically the same r value for α-cumyl system, the r value does not change with electronic effect of α-alkyl substituents. This provides the reasonable assumption of the r value of unity for coplanar and tertiary benzylic cations, regardless of varying α-alkyl group. Thus the reduced r value of **1** from 1.00 is attributed to the decreased resonance interaction between
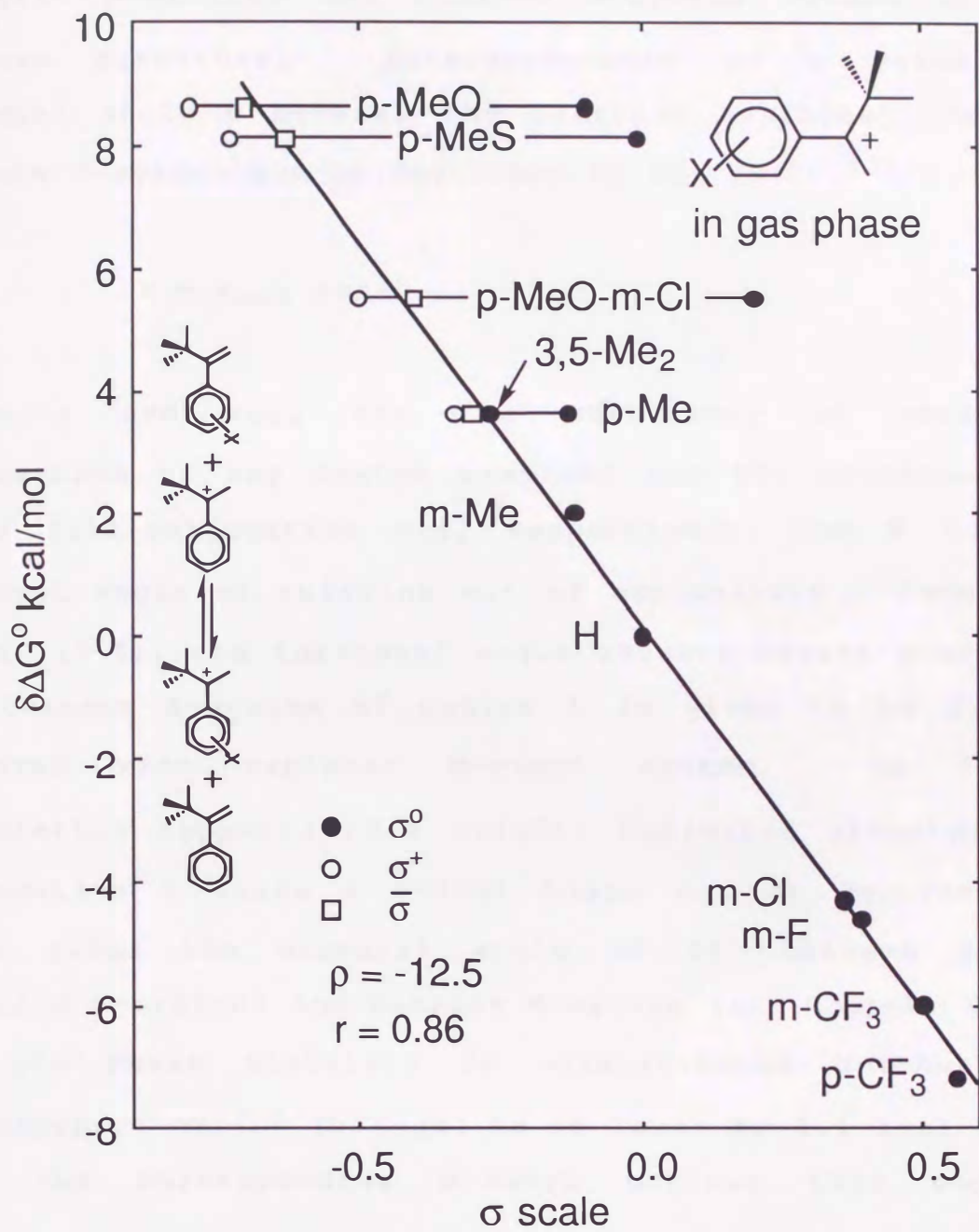
Fig. 3-2. LArSR plot for the gas phase stabilities of α-t-butyl-α-methylbenzyl cations.

benzylic p-orbital and benzene π-system caused by the twisted structure. Interdependence of r value and dihedral angle θ between the benzylic p-orbital and the benzene π-system can be described by Eq. (3-8).[13]

$$r = r_{max} \cos^2\theta \qquad\qquad (3-8)$$

where r and r_{max} are the efficiency of resonance interaction of any system examined and the corresponding ideal full-conjugative one, respectively, and θ is the dihedral angle of twisting out of coplanarity. According to Eq. (3-8), the torsional angle between vacant p-orbital and benzene π-system of cation **1** is given to be 22° as compared with coplanar α-cumyl system. Ab initio calculation supports this result; optimized structure of carbocation **1** using a 6-31G* basis set at Hartree-Fock level gives the dihedral angle of 24° between vacant benzylic p-orbital and benzene π-system (see Chapter 4). The gas phase stability of unsubstituted α-t-butyl-α-methylbenzyl cation is found to be lower by 1.1 kcal mol^{-1} than the corresponding α-cumyl cation; this may be attributed to polar effect or increased steric hindrance due to replacing the α-methyl group by bulky t-butyl group, or the loss of resonance stabilization by reduced overlapping of both p and π-orbitals due to bulkiness around the cation center in **1**. The LArSR r values and relative stabilities of parent substrates (ring

substituent = H) for α-substituted benzylic cations were summarized in Table 3-2. Only α-t-butyl-α-methylbenzyl system (1) shows different behavior; the parent (1) cation is more destabilized than α-cumyl cation despite its reduced r value. As shown in Fig. 3-3, the plot for 1 deviates clearly from the line which is nicely correlated with plots of other systems. Consequently good relation between the r value and the intrinsic stability discriminates resonance hindered system such as 1. In turn, it is concluded that this linear relationship is generally retained for benzylic system as far as the

Table 3-2. The r Values and Relative Gas Phase Stabilities of Benzylic Cation Systems.

α-Subst.	r value	Relative Stability[a] / kcal mol^{-1}
CF3,H[b]	1.54	-19.5
CF3, Me[c]	1.41	-16.2
H,H[d]	1.29	-12.0
Me,H[e]	1.14	-5.2
Me,Me[f]	1.00	0.0
Et,Me[g]	1.01	0.4
t-Bu, Me[h]	0.86	-1.1

a) Relative to α-cumyl cation.   b) Ref. 8.   c) Ref. 7.   d) Ref. 6.
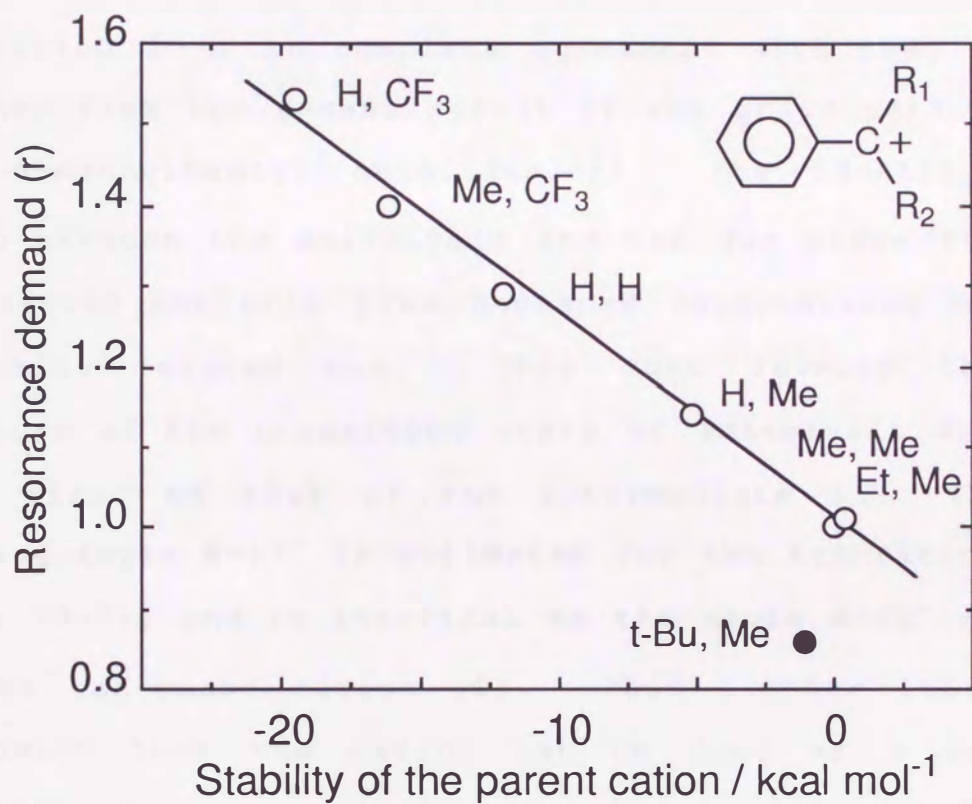e) Ref. 5.   f) Ref. 3.   g) Ref. 4.   h) Ref. 1.

Fig. 3-3. Linear relationship between r value and stabilities of the unsubstituted member of each series. A closed circle denotes the twisted system.

benzene π-orbital and a vacant p-orbital lie on the same plane. That is, the intrinsic stability of the parent benzylic carbocation is a factor which govern the resonance demand.

The r value of 0.86 for the gas-phase stability of carbocation **1** is in complete agreement with that of 0.91 obtained from the recent result of the solvolysis of α-t-butyl-α-methylbenzyl chlorides.[11) The identity of r values between the solvolysis and the gas phase stability is observed not only free coplanar carbocations but also sterically twisted one. This fact reveals that the structure of the transition state of solvolysis should be quite close to that of the intermediate **1**. Thus the twisting angle $\theta=17°$ is estimated for the transition state by Eq. (3-8), and is identical to the angle $\theta=22°$ assigned for the gas-phase cation (**1**). This further leads to a conclusion that the cation can be used as a model of resonance structure of the transition state of benzylic solvolysis. This identity of r value between the solvolysis reactivity and the corresponding gas-phase cation stability provides quite important information concerning the real picture of the solvolysis transition state. Although ρ values of gas phase cations are twice as large as those for the solvolysis, the degree of charge-delocalization into the aryl ring will remain essentially the same in the gas phase as in the solution. The solvation of the cation lowers the response to

substituent perturbation, essentially without the change in intramolecular charge-delocalization. Furthermore, the charge delocalization in the S_N1 transition state in the benzylic solvolysis should also quite close to those of the carbocation intermediate.

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