Substituent Effects on the Solvolysis of 2,2,2-Trifluoro-1,1-diphenylethyl Tosylates. II.[1] 3-Chlorophenyl- and 3,5-Dichlorophenyl-Fixed Systems

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The solvolysis rates of 2,2,2-trifluoro-1-(3-chlorophenyl)-1-(substituted phenyl)ethyl and 2,2,2-trifluoro-1-(3,5-dichlorophenyl)-1-(substituted phenyl)ethyl tosylates or bromides were conductimetrically measured at 25.0 °C in 80% aqueous ethanol. The 3-chlorophenyl-fixed series showed a bilinear Yukawa–Tsuno correlation with $\rho = -4.81$ and $r = 1.41$ for substituents more deactivating than 3,5-dimethyl, and with $\rho = -6.19$ and $r = 1.57$ for the substituent range more activating than 4-methyl. The bilinear correlation was interpreted in terms of the changing coplanarity of the two aryl rings. The 3,5-dichlorophenyl-fixed substrates gave an excellent linear Yukawa–Tsuno correlation for the substituents ranging from 4-MeO to 4-Cl with $\rho = -5.95$ and $r = 1.69$. The variable aryl rings in this series show the largest extent of resonance interaction with the extraordinary deactivated carbenium ion center by α-CF_3 and α-(3,5-dichlorophenyl) groups in the transition state. The optimization of the geometries of 2,2,2-trifluoro-1,1-diphenylethyl cation and some ring-substituted derivatives was performed at the RHF/6-31G* level. The symmetric diaryl cations have equivalently twisted conformations, while in unsymmetric ones the more stabilizing aryl group is less twisted from the plane of the positive sp^2 carbon. The observed variation of r and ρ parameters is accommodated by geometrical changes of the incipient cation.

In the solvolyses of benzylic substrates carrying strongly electron-withdrawing α-substituents, such as 2,2,2-trifluoro-1-methyl-1-phenylethyl tosylates(*p*-toluenesulfonates) (**1**) and 2,2,2-trifluoro-1-phenylethyl tosylates (**2**), the strong destabilization of the carbocationic transition state by the α-CF_3 group should provide a high demand for positive charge delocalization into the α-aryl π-system.[2] This has been demonstrated by an excellent correlation with a high r value of the Yukawa–Tsuno (Y–T) equation,[3]

$$\log(k/k_0) = \rho(\sigma^\circ + r\Delta\overline{\sigma}_R^+) \quad (1)$$

where the r value is a parameter measuring the resonance demand; i.e., the degree of resonance interaction between the aryl group and the reaction site in the rate-determining transition state.[2–6] The $\Delta\overline{\sigma}_R^+$ is the resonance substituent constant defined by $\sigma_p^+ - \sigma_p^\circ$.[3b] Thus r=0 refers to σ° and r=1.00 to the Brown σ^+.[7]

In the forgoing paper,[1] the substituent effects on the solvolyses of 2,2,2-trifluoro-1-phenyl-1-(substituted phenyl)ethyl tosylates (**3**) and 2,2,2-trifluoro-1,1-bis(substituted phenyl)ethyl tosylates (**4**) were analyzed on the basis of the Y–T equation. In Chart 1, the substituent(s) Y are usually fixed and X is varied for the analysis. The monosubstituted series **3** did not give a single linear Y–T correlation, but resulted in a clearly bilinear correlation with $\rho = -4.3$ and $r = 1.26$ for the range of deactivating substituents, and $\rho = -6.1$ and $r = 1.45$ for the range of more activating ones than 3,4-dimethyl. On the other hand, the symmetrically disubstituted series **4** gave an excellent linear Y–T correlation for the whole substituent range with a ρ value of −4.15 and an r value of 1.19. These correlation results led us to the conclusion that the two aryl rings in **4** remain in the same conformation with respect to deviation from coplanarity with the carbenium ion center in the transition state, and are both equally effective in stabilizing the rate-determining transition state by delocalization of the positive charge.

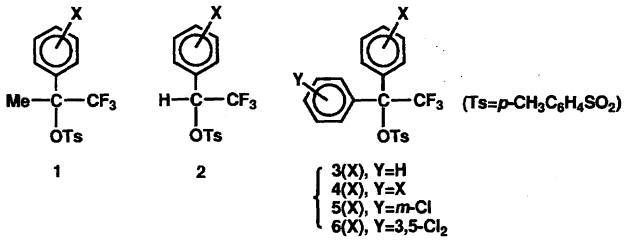

Chart 1.

Significant non-equivalence in the aryl substituent effects has also been observed in pK_{R^+} values or solvolysis rates of unsymmetrically substituted triphenylmethyl systems.[8] The pK_{R^+} values for the symmetrically trisubstituted triphenylmethanols were reported to give a completely linear Y–T correlation for the substituent range from 4-dimethylamino to 4-nitro.[3b,5b] On the other hand, less satisfactory Y–T correlations were obtained for the pK_{R^+} values of monosubstituted triphenylmethanols.[3b,5b] The three aryl rings in the triarylmethyl cation are twisted out of the plane of the carbocation center in a propeller fashion: Each aryl group of the

symmetric cations is twisted to the same degree, while the better donor group of the monosubstituted triphenylmethyl cations keeps more coplanarity with the plane of the positive sp^2 center to attain higher π-conjugative stability.

Our investigations of the behavior of carbocations in the gas phase have confirmed that the Y–T equation can be applied to substituent effects on the gas-phase stabilities of benzylic cations exactly in the same manner as it was applied to the solution phase,[9a] and that varying r values for the gas-phase stabilities of a series of benzylic carbenium ions have a magnitude identical to those of the corresponding k_c solvolyses.[2b,5,9b] Thus, the carbenium ion can be used as an appropriate model of the transition state structure of solvolysis, particularly regarding the resonance structure. The resonance demand parameter r should be related closely to the degree of π-overlapping between the aryl-π-orbitals and the incipient benzylic carbenium vacant orbital, and in fact the reduced r values for solvolyses of sterically congested α,α-dialkylbenzyl series were related to the inefficiency of benzylic resonance interaction.[10] In the present α-CF_3-benzhydryl system, where the carbenium center remains sterically under the same circumstances regardless of the fixed Y-groups, the non-planar conformation of the transition state should be determined by relative delocalization effects of two aryl groups. Thus the conformational dependence of the delocalization is better understood by the orbital overlapping in the carbenium ion intermediate rather than in the solvolysis transition state. The geometries of carbenium ions in our studies now can be estimated by the advanced ab initio MO calculation. Thus the optimization at the RHF/6-31G* level has been performed for several related carbenium ions which are twisted out of coplanarity.[11]

In order to clarify the conformational dependence of r parameter, more data for the unsymmetrically substituted X≠Y series of the α-CF_3-benzhydryl system are required. Accordingly, we now report the Y–T analysis of substituent effects on the solvolysis of the 1-(3-chlorophenyl)-2,2,2-trifluoro-1-(substituted phenyl)ethyl tosylates (**5**) and 1-(3,5-dichlorophenyl)-2,2,2-trifluoro-1-(substituted phenyl)ethyl tosylates (**6**) as the more deactivated diaryl systems. The effects of resonance demand on the reactivity and the conformation in these solvolyses are discussed in comparison with those observed for the monosubstituted diphenyl series **3** and the symmetric one **4**,[1] together with the α-(trifluoromethyl)benzyl analogue of **1** and **2**[2] (Chart 1).

Results

Kinetics. Rate constants for solvolyses of the tosylates of **5** and **6** or the corresponding bromides were measured conductimetrically at 25.0 °C in 80 vol% aqueous ethanol (80E) with initial concentrations of ca. 10^{-4} mol dm^{-3} of substrates under the same conditions as those for **1**, **3**, and **4** in the previous studies.[1,2a] All kinetic runs accurately followed first-order kinetics over 2.5 half-lives, and the reproducibility of rate constants from repeated runs was estimated to be within 1%. The rates for the reactive substrates were determined for the corresponding bromides, as listed in Tables 1 and 2, and were converted into the rates for the corresponding tosylates at 25 °C on the basis of the tosylate/bromide

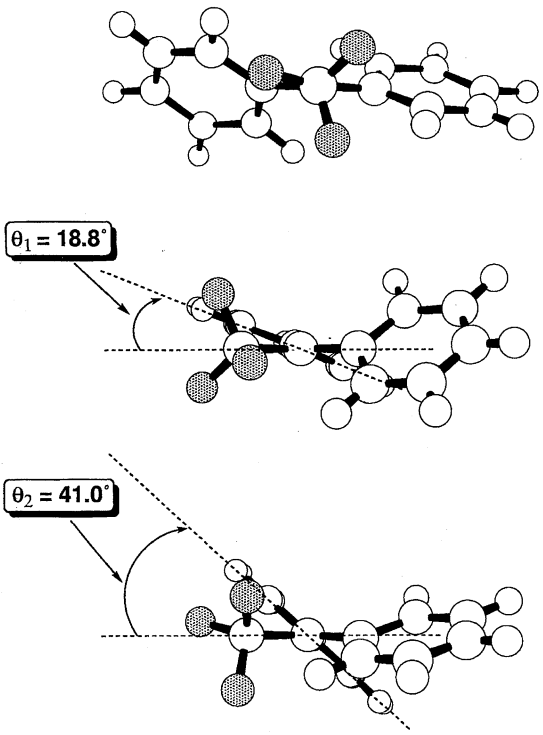

Fig. 1. Optimized structure of 2,2,2-trifluoro-1,1-diphenylethyl cation **3C**$^+$ **(H)** at RHF/6-31G* level.

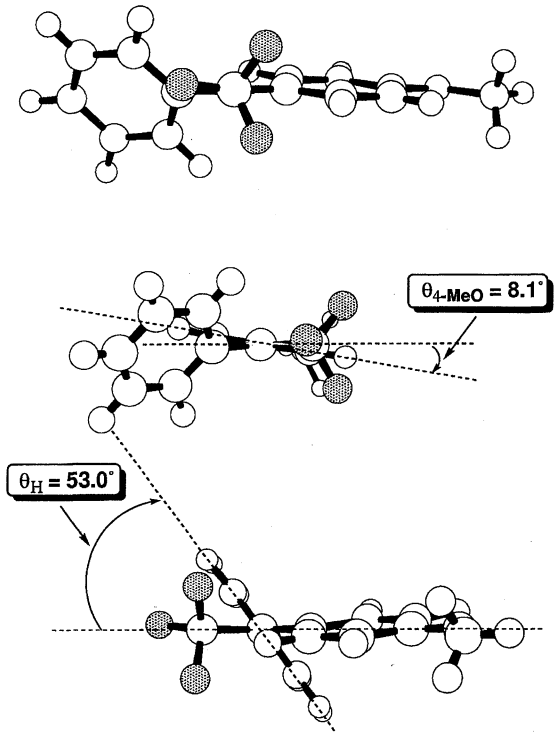

Fig. 2. Optimized structure of 2,2,2-trifluoro-1-(4-methoxyphenyl)-1-phenylethyl cation **3C**$^+$ **(4-MeO)** at RHF/6-31G* level.

Table 1. Solvolysis Rates of 1-Aryl-1-(3-chlorophenyl)-2,2,2-trifluoroethyl Systems in 80% Aqueous Ethanol

Subst.	Temp	$10^5 k_t/s^{-1}$		$\Delta H_{25}^{\ddagger}$ a)	$\Delta S_{25}^{\ddagger}$ a)
X	°C	Tosylates	Bromides	kcal mol^{-1}	cal K^{-1} mol^{-1}
4-MeO	25.0	39260000 b)	92.53	21.7	0.4
	5.0		6.183		
4-MeS	25.0	12780000 b)	30.12	22.0	−0.9
	5.0		1.941		
4-PhO	25.0	317500 b)	0.7482	23.7	−2.5
	45.0		9.853		
4-MeO-3-Cl	25.0	203800 b)	0.4803		
4-MeS-3-Cl	25.0	88380 b)	0.2083 c)	23.6	−5.5
	45.0		2.699		
	55.0		8.693		
	65.0		25.87		
3,4-Me$_2$	25.0	1803 b)	0.004250 c)	26.3	−3.9
	55.0		0.2703		
	65.0		0.9267		
	75.0		2.899		
4-Me	25.0	623.4			
3,5-Me$_2$	25.0	30.12		(23.7	4.9)
	5.0	1.576			
4-F	25.0	22.27		(23.4	3.1)
	5.0	1.215			
3-Me	25.0	12.73		(23.5	2.3)
	45.0	163.5			
H	25.0	5.279 d)			
4-Cl	25.0	3.836		(24.1	2.2)
	45.0	52.83			
3-Cl	25.0	0.07169 c,d)			

a) Activation parameters in parentheses are those for tosylates and 1 cal=4.184 J. b) Estimated from bromides reactivities based on the ratio of tosylate/bromide=4.2432×10^5 for **4** (3,5-Me$_2$) as reported in Ref. 1. c) Extrapolated from other temperatures. d) Rate data reported in Ref. 1.

rate ratio=4.243×10^5 calculated from the data obtained for **4**(3,5-Me$_2$).[1)]

As shown in Table 1, the solvolysis rate of the series **5** members varies over a range of ca. 10^8 in reactivity with varying X-substituents in 80E at 25 °C, indicating that the solvolysis rate is highly sensitive to substituent change. The rate change of the 3,5-dichlorophenyl-fixed series **6** covers a range of reactivity of ca. 10^7 for the change in the X-substituent from 4-MeO to H (or 4-Cl) (Table 2), and is more sensitive than in the 3-chlorophenyl-fixed series **5**.

Calculations. The geometries of the carbenium ions of the present system, the parent α-CF$_3$-benzhydryl cation **3C**$^+$ (H), its mono-3-chloro derivative ion **3C**$^+$ (3-Cl), the mono-4-methoxy derivative **3C**$^+$ (4-MeO), and the symmetrical di-4-methoxy derivative ion **4C**$^+$ (4-MeO) were initially examined with the ab initio MO calculations at the RHF/3-21G level. The minimum energy conformations were refined at the 6-31G* level and the potential energies associated with rotations about the C$_{ar}$–C$^+$ bonds of carbenium ions were also evaluated at the 6-31G* level. The results of these calculations are summarized in Table 3.

Geometries of all the optimized structures located at the 6-31G* level will be presented in a separate paper.[12)] The optimized structures of the carbenium ion **3C**$^+$ (H) and its mono-4-methoxy substrate, **3C**$^+$ (4-MeO), are shown in Figs. 1 and 2. In these optimized structures, the two phenyls of the parent carbenium ion **3C**$^+$ (H) are rotated by 19° or by 41° from the plane of the sp^2 carbenium center (Fig. 1). Essentially the same geometry was obtained for the optimized conformer of symmetrically di-4-methoxy-substituted carbenium ion **4C**$^+$ (4-MeO); the two 4-methoxyphenyl rings being twisted by 17° or by 40° with respect to the C$^+$–CF$_3$ bond.

The optimized structure of benzhydryl carbocation evaluated at the 6-31G* level has a potential minimum of C_2 symmetry; the two phenyl rings are rotated about the Ph–C$^+$ bonds by 16°. A similar propeller-like structure is well documented for triarylmethyl carbocations. Thus the doubly twisted conformations optimized for the above **3C**$^+$ (H) and **4C**$^+$ (4-MeO) can be regarded as the propeller-shape structure of slightly distorted C_2 symmetry, due to non-equivalent proximity effect of CF$_3$ group to both phenyl rings. The optimization at the MP2/6-31G*//RHF/6-31G* level of **3C**$^+$ (H) indicates a propeller-conformation with equivalent rotations of the two phenyls by 23° and 38° and in fact the enforced equivalent-propeller conformation (both twisted by 30°) is only a little more unstable (less than 1.2 kcal mol^{-1}) than the above optimized frozen conformer of **3C**$^+$ (H) (Table 3).

When constraining one of the phenyl groups in **3C**$^+$ (H) coplanar (θ_1=0°), the second phenyl is forced to be twisted further out of coplanarity to give a potential minimum at

Table 2. Solvolysis Rates of 1-Aryl-1-(3,5-dichlorophenyl)-2,2,2-trifluoroethyl Systems in 80% Aqueous Ethanol

Subst.	Temp	$10^5 k_t/s^{-1}$		$\Delta H_{25}^{\ddagger}$ [a]	$\Delta S_{25}^{\ddagger}$ [a]
X	°C	Tosylates	Bromides	kcal mol^{-1}	cal K^{-1} mol^{-1}
4-MeO	25.0	10470000[b]	24.66	22.1	−0.8
	5.0		1.566		
4-MeS	25.0	4361000[b]	10.28	21.9	−3.4
	45.0		111.6		
4-PhO	25.0	84320[b]	0.1987[c]	22.9	−8.0
	45.0		2.395		
	55.0		7.382		
	65.0		21.48		
4-MeO-3-Cl	25.0	57500[b]	0.1355[c]	23.6	−6.1
	45.0		1.760		
	55.0		5.766		
	65.0		16.97		
4-MeS-3-Cl	25.0	30780[b]	0.07253[c]	23.8	−6.9
	45.0		0.9638		
	55.0		3.085		
	65.0		9.404		
3,4-Me$_2$	25.0	185.3		(22.7	5.2)
	5.0	10.94			
4-Me	25.0	71.94		(23.0	4.3)
	5.0	4.098			
4-*t*-Bu	25.0	23.20		(23.4	3.5)
	45.0	297.3			
3,5-Me$_2$	25.0	2.179		(24.1	1.1)
	45.0	30.02			
4-F	25.0	1.938		(23.9	0.1)
	45.0	26.09			
3-Me	25.0	0.7588		(24.7	0.8)
	45.0	11.08			
H	25.0	0.2736[d]			
4-Cl	25.0	0.2755		(24.9	−0.3)
	35.0	1.190			
	45.0	4.333			
	55.0	14.22			

a) b) c) d) See footnotes of Table 1.

θ_2=53°. The potential energy minimum for this forced conformation is significantly (3 kcal mol^{-1}) higher than that of the most stable (doubly twisted) conformer.

On the other hand, the mono-4-methoxy-carbenium ion **3C**$^+$ (4-MeO) has an optimized structure where the 4-methoxyphenyl is much closer to the plane ($\theta_{4\text{-MeO}}$=8°), while the phenyl ring is forced to be more twisted (θ_H=53°) (Fig. 2 and Table 3). This conformation, when constraining the 4-methoxyphenyl ring to be coplanar, at $\theta_{4\text{-MeO}}$=0°, is 3.3 kcal mol^{-1} more stable than the doubly twisted conformation ($\theta_{4\text{-MeO}}=\theta_H$=30°) or 8 kcal mol^{-1} more stable than the phenyl-coplanar and 4-methoxyphenyl-twisted one (θ_H=0° and $\theta_{4\text{-MeO}}>45°$).

According to the optimized structure of the mono-3-chloro derivative **3C**$^+$ (3-Cl), the unsubstituted phenyl ring should be favored to show more coplanarity with the plane of the carbenium center rather than the 3-chlorophenyl ring, while the θ_H value is not significantly smaller than the lower θ value of the more coplanar phenyl in the equivalently twisted conformation of **3C**$^+$ (H). In fact, either the reverse conformation, θ_H=45° and $\theta_{3\text{-Cl}}$=16°, or the enforced conformation of equivalent rotation with $\theta_H=\theta_{3\text{-Cl}}$=30° appears less stable by 1.8 kcal mol^{-1}.

In the diphenylcarbenium system, the energy loss for the deviation of one phenyl ring from coplanarity must be largely compensated for by the energy gain by synchronous rotation toward increased coplanarity of the other ring. This therefore causes remarkable lowering in the potential barrier of rotation between stable conformations.

The sum of the angles of rotation of the two aryl-rings in the optimized structures, $\theta_X+\theta_Y$, remains constant at about 60° in a good approximation, regardless of the substituents. When the substituents X and Y are the same or electronically equivalent, especially in resonance character, both rings tend to take symmetrically rotated conformations; otherwise the more strongly electron-donating aryl comes closer to the coplanar conformation. The minimum steric repulsion for the single aryl planar conformation in the diarylcarbenium ions appears generally to result in a twisting angle of ca. 8° from the result of calculations.

Table 3. Geometric Parameters and Relative Stabilities for **3C**$^+$ (H), **3C**$^+$ (4-MeO), **3C**$^+$ (3-Cl), and **4C**$^+$ (4-MeO) calculated at RHF/6-31G* [a)]

Cations	Torsion angle/°		Rel. energy	Bond length/Å		
	θ_Y [b)]	θ_X [c)]	kcal mol^{-1}	C$^+$–C$_Y$ [b)]	C$^+$–C$_X$ [c)]	C$^+$–CF$_3$
4C$^+$ (X=Y=4-MeO)	16.5	40.1		1.401	1.431	1.540
3C$^+$ (X=Y=H)	18.8	41.0	0.0	1.413	1.435	1.544
	30	30	1.2	1.431	1.423	1.546
	30	35.9 [d)]	0.9	1.424	1.427	1.544
	0	53 [e)]	2.7	1.395	1.460	1.548
3C$^+$ (X=4-MeO, Y=H)	53.0	8.1	0.0	1.470	1.371	1.540
	60	0	0.9	1.480	1.365	1.541
	30	30	4.2	1.444	1.400	1.545
	0	45	9.1	1.422	1.427	1.548
3C$^+$ (X=3-Cl, Y=H)	15.5	44.9	0.0	1.402	1.447	1.544
	30	30	1.8	1.424	1.431	1.547
	44.9	15.5	1.8	1.440	1.413	1.546

a) Underlined data indicate those of the optimized structure. b) Between Y-Phenyl and C$^+$. c) Between X-phenyl and C$^+$ d) θ_{H_2} for energy minimum with one phenyl fixed at θ_{H_1}=30°. e) θ_{H_2} for energy minimum with one phenyl fixed at θ_{H_1}=0°.

Table 4. Correlation Analyses of Substituent Effects [a)]

No.	Substrates (R) [c)]	Range of subst.	n [d)]	Yukawa–Tsuno equation ρ	r	R	SD	Brown $\rho^+\sigma^+$ equation [b)] ρ^+	R	SD
1	**1** (CH_3)	4-OCH$_2$CH$_2$-3–4-CN	28	−6.29±0.05	1.39±0.02	0.9998	±0.07	−7.54±0.21	0.990	±0.49
2	**2** (H)	4-MeO-3-Me–3,5-Me$_2$	17	−6.05±0.19	1.53±0.07	0.998	±0.15	−8.27±0.91	0.921	±0.85
3	**3** (Ph)	4-MeO–3,5-Cl$_2$	18	−4.37±0.21	1.67±0.13	0.996	±0.24	−5.93±0.33	0.976	±0.60
4	**3** (Ph)	4-Me–3,5-Cl$_2$	12	−4.33±0.08	1.26±0.08	0.9990	±0.07	−4.49±0.10	0.997	±0.11
5	**3** (Ph)	4-MeO–3,4-Me$_2$	6	−6.08±0.42	1.45±0.17	0.996	±0.12	−7.39±1.52	0.925	±0.60
6	**4** (X-Ph)	4-MeO–3-Cl	14	−4.15±0.08	1.19±0.04	0.9994	±0.12	−4.74±0.14	0.995	±0.33
7	**5** (3-Cl-Ph)	4-MeO–3-Cl	13	−5.32±0.32	1.65±0.14	0.997	±0.22	−7.93±0.61	0.969	±0.71
8	**5** (3-Cl-Ph)	3,5-Me$_2$–3-Cl	6	−4.81±0.11	1.41±0.08	0.9993	±0.05	−4.87±0.54	0.976	±0.23
9	**5** (3-Cl-Ph)	4-MeO–4-Me	7	−6.19±0.52	1.57±0.20	0.996	±0.19	−8.92±1.82	0.910	±0.81
10	**6** (3,5-Cl$_2$-Ph)	4-MeO–4-Cl	13	−5.95±0.31	1.69±0.12	0.998	±0.18	−9.59±0.87	0.958	±0.82
11	**6** (3,5-Cl$_2$-Ph)	4-MeO–4-Cl	11 [e)]	−6.11±0.24	1.61±0.09	0.9991	±0.12			

a) Substituent parameters, σ°, $\Delta\overline{\sigma}^+_R$, and σ^+, employed in the present analysis are mostly the standard values except for the correction of 0.03—0.04 σ unit for the resonance parameters of 4-MeS derivatives characteristic of highly electron-deficient systems.[1,2] Literature σ value of 0.701 for 3,5-dichloro substituent (X. Creary, *J. Am. Chem. Soc.*, **103**, 2463 (1981)) was used. b) r=1.00 in the Y–T Eq. c) R in X–PhCR(CF$_3$)–OTs d) Number of substituents involved. e) Excluding 4-MeS and 4-MeS-3-Cl.

Analysis of Substituent Effects. Correlation analysis of substituent effects has been carried out for the series **5**, **6**, and closely related series by the ordinary least-squares procedure based on Eq. 1; the results are summarized in Table 4. For comparison, the Brown $\rho^+\sigma^+$ equation (r=1.00) was also applied to these sets, which gave poorer correlations (Table 4).

The behavior of X-substituents on the solvolysis of **6** is illustrated by the Y–T plot in Fig. 3. The σ^+ points (open circles) of para π-donor substituents result in a significantly split pattern. The σ^+ plots for this solvolysis are neither randomly scattered nor smoothly curved; the discontinuously split pattern of the σ^+ plot in principle is incompatible with a simple deviation from the correlation for single mechanism. In fact, the least-squares application of Eq. 1 to the series **6** affords a linear correlation of r=1.69±0.12, with correlation coefficient 0.998 and SD=±0.18 (Entry 10 in Table 4). The Y–T plot (squares) indicates no serious deviation from the resonance effect correlation over the whole range of X-substituents, except for the 4-MeS and 4-MeS-3-Cl substituents, which require slightly larger $\Delta\overline{\sigma}^+_R$ values.[1,2]

The substituent effect in the solvolysis of **5** in Fig. 4 is not correlated linearly with σ^+; the σ^+ points (open circles) of para π-donor substituents all deviate significantly in the direction of rate enhancement from the ρ_m correlation line of −4.8. Only for the range of substituents less reactive than 3,5-Me$_2$ does this ρ correlation line divide all the resonance line-segments at a constant external ratio, r=1.41 (Entry 8 in Table 4) for the series **5**. However, the Y–T plots for the strong *p*-π-donor class substituents against a Y–T $\overline{\sigma}$ scale

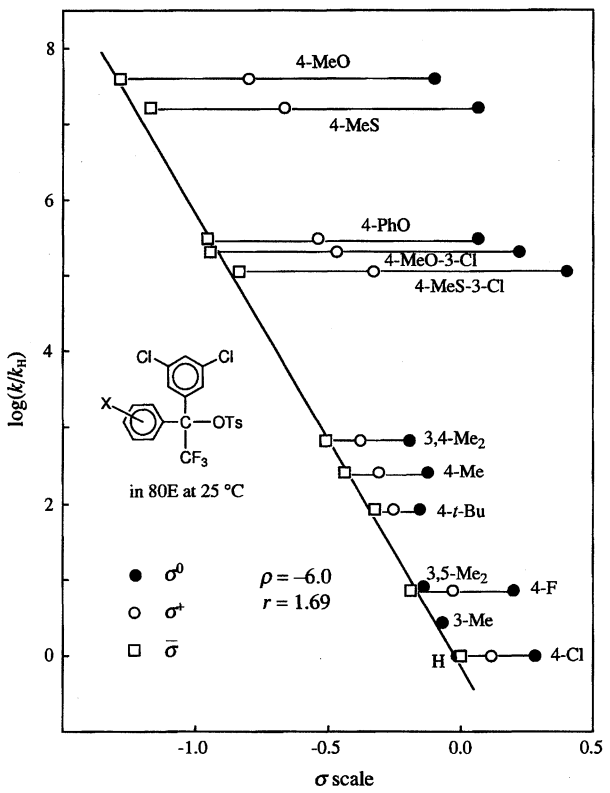

Fig. 3. The Y–T plot for the solvolysis of 1-aryl-1-(3,5-dichlorophenyl)-2,2,2-trifluoroethyl tosylates (**6**) in 80% aq EtOH at 25.0 °C; open circles, σ^+, closed circles, σ°, and open squares, $\overline{\sigma}$ for r=1.69.

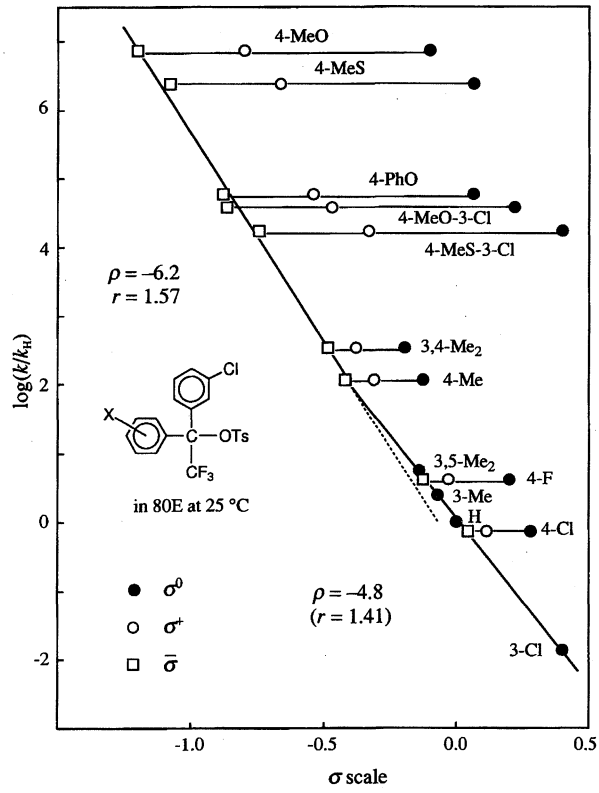

Fig. 4. The Y–T plot for the solvolysis of 1-aryl-1-(3-chlorophenyl)-2,2,2-trifluoroethyl tosylates (**5**) in 80% aq EtOH at 25.0 °C; open circles, σ^+, closed circles, σ°, and open squares, $\overline{\sigma}$ (r=1.57 for strong para π-donors and r=1.41 for weak ones).

with the same r value (not shown in Fig. 4) still appear to deviate upward from the extrapolated ρ_m line. A different r value must be operating in this range of substituents more activating than 4-Me as Entry 9 in Table 4, which gives a separate Y–T correlation with r value of 1.57±0.20 and ρ=−6.2±0.5; although the precision (R=0.996 and SD=±0.19) is slightly low, this is due to severe limitations of the range of substituent change of this partial correlation.

The solvolysis of **1** was correlated by the Y–T equation,[2a] with excellent precision (Entry 1 in Table 4). While the set of $\log(k/k_0)_6$ values for a series of X for **6** does not give a single linear correlation against $\log(k/k_0)_1$ for **1**, the same set gives an excellent correlation, if a correction for the different resonance contribution is applied, as in the following equation,

$$\log(k/k_0)_6 = (0.98 \pm 0.07)\log(k/k_0)_1 - (1.65 \pm 0.26)\Delta\overline{\sigma}_R^+. \quad (2)$$

This indicates that, while the r value for the series **6** is significantly higher than that for **1**, the ρ values are identical for both series.

On the other hand, the plot of $\log(k/k_0)_5$ values for a series of X-substituents in **5** against $\log(k/k_0)_1$ values for the corresponding substituents in **1** is bilinear, in contrast to the linear correlation (2) for **6**. The effect of a limited range of X-substituents more electron-donating than 4-alkyl in the **5** is correlated linearly with a unit slope by Eq. 3,

$$\log(k/k_0)_5 = (1.02 \pm 0.07)\log(k/k_0)_1 - (0.86 \pm 0.36)\Delta\overline{\sigma}_R^+ - 0.56, \quad (3)$$

which has a precision of SD=±0.17 and R=0.998, while the effect of the other electron-withdrawing range of X-substituents is described by a separate correlation with a reduced slope of 0.82. The bisected correlation implies that the ρ-value for the former range of strong π-donor substituents is the same as those for the series **6** as well as **1**, despite their significantly different r values. We have obtained a similar correlation between **1** and the monosubstituted series **3**.[1] Whereas the r value still changes significantly within respective Y-series, this common ρ value assigned for the range of electron-donating substituents should be the reaction constant characteristic of extremely electron-deficient benzylic solvolyses (Entries 1, 2, 5, 9, and 10 in Table 4).

These results are consistent with the results from the Y–T correlation analysis as shown in Table 4. They provide strong evidence for a constant interaction mechanism for the substituent effect in the series **6** over the whole range of substituents involved. The changes in both r and ρ values indicate a change in the interaction mechanism of the substituent effect within the reactivity range, brought about by varying X-substituents. The nonlinear Y–T correlation obtained for the series **5** may be the latter case; the substituent effects on respective ranges of substrates can be described by different partial Y–T correlations, as in Fig. 4. However, it seems

unlikely that within the same range of reactivities where the electron-deficiency of the reaction center remains apparently the same as that for the symmetric series **4**, unsymmetrically substituted series **3** and/or **5**, particularly, would involve a significant changeover in the substituent interaction mechanism.

Discussion

As we have already pointed out, highly electron-deficient carbocation reactions are generally characterized by a high resonance demand r of 1.3—1.5 in Eq. 1 with the ordinary size of ρ value.[2,5] The Y–T correlations for a series of typical benzylic solvolyses reveal that the resonance demand usually increases as the carbocation becomes unstable.[5] The ρ value tends to increase with enhanced destabilization of incipient cation, attaining a ceiling value of -6,[2b,5] which is in all the cases distinctly lower than the reported ρ^+ values based on the σ^+ analysis.[13] The r value for the effect of X-substituents in the coplanar phenyl increases with deactivation by electron-withdrawing Y substituent in the fixed aryl-group, e.g., for Y=H, 3-Cl, and 3,5-Cl_2. The r value of 1.69 given for the series **6** must be related to the resonance demand characteristic of the solvolysis forming extremely deactivated carbenium ions; a slightly lower r value of 1.61 is obtained by excluding the 4-methylthio substrates with a slightly improved precision (Entry 11 in Table 4). The resonance demand r of 1.6—1.7 for this system, the ceiling value observed in benzylic solvolyses, is ascribed to the highest extreme of the demand for the exalted resonance stabilization of the transition state of the extremely electron-deficient system, while keeping the ρ value constant at ca. -6.

In Fig. 5 are displayed the effects of varying X-substituents in solvolyses of the 1,1-diaryl-2,2,2-trifluoroethyl system for a series of subsidiary Y groups, **3**, **4**, **5**, and **6**. The substituent effects of strong p-π-donors in individual series are also plotted against the best-fit Y–T $\overline{\sigma}$ scales with individual r values; r=1.45 for **3**, r=1.57 for **5** and r=1.69 for **6**, and the effects of substituents in the symmetric diaryl series **4** as a reference are plotted against $\overline{\sigma}$ values with r=1.19.

The two aryl groups in the present 1,1-diaryl-2,2,2-trifluoroethyl system cannot simultaneously attain the coplanar conformation in full conjugation because of the steric congestion in this diarylcarbenium transition state as observed for **3** and **4** in the previous paper.[1] It is known that in diphenylcarbenium ions the molecule adopts a propeller-shaped twisted conformation to be relieved from the steric repulsion, but also that the twist angle will be a minimum to favor the positive charge delocalization into the ring.

Any symmetrically disubstituted diphenylcarbenium ion **4**C^+ has a preferred conformation in which the two phenyl rings are twisted essentially equivalently out of the plane of the C^+-center. For unsymmetrically substituted diphenylcarbenium ions, the propeller shape is not symmetrical and the X-substituted ring with electron-donating groups becomes close to coplanar with the carbenium α-carbon due to an enhanced delocalization of the ring electrons. This will lower the electron demand on the Y-aryl ring, which

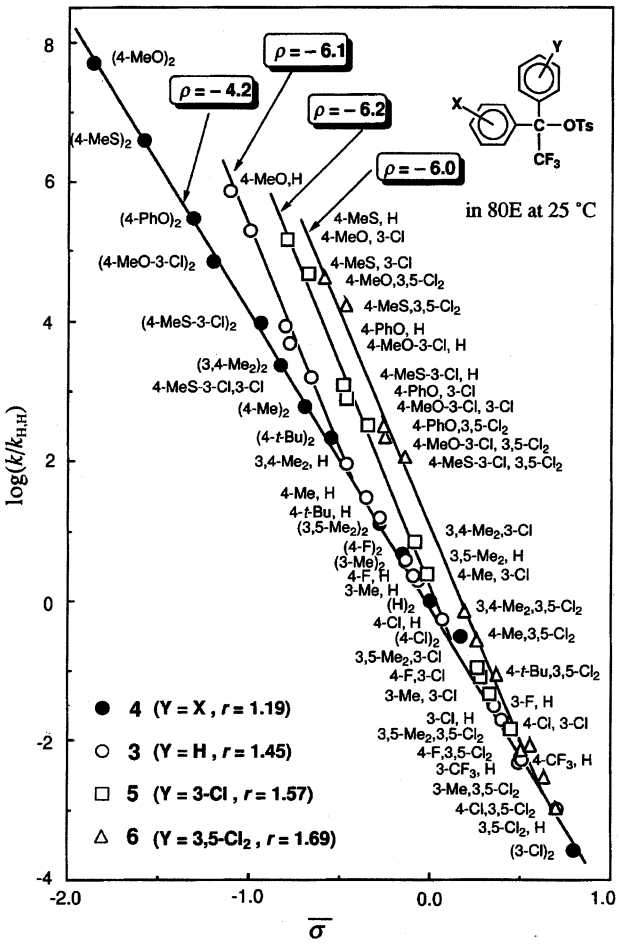

Fig. 5. Substituent effects on the solvolysis of 1,1-diaryl-2,2,2-trifluoroethyl tosylates in 80% aq EtOH at 25 °C; open circles, (**3**), closed circles, (**4**), open squares, (**5**), and open triangles, (**6**).

in turn will be forced further out of the plane. The deviant behavior of the two aryl groups should be ascribed to loss of coplanarity with the carbenium center, depending mainly upon their different resonance capabilities (Fig. 6). But the correlation for the range of non-activating to deactivating X-substituents should be referred to the substituent effect from the twisted X-aryl ring in **5**. Even so, the fixed (Y=3-Cl) ring may not enter into nor deviate more out of coplanarity but will keep an equivalently twisted conformation with variable

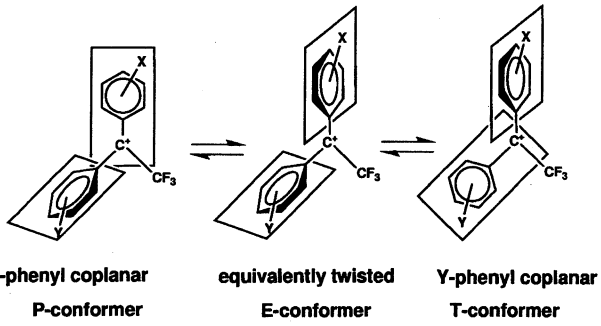

Fig. 6. Coplanarity change in 1,1-diaryl-2,2,2-trifluoroethyl cation.

X-aryl ring as in the symmetric diaryl system **4**.

In the series **6**, all variable X-substituents are more strongly π-donating than 3,5-dichloro substituent of the fixed aryl Y. Thus the conformation of the transition state as well as the carbenium intermediate should be assigned to the conformation with the X-aryl being coplanar and the Y-aryl (Y=3,5-Cl_2) being twisted by $\theta_Y \gg 30°$, which is close to the geometry optimized for the mono-4-methoxy carbenium ion of **3C**$^+$ (4-MeO) as in Fig. 2. Thus the r value of 1.69 should be a reflection of the effect of X-substituents of the coplanar aryl group.

For the range of X-substituents from 4-MeO to 3,4-Me_2 in the monosubstituted series **3**(X), the conformation should be closely related to the optimized geometry of the mono-4-MeO carbenium ion **3C**$^+$ (4-MeO) in Fig. 2. The **3C**$^+$ (X) ion of which the X substituents are of comparable polarity to the fixed substituent Y should have the same conformation as the optimized one of equally twisted structure ($\theta_X=\theta_Y=30°$) in Fig. 1. The r value of 1.45 for the electron-donative substituent range in **3** (Entry 5 in Table 4) may be referred to the effect of coplanar-aryl substituents ($\theta_X \doteqdot 0°$), and the r of 1.26 for weakly electron-donating substituents (Entry 4 in Table 4) may be referred to the effect of substituents X in the aryl twisted by $\theta=30$—$35°$.

In the case of the series **5**, the conformations are assigned in a similar way for a series of X-substituents; since the conformation of the symmetrical **5**(3-Cl) should be assigned as an equivalently twisted one, i.e., $\theta_X \doteqdot \theta_Y=30$—$35°$, that for strongly π-donating substituents should be essentially coplanar, while that for the remainder will be twisted appreciably but no more than 30°. The r value of 1.57 for the range of strong π-donor substituents from 4-MeO to 4-Me may be related to the effect of the coplanar X-substituted aryl group $\theta_X \doteqdot 0°$. The slightly reduced r value (Entry 8 in Table 4) assigned for the range from 4-Me to H or 4-Cl, though not so accurate, may be related to the effect of the conformer being a little more coplanar ($\theta_X \doteqdot 20$—$25°$) than the equivalently twisted one.

Whereas the variation in the aryl-coplanarity in the present cation system provides a plausible explanation for the varying resonance demand for respective series, it is noteworthy that the ρ-value is subject to change from series to series and also within individual series of substituent effects. Nevertheless, the bilinear correlation within individual Y-series (in Fig. 5) evidently occurs but can hardly be attributed to any mechanistic change. The variation of ρ value in a series of solvolyses of closely related mechanism is often ascribed to the shift of the transition state coordinate.[14] The reduction of ρ value observed in highly congested α,α-dialkylbenzyl solvolyses was interpreted in terms of the relief of the ground state strain of reactant at the transition state.[14] In the present diarylcarbenium system, however, the steric congestion around the reaction site should be maintained constant throughout the series regardless of aryl-substituents, in the ground state reactant as well as in the transition state or the intermediate. The Hammond shift of transition state coordinate by substituents does not appear to be significant for the whole range of substituent change, because of the excellent linear correlation for the range from 4-methoxy to 3-chloro substrates in the symmetric series **4**.

Clearly the ρ values also are closely related to the geometry, i.e., the angular deviation from coplanarity in the intermediate. It is important that the strong π-donor X-substituents in any series, **3**, **5**, and **6**, regardless of Y-substituents, all afford the same ρ value as high as -6.1, which is characteristic of extremely electron-deficient carbocation systems (e.g., **1** and **2**). Those substituent effects should be related to the optimal substituent effects of X-groups in the coplanar aryl ring. On the other hand, the range of less electron-donating X substituents in any series is found again to give a constant ρ value of -4.2, which may be related to the value for the substituent effects of aryl groups twisted by $\theta \doteqdot 30°$. The same ρ value is assigned to the symmetric diaryl series **4** with constant geometry ($\theta_X=\theta_Y \doteqdot 30°$). From a statistical point of view, these estimates of ρ values should be rather reliable and little dependent upon the r-values applied; the ρ value evaluated for the former substituent range relies essentially upon the polarity (or non-resonance) effects of the substituents of the 4-methoxy and 4-methylthio analogues having nearly same $\Delta\overline{\sigma}_R^+$ values. The ρ value for the latter substituent range depends almost exclusively on meta substituents which are not susceptible to the resonance demand of the system. Even in the gas-phase carbenium ion systems, the steric loss of coplanarity brings about a significant decrease in the ρ as well as r values.[10b,15] The significant diminution of ρ-value caused by simple rotation from coplanarity essentially without change in the substituent–carbenium center distance (X_{Ar}–C^+) cannot be interpreted by the ordinary field-effect theory.[16] It follows that either the extent of π-delocalization to the carbenium p-orbital or the π-bond order of C_{ar}–C_α bond plays a significant part in the attenuation of the polar effect of substituents.

Experimental

Materials: 1-(3-Chlorophenyl) and 1-(3,5-dichlorophenyl)-2,2,2-trifluoro-1-ethanones required for preparation of alcohol precursors of solvolysis substrates were synthesized according to Stewart's procedure of the Grignard reaction of 3-chloro- and 3,5-dichlorobromobenzenes with trifluoroacetic anhydride at -78 °C in a dry ice-acetone bath, respectively.[17]

2,2,2-Trifluoro-1-phenyl-1-ethanones were converted into the corresponding 1-aryl-1-(3-chlorophenyl or 3,5-dichlorophenyl)-2,2,2-trifluoroethanols by the Grignard reaction with substituted phenylmagnesium bromide at ice-bath temperature. The tertiary alcohols obtained were purified by column chromatography on silica gel.

1,1-Diaryl-2,2,2-trifluoroethyl tosylates were synthesized according to Tidwell's method[13,18] as described in the previous paper[1] and were purified by recrystallization from ether–hexane.

1,1-Diaryl-2,2,2-trifluoroethyl bromides were prepared from the alcohols and phosphorus tribromide by essentially the same procedure reported by Liu et al.[19] as described before.[1] The bromide was purified through column chromatography on alumina. Some of bromides were only slightly purified and were directly utilized for kinetic measurements.

Physical constants and analytical data of alcohols, tosylates, and bromides are summarized in Table 5.

Table 5. Physical and Analytical Data of 1,1-Diaryl-2,2,2-trifluoroethyl Alcohols, Tosylates, and Bromides

Subst.		Mp	Carbon/%		Hydrogen/%	
X	Y	°C	Found	Calcd	Found	Calcd
Alcohols						
4-MeO	3-Cl	Liq.	56.63	56.89	3.86	3.82
4-MeS	3-Cl	Liq	54.26	54.14	3.73	3.63
4-PhO	3-Cl	57.8—59.0	63.59	63.42	3.79	3.73
4-MeO-3-Cl	3-Cl	69.7—70.0	51.33	51.31	3.24	3.16
4-MeS-3-Cl	3-Cl	85.0—87.5	49.17	49.06	3.07	3.02
3,4-Me_2	3-Cl	Liq.	60.91	61.06	4.60	4.48
3,5-Me_2	3-Cl	Liq	61.22	61.06	4.70	4.48
4-Me	3-Cl	Liq.	59.76	59.91	4.08	4.02
3-Me	3-Cl	54.0—56.0	59.84	59.91	3.99	4.02
4-F	3-Cl	54.9—56.7	55.18	55.19	3.09	2.98
4-Cl	3-Cl	Liq.	52.48	52.36	2.96	2.82
4-MeO	3,5-Cl_2	Liq.	51.47	51.31	3.24	3.16
4-MeS	3,5-Cl_2	106.3—107.6	49.27	49.06	3.03	3.02
4-PhO	3,5-Cl_2	Liq.	57.97	58.13	3.05	3.17
4-MeO-3-Cl	3,5-Cl_2	109.5—109.9	46.76	46.72	2.63	2.61
4-MeS-3-Cl	3,5-Cl_2	126.0—128.2	45.08	44.85	2.57	2.51
3,4-Me_2	3,5-Cl_2	Liq.	54.78	55.04	3.78	3.75
3,5-Me_2	3,5-Cl_2	88.0—88.8	55.08	55.04	3.86	3.75
4-Me	3,5-Cl_2	Liq.	53.54	53.76	3.24	3.31
3-Me	3,5-Cl_2	Liq.	53.62	53.76	3.39	3.31
4-*t*-Bu	3,5-Cl_2	60.5—62.5	57.47	57.31	4.62	4.54
4-F	3,5-Cl_2	Liq.	49.71	49.59	2.42	2.38
4-Cl	3,5-Cl_2	Liq.	47.61	47.29	2.37	2.27
Tosylates						
3,5-Me_2	3-Cl	61.5—62.0	58.84	58.91	4.33	4.30
4-Me	3-Cl	41.8—42.3	58.00	58.09	4.02	3.99
3-Me	3-Cl	68.2—68.9	58.08	58.09	4.03	3.99
4-F	3-Cl	70.8—72.6	54.97	54.97	3.33	3.29
4-Cl	3-Cl	76.9—79.2	53.02	53.07	3.22	3.18
3,4-Me_2	3,5-Cl_2	66.9—67.4	54.98	54.88	3.88	3.80
3,5-Me_2	3,5-Cl_2	94.4—95.8	54.94	54.88	3.76	3.80
4-*t*-Bu	3,5-Cl_2	67.3—68.0	56.44	56.50	4.37	4.36
4-Me	3,5-Cl_2	72.0—73.8	54.15	54.00	3.56	3.50
3-Me	3,5-Cl_2	105.0—107.0	53.71	54.00	3.55	3.50
4-F	3,5-Cl_2	94.8—96.5	51.23	51.13	2.78	2.86
4-Cl	3,5-Cl_2	133.5—135.3	49.57	49.48	2.82	2.77
Bromides						
4-MeS	3-Cl	35.0—35.5	45.72	45.53	2.89	2.80
3,4-Me_2	3-Cl	49.9—51.5	50.90	50.89	3.49	3.47

Solvents:[1,2a] Commercial 95% ethanol was dehydrated twice by heating under reflux with magnesium ethoxide and distilled. Deionized water was refluxed with $KMnO_4$ and the distillate was redistilled immediately before use. Eighty percent aqueous ethanol (80E) was prepared by mixing corresponding volumes of ethanol (80) and water (20) at 25 °C.

Kinetic Measurements: Solvolysis rates were measured by a conductimetric method as described before.[1,2a] The first-order rate constants were determined by the least-squares computer program; the precision of fit to first-order kinetics was generally satisfactory over 2.5 half-lives, with a correlation coefficient >0.99998.

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