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The Estimation of the Electronic Effects of Cyclopropyl and 2,2-Dichlorocyclopropyl Groups

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The normal substituent constant, σ^0, and the resonance substituent constant, $\Delta\bar{\sigma}_R^+$, in the Yukawa and Tsuno treatment of cyclopropyl and 2,2-dichlorocyclopropyl were determined by the ionization of *m*-, *p*-substituted phenylacetic acids in 50% aqueous ethanol and by the solvolysis of α-(*m*-, *p*-substituted phenyl) ethyl chlorides in 80% aqueous acetone. For cyclopropyl, the obtained σ^0 value indicates an inductive electron-attracting behavior, while the $\Delta\bar{\sigma}_R^+$ value indicates a marked enhancement of the electron-releasing resonance effect on the electron deficient reaction center compared with alkyl groups. A minor resonance contribution was observed for the 2,2-dichlorocyclopropyl group.

It is well known that cyclopropane derivatives are remarkably different in their chemical properties compared with other cycloalkanes and alkanes. Of particular interest is the fact that the cyclopropane ring may enter into conjugated systems. Since Walsh[1] concluded, from his molecular orbital caluculations, that the cyclopropane ring posessed properties of a π bond character, numerous spectroscopic[2,3] and kinetic studies[4–11] have been carried out to examine the electronic properties of the cyclopropane ring. However, the influence of the cyclopropane ring is complicated by steric, inductive, and resonance effects. In order to attain a better understanding of the chemical behavior of the cyclopropane ring, it appeared to be of interest to estimate strictly the electronic contribution of the cyclopropyl group, using a system in which the steric factor is neglected.

The purpose of the present work has been to evaluate the electronic effect of the cyclopropyl group on the basis of a linear free-energy relationship. The σ^0-values[12–14] of cyclopropyl and 2,2-dichlorocyclopropyl have been determined from the dissociation of *m*-, *p*-substituted phenylacetic acids in 50% aqueous alcohol at 25°C, while the $\Delta\bar{\sigma}_R^+$ value in the Yukawa and Tsuno equation[14] has been determined from the solvolysis of α-(*m*-,*p*-substituted phenyl) ethyl chlorides in 80% aqueous acetone at 45°C.

Experimental

Materials. The materials were identified by means of spectroscopic and gas-chromatographic measurements and by elemental analyses. The NMR spectra were measured on a JEOL JMN-C-60HL (60MHz) spectrometer in CCl_4, with tetramethylsilane as the internal standard.

The unsubstituted and *p*-nitrophenylacetic acids were obtained commercially. The *m*-nitro derivative was obtained by the hydrolysis of the appropriate nitrile. The other phenylacetic acid derivatives were prepared by a modified Willgerodt reaction, using sulfur and morpholine, from the appropriate acetophenones. The acids were purified by recrystallization. The melting points are listed in Table 1. The syntheses of cyclopropylbenzene derivatives will be described below.

2,2-Dichlorocyclopropylbenzene. Sodium *t*-butoxide (145g) was vigorously stirred into a solution of styrene (73 g) and chloroform (167 g) in 500 ml of *n*-hexane cooled in water bath. The reaction mixture was then hydrolyzed by being added to 500 ml of ice-water. The hexane layer and hexane extracts were combined and dried with silica gel pellets, and the hexane was removed under reduced pressure. The product was distilled through a Widmer column fitted with a glass spiral core. Yield 92 g (70% from styrene). Bp 120°C/20 mmHg, NMR: δ 1.53—2.02 (2H, multiplet), 2.60—2.95 (1H, triplet), 7.15 (5H, singlet).

Cyclopropylbenzene. To a solution of 2,2-dichlorocyclo-

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TABLE 1. MELTING POINTS OF PHENYLACETIC ACIDS

Substituent	Mp (°C)
H	78—79
p-$\mathrm{CH_3}$	90—92 (92—93)[a,b,c]
p-$\mathrm{C_2H_5}$	91 (91.5—92)[c]
p-c-$\mathrm{C_3H_5}$	84.5
p-c-(2,2-$\mathrm{Cl_2}$-$\mathrm{C_3H_3}$)	110—111
p-$\mathrm{C_6H_5O}$	161 (79.5)[c]
p-Br	114 (114—114.5)[c,d]
p-$\mathrm{NO_2}$	154—155 (153)[e,f]
m-Br	101—102.5 (101—101.5)[c,f]
m-$\mathrm{NO_2}$	117—118 (118.5—119)[a,g]

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propylbenzene (50 g) in 2-propanol (100 g), sodium metal (23 g) was added. A vigorous exothermic reaction then occurred. The mixture was allowed to stand overnight and then hydrolyzed by the addition of ice water. Cyclopropylbenzene was obtained by the hexane extraction and distillation of the dried hexane extract. Yield, 18 g (67%). Bp 77°C/30 mmHg, NMR: δ 0.50—1.00 (4H, multiplet), 1.53—2.03 (1H, multiplet), 6.71—7.37 (5H, complicated).

p-*Cyclopropylacetophenone.* Cyclopropylbenzene was acetylated in accordance with the procedure given in the literature. Pure p-cyclopropylacetophenone (GLC analysis) was obtained by fractional distillation. Bp 130°C/7 mmHg (lit, bp 114—119°C/2.5—2.9 mmHg,[15] 142°C/12 mmHg,[16] 142—145°C/9 mmHg,[17] Mp 36°C (lit, 35—36°C,[15] 36°C[16,17]) NMR: δ 0.60—1.25 (4H, multiplet), 1.62—2.21 (1H, multiplet), 2.40 (3H, singlet), 6.86—7.73 (two 2H doublets, J=8 Hz).

p-*Cyclopropylphenylacetic Acid.* p-Cyclopropylacetophenone (32 g), morpholine (30 g) and sulfur (11.2 g) were refluxed for 14 hr. Ethanol (99%, 130 ml) was then added. The mixture was heated to 80°C and filtered while hot. p-Cyclopropylphenylthioacetomorpholide was crystallized spontaneously on cooling in the filtrate. Yield, 44 g (85%). Mp 107—108°C.

The morpholide was refluxed with 300 ml of 15% potassium hydroxide for 12 hr. The alkaline solution was then acidified, and the precipitate was recrystallized from benzene. Yield, 24 g (83%). Mp 84—85°C, Found: C, 74.84; H, 6.86%. Calcd: C, 74.98; H, 6.86%.

Ethyl ester: Bp 145°C/10 mmHg, NMR: δ 0.50—0.95 (4H, multiplet), 1.17 (3H, triplet, J=8 Hz), 1.55—2.02 (1H, multiplet), 3.40 (2H, singlet), 4.02 (2H, quartet, J=7 Hz), 6.80—6.87 (4H, complicated).

p-*2,2-Dichlorocyclopropylacetophenone.* 2,2-Dichlorocyclopropylbenzene was converted to p-2,2-dichlorocyclopropylacetophenone in chloroform, using aluminum chloride and acetyl chloride at 10°C. Bp 153°C/23 mmHg, NMR: δ 1.93 (1H, doublet, J=9 Hz), 1.96 (1H, doublet, J=9 Hz), 2.50 (3H, singlet), 2.92 (1H, triplet, J=9 Hz), 7.19—7.93 (two 2H doublets, J=8 Hz).

p-*2,2-Dichlorocyclopropylphenylacetic Acid.* p-2,2-Dichlorocyclopropylacetophenone (48 g), morpholine (30 g), and sulfur (11.2 g) were refluxed gently for 20 hr. 99% Ethanol (40 ml) was then added, and the mixture was cooled with an ice bath. However, morpholide was not precipitated, but a pasty mass. To this, a 15% sodium hydroxide solution (400 ml) was added, and the mixture was refluxed for 7 hr. The mixture was filtered rapidly while hot with suction and acidified with diluted hydrochloric acid. Attempts to crystallize the resultant precipitate were unsuccessful. Methyl p-2,2-dichlorocyclopropylphenylacetate (9 g) was obtained by refluxing a mixture of the precipitate, methanol (50 ml), and concentrated sulfuric acid (5 ml) for 6 hr. Bp 122°C/2 mmHg. NMR: δ 1.68—2.05 (2H, multiplet), 2.62—2.98 (1H, triplet), 3.50—3.64 (2H, one doublet, 3H singlet), 7.20 (4H, singlet). The ester (6.5 g) was converted to the appropriate acid by alkaline hydrolysis. Yield, 4 g. Mp 110—111°C. Found: C, 54.05; H, 4.03; Cl, 29.14%. Calcd: C, 53.90; H, 4.11; Cl, 28.83%.

*α-(*p-*Cyclopropylphenyl)ethyl Alcohol.* p-Cyclopropylacetophenone (10 g) was converted to α-(p-cyclopropylphenyl)-ethyl alcohol (7 g) by $\mathrm{LiAlH_4}$ (0.8 g) reduction according to the usual procedure. Bp 109°C/3.5 mmHg. Found: C, 81.53%; H, 8.70%. Calcd: C, 81.43%; H, 8.69%. NMR: δ 0.40—1.12 (4H, multiplet), 1.20—1.40 (3H, doublet, J=6 Hz), 1.58—2.02 (1H, multiplet), 4.04—4.13 (1H, singlet), 4.38—4.78 (1H, quartet, J=8 Hz), 6.75—7.20 (4H, complicated).

*α-(*p-*Cyclopropylphenyl)ethyl Chloride.* Hydrogen chloride was passed over a solution of 7 g of α-(p-cyclopropylphenyl)-ethyl alcohol in 30 ml of dichloromethane for ten minutes. The mixture was then treated with anhydrous calcium chloride after which hydrogen chloride was again passed over for ten minutes. The reaction mixture was then filtered rapidly, and the dichloromethane and dissolved hydrogen chloride was removed under a reduced nitrogen pressure. The product was utilized for the rate measurement without further purification. Found: C, 72.88; H, 7.46; Cl, 19.44%. Calcd: C, 73.12; H, 7.24; Cl, 19.62%. NMR: δ 0.44—1.08 (4H, multiplet), 1.55—2.08 (1H, multiplet), 1.60—1.80 (3H, doublet, J=7 Hz), 4.72—5.13 (1H, quartet, J=7 Hz), 6.60—7.35 (4H, two doublets, J=8 Hz, further splits).

*α-(*m-*Cyclopropylphenyl)ethyl Alcohol.* The Grignard reagent from m-bromocyclopropyl benzene (15 g)[8] and magnesium (1.95 g) was treated with acetaldehyde (3.5 g). The mixture was then decomposed with a saturated ammonium chloride solution. Subsequent work-up by the usual method gave α-(m-cyclopropylphenyl) ethyl alcohol. Yield, 11 g. Bp 103°C/1 mmHg. NMR: δ 0.58—1.21 (4H, multiplet), 1.35—1.56 (3H, doublet, J=7 Hz), 1.70—2.20 (1H, multiplet) 2.96—3.20 (1H, singlet), 4.55—4.95 (1H, quartet, J=7 Hz), 6.80—7.35 (4H, complicated).

*α-(*m-*Cyclopropylphenyl)ethyl Chloride.* α-(m-Cyclopropylphenyl)ethyl alcohol (10 g) was converted to the appropriate chloride (7 g) by the method described above for the synthesis of α-(p-cyclopropylphenyl)ethyl chloride. Bp 78°C/3 mmHg. Found: C, 72.79; H, 7.20; Cl, 19.49%. Calcd: C, 73.13; H, 7.25; Cl, 19.62%. NMR: δ 0.45—1.16 (4H, multiplet), 1.47—2.13 (1H, multiplet), 1.71—1.80 (3H, doublet, J=6 Hz), 4.75—5.15 (1H, quartet, J=6 Hz), 6.70—7.30 (4H, multiplet).

*α-(*p-*2,2-Dichlorocyclopropylphenyl)ethyl Alcohol.* The treatment of p-2,2-dichlorocyclopropylacetophenone (10 g)

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with $LiAlH_4$ in ether gave α-(*p*-2,2-dichlorocyclopropylphenyl)ethyl alcohol (7.5 g). Bp 145°C/2.5 mmHg. Mp *ca* 35°C. Found: C, 57.18; H, 5.09; Cl, 30.68%. Calcd: C, 57.16; H, 5.23; Cl, 30.68%. NMR: δ 1.18—1.40 (3H, doublet, *J*=6.5 Hz), 1.65—2.05 (2H, multiplet), 2.58—3.00 (1H, triplet, *J*=9.5 Hz), 3.75—3.88 (1H, singlet), 4.40—4.82 (1H, quartet, *J*=6.5 Hz), 6.76—7.40 (4H, multiplet).

α-(p-2,2-Dichlorocyclopropylphenyl)ethyl Chloride. α-(*p*-2,2-Dichlorocyclopropylphenyl)ethyl alcohol (7 g) was converted to α-(*p*-2,2-dichlorocyclopropyl)ethyl chloride (5 g) with hydrogen chloride in dichloromethane. The dichloromethane and dissolved hydrogen chloride were removed under reduced pressure. The product was then used directly for the rate measurement without any further treatment. Found: C, 54.02; H, 4.15; Cl, 42.83%. Calcd: C, 52.93; H, 4.40; Cl, 42.62%. NMR: δ 1.20—2.10 (2H, multiplet), 1.70—1.90 (3H, doublet, *J*=7 Hz), 2.63—3.02 (1H, triplet, *J*=9.5 Hz), 4.82—5.20 (1H, quartet, *J*=7 Hz), 7.00—7.53 (4H, complicated).

Measurements of pK_a. The pK_a values of the phenylacetic acids were determined by the potentiometric titration of the acid with sodium hydroxide in 50% (v/v) ethanol, using a pH meter (Hitachi Horiba F-5) with glass and with reference electrodes. The titration cell was a flat-bottomed, 100 ml beaker equipped with a water jacket maintained at 25.00±0.02°C. The base was added from the titration buret graduated to 0.01 ml. The sample was stirred magnetically. The pH meter and electrodes were standardized before each run against a pH 7 buffer (a neutral phosphate standard solution) and checked against a pH 4 buffer (a phthalate standard solution). Each new batch of commercial buffer was compared with previous sample before use. The electrodes were kept immersed in the solvent for a day before the measurements. The solvent was prepared in a large quantity. A sample of each acid was weighed and dissolved in the solvent (9.0×10^{-3}mol/l). A 25 ml portion of the solution was pipetted out and transferred into the titration, cell. After the cell had been equilibrated thermally, the acid solution was titrated with a 0.02N carbonate free sodium hydroxide solution in the same solvent. The pH was measured after each small addition of the base until pH 11. The measurements were repeated two or three times. The pK_a calculations were carried out by the method described in the literature.[8,18] Identical pK_a values were obtained from the pH at one-fourth and three-fourths neutralization. No correction was made for the liquid-junction potential.

Kinetic Measurements. The rates of the solvolysis of α-phenylethyl chlorides were determined in an 80% (v/v) aqueous acetone solution.[19] An accurately-weighed amount of chloride was made up to volume in a volumetric flask (150 ml, 0.02 mol/l). The mixture was then transferred to a reaction vessel immersed in a thermostated bath. Kinetic runs below 45°C were conducted in a 200 ml flask. When the solution had reached the temperature of the thermostat, a 10 ml portion was pipetted out, transferred into 50—100 ml of cold dry acetone (to stop the reaction) and free hydrogen chloride titrated with 0.02N sodium hydroxide, using bromocresol purple as the indicator. For the runs at 55°C and 65°C, the sealed-ampule technique was used. The reactions were continued until at least 70% completion. The rate constants were calculated from the integrated form of the first-order rate equation. The rate constants from different runs agreed within 1%.

Results and Discussion

Normal Substituent Constants of Cyclopropyl and 2,2-Dichlorocyclopropyl Groups. It is desirable to determine the σ^0 from the dissociation of phenylacetic acids in water, as well as the σ from that of benzoic acid in water.[13] The substituent effect is, however, too small in these equilibria in water for us to obtain precise σ^0 values.[13,14] 50% ethanol was chosen as the medium, because in this solvent substituents influence the acid dissociation by a factor of 1.5 more than in water.[18,20] It was hoped that this solvent would result in a uniform deviation from the thermodynamic pK_a values and offer the advantage of the solubility of the acids. The ionization constants thus measured are given in Table 2. It is noteworthy that *p*-cyclopropylphenylacetic acid is measurably stronger than the *p*-alkyl derivatives.

TABLE 2. APPARENT DISSOCIATION CONSTANTS OF PHENYLACETIC ACIDS IN 50% ETHANOL AT 25°C

Substituent	pK_a (±0.01)	Substituent	pK_a (±0.01)
H	5.63	*p*-C_6H_5O	5.60
p-C_2H_5	5.78	*p*-NO_2	5.01
p-CH_3	5.74	*m*-Br	5.40
p-*c*-C_3H_5	5.72	*p*-Br	5.38
p-*c*-(2,2-Cl_2-C_3H_3)	5.60	*m*-NO_2	5.11

The effects of substituents can be correlated linearly with those on the dissociation of phenylacetic acids in water,[21] as is illustrated in Fig. 1. As would be anticipated, a precisely linear correlation is observed for σ^0, with a ρ value of 0.775 (correlation coefficient,

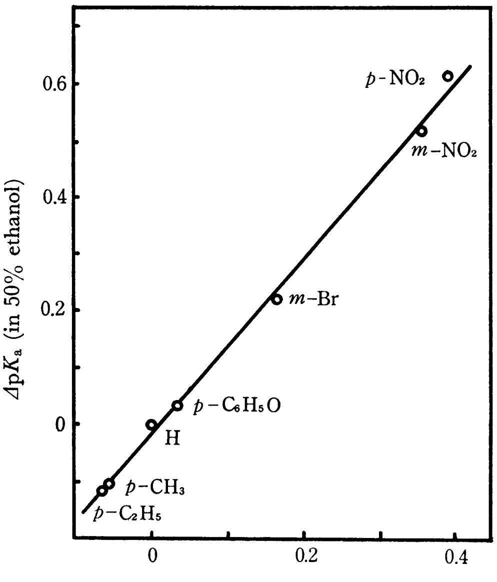

Fig. 1. Linear free energy relation for dissociation of phenylacetic acids at 25°C.

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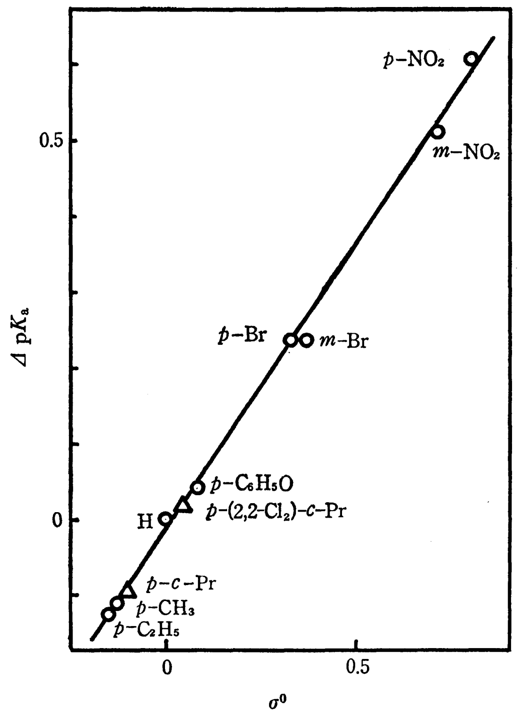

Fig. 2. Correlation of dissociation of phenylacetic acids in 50% ethanol with σ^0.

0.994, Fig. 2). It seemed reasonable to determine the σ^0 values for cyclopropyl and 2,2-dichlorocyclopropyl groups on the basis of this correlation.

TABLE 3. SUBSTITUENT CONSTANTS OF ALKYL GROUPS

Substituent	σ^0	σ	σ^+	$\Delta\bar{\sigma}_R{}^+$
H	0.000	0.000	0.000	0.000
p-CH_3	−0.124[a]	−0.170[b]	−0.311[c]	−0.187[a]
p-i-C_3H_5	−0.156[a]	−0.15[b]	−0.280[c]	−0.124[a]
p-c-C_3H_5	−0.10± 0.01[d]	−0.22[d]	−0.45[d]	−0.35[d]
p-(2,2-Cl_2-c-C_3H_5	+0.05[d]		−0.02[d]	−0.07[d]
p-t-C_4H_9	−0.174[a]	−0.197[b]	−0.256[c]	−0.082[a]
p-C_6H_5	+0.062[a]	−0.01[b]	−0.156[c]	−0.218[a]
m-CH_3		−0.069[b]		
m-c-C_3H_6		−0.036[d]		

a) Ref. 13.
b) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reaction," John Wiley & Sons, New York (1963), Chapt. 6, p. 128.
c) Ref. 23.
d) Present study.

The obtained σ^0 value for cyclopropyl (Table 3) shows more electron-withdrawing behavior than in other p-alkyl groups. This is inconsistent with Pews and Ojha's report, in which the σ^0 values for the cyclopropyl and ethyl groups, determined from the ^{19}F NMR chemical shift of fluorobenzenes,[3] are nearly identical. The tendency observed in present study, however, is in agreement with that of σ_m[8] and the kinetic results of the solvolysis, where the direct conjugative interaction between substituent and reaction site makes no contribution.[7,8,10] The relative electron-withdrawing effect of cyclopropyl is attributable to the inductive-electron attracting effect of the three-membered ring, which is constructed with a slightly increased electronegative carbon atom compared with the alkyl groups. This result is a proof of the proposed molecular orbital structures of cyclopropane,[1,22] in which the exo orbital of cyclopropane possesses considerably more s orbital character than sp^3. The σ^0 values of 2,2-dichlorocyclopropyl show a considerably strong inductive effect of the group caused by the highly electronegative chlorine atom. This is incompatible with the σ^* values[11] calculated from the pK_a of 2,2-dichlorocyclopropylacetic acid. The σ^0 values are useful for the estimation of the resonance effect of cyclopropyl and 2,2-dichlorocyclopropyl groups.

Resonance Effect of Cyclopropyl and 2,2-Dichlorocyclopropyl Groups. Considerable interest has been shown in the solvolysis of cyclopropyl carbinyl derivatives,[4] in which the cyclopropyl group exhibits large rate accelerations. In the cyclopropyl carbinyl system, however, the interpretation of the effect of the group is complicated by the immediate proximity of the positive reaction center. In order to estimate the electronic effects of cyclopropyl, the substituent constant,[23] σ^+, has been determined by several workers.[5,7,8,24] Each derived value, however, is more different than the general error in σ^+ values.

Thus, in order to probe the interaction mechanism of cyclopropyl with a cationic center more precisely, it was felt that substituent constants should be derived from the representative solvolysis reaction, in which experimental errors has been minimized. The solvolysis of α-phenylethyl chlorides[25] in 80% aqueous acetone was selected for this study because, in this reaction, the relative rates may be calculated from

TABLE 4. RATE CONSTANTS AND DERIVED DATA FOR SOLVOLYSIS OF α-PHENYLETHYL CHLORIDE IN 80% AQUEOUS ACETONE

Substituent	Temp (°C)	$k\times10^5$ (sec^{-1})	E_a (kcal)	log A
H	45	0.729 (1.00)[a]	22.3	10.1
p-c-C_3H_5	10	5.84	19.4	10.7
	20	18.9		
	30	56.6		
	45	258[b] (353)[a]		
p-2,2-Cl_2-c-C_3H_5	45	0.905 (1.24)[a]	22.4	10.4
	55	2.67		
	65	7.85		
m-c-C_3H_5	45	1.10 (1.50)[a]	24.3	11.7
	55	3.41		
	65	8.94		

a) Relative rate at 45°C.
b) Extrapolated from Arrhenius equation.

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[22] C. A. Coulson and W. Moffit, *J. Chem. Phys.*, **15**, 151 (1947).

[23] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **79**, 1913 (1957); *ibid.*, **80**, 4947 (1958); H. C. Brown, "Advances in Physical Organic Chemistry," Vol. 1, Academic Press, New York (1963), Chapt. 2, p. 34.

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[25] Ref. 13, 14, Y. Yukawa, Y. Tsuno, and Y. Kusuyama, To be published in detail.

Table 5. Relative rates of solvolysis of α-(p-alkylphenyl)ethyl chlorides in 80% aqueous acetone at 45°C.

H	1.00	p-c-C_3H_5[b]	353
p-CH_3[a]	41.5	p-2,2-Cl_2-c-C_3H_3[b]	1.24
p-C_2H_5[a]	34.0	p-C_6H_5[a]	11.1
p-i-C_3H_7[a]	34.1	m-CH_3[a]	2.11
p-t-C_4H_9[a]	19.3	m-c-C_3H_5[b]	1.51

a) Ref. 25.
b) Present work.

only Arrhenius equation and because the results previously obtained have been sufficient to elucidate the substituent effects.[13,14]

The observed rate constants are listed in Tables 4 and 5. The solvolysis of the p-cyclopropyl derivative is 353 times faster than that of the parent phenylethyl chloride and 234 times faster than the m-cyclopropyl derivatives (45°C). This marked exaltation of the p-cyclopropyl group is consistent with the results of other experimental studies of cyclopropyl systems[5,7,8] and indicates the strong contribution of the resonance effect to the transition state.

In the *para* position, some rate accelerations of p-alkyl groups have been observed, usually in electrophilic reactions; these accelerations have been attributed to hyperconjugation.[26] However, the exaltation of cyclopropyl in this study is remarkably larger than this effect. The p-cyclopropyl derivative is 10 times faster than the p-isopropyl homologue.

The solvolysis rate is depressed by a factor of 0.036 on 2,2-dichloro substitution on the p-cyclopropyl group. The relative rate of the p-2,2-dichlorocyclopropyl derivative for unsubstituted α-phenylethyl chloride is 1.24. No marked participation in the *gem*-dichlorocyclopropyl carbinyl chloride solvolysis has been observed in Robinson's work,[11] and it has been described as anomalous in comparison with other substituted cyclopropyl carbinyl solvolyses. The inductive effect of cyclopropyl increases upon the substitution of a more negative chlorine atom, and this decreases the solvolysis rate. However, the inductive effect may be decreased by the transmission of the cyclopropyl; if so, it will be impossible for it to affect the reaction center strongly. The observed results described above indicate the major importance of the resonance effect for the cyclopropyl and the depression of the effect for the 2,2-dichlorocyclopropane ring.

Product studies of α-(p-cyclopropylphenyl) and α-(p-2,2-dichlorocyclopropylphenyl)ethyl chloride solvolysis were conducted by means of an NMR examination. Only α-(p-cyclopropylphenyl) and α-(p-2,2-dichlorocyclopropylphenyl)ethyl alcohol respectively were detected.

The resonance effect of the substituents may be evaluated strictly in terms of the following linear free-energy relationship, presented by Yukawa and Tsuno:[13,14]

$$\log k/k_0 = \rho(\sigma^0 + r\varDelta\bar{\sigma}_R^+) \qquad (1)$$

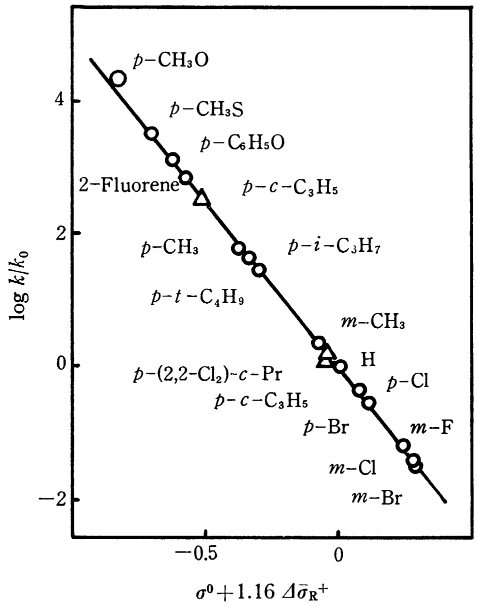

Fig. 3. Application of Eq. (1) to the solvolysis of α-phenylethyl chlorides.

where r is a constant depending on the resonance requirement of the reaction and where $\varDelta\bar{\sigma}_R^+$ measures the capacities of the substituents to supply electrons by resonance. The application of the equation to the solvolysis of α-phenylethyl chlorides gave an excellent correlation,[25] with a correlation coefficient of 0.999, as is shown in Fig. 3.

$$\log k/k_0 = -4.95(\sigma^0 + 1.16\varDelta\bar{\sigma}_R^+) \qquad (2)$$

On the basis of this correlation, the resonance contributions of cyclopropyl and 2,2-dichlorocyclopropyl were estimated using σ^0 values obtained as has been described above (Table 3).

The $\varDelta\bar{\sigma}_R^+$ for cyclopropyl indicates a marked contribution of the resonance effect. The magnitude relative to the alkyl groups is about twofold and shows the ability for a strong interaction with an electron-deficient center without ring opening. Thus, the striking exaltation in the cyclopropyl carbinyl systems is partly attributable to the behavior of the cyclopropane ring itself, although ring-opening products were generally produced. The perturbation of cyclopropyl over the hyperconjugative effect of alkyl groups may be evaluated by substructing the $\varDelta\bar{\sigma}^+_{R\,i\text{-Pr}}$ from the $\varDelta\bar{\sigma}^+_{R\,c\text{-Pr}}$. Thus, the value thus obtained (−0.226) indicates a remarkable ring-closure effect and an extra-delocalization of the intra-cyclic orbital of the cyclopropane ring. This situation is compatible with the two proposed molecular orbital models of cyclopropane.[1,22] The structure suggests that intra bonds possess considerable p orbital character and that they interact with the extra p orbitals of groups linked to the ring. Therefore, the mode of the contribution is different from the exalted hyperconjugation[27] and/or the σ-π vertical stabilization.[28]

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[26] J. W. Baker, "Hyperconjugation," Oxford Univesity Press, London (1952), p. 48.

[27] J. D. Roberts and R. H. Mazur, *J. Amer. Chem. Soc.*, **73**, 2509 (1951).

[28] T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton,. and R. S. Brown, *ibid.*, **93**, 5715 (1971).

The contribution of the resonance of 2,2-dichlorocyclopropyl is minor. The decrease in the contribution of the resonance $(\Delta\bar{\sigma}_{\mathrm{R}\ p\text{-}c\text{-}\mathrm{Pr}} - \Delta\bar{\sigma}_{\mathrm{R}\ p\text{-}(2,2\text{-dichloro-}c\text{-}\mathrm{Pr})})$ is found to be two times that of the inductive effect $(\sigma^0{}_{p\text{-}c\text{-}\mathrm{Pr}} - \sigma^0{}_{p\text{-}(2,2\text{-dichloro-}c\text{-}\mathrm{Pr})})$. The low reactivity of *p*-2,2-dichlorocyclopropyl is attributable mainly to the depression of the resonance effect by substitution with the chlorine atom. The decrease in the resonance is nearly identical with the ring-closure effect described above. It appears that, in the cyclopropyl, the developing charge was delocalized over the ring. However, in the 2,2-dichlorocyclopropyl, the chlorine atom interacts with the cyclopropane ring and the internal cyclopropane bond scarcely interacts at all with the reaction center. The exact interaction mechanism remains to be elucidated.

The solvolysis of the *m*-cyclopropyl derivative is slower than that of the *m*-methyl derivative. This fact fits previous evidence that cyclopropyl exhibits electron-attracting behavior in a system to which direct interaction with the reaction center cannot contribute as much as alkyl groups.[7,8,10,29]

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[29] T. Sharpe and J. C. Martin, *J. Amer. Chem. Soc.*, **88**, 1815 (1966).