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The Substituent Effect. XI. Solvolysis of 5-, 6-, and 7-Substituted 1-(1-Naphthylethyl) Chlorides

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Fourteen 5-, 6-, and 7-substituted 1-(1-naphthylethyl) chlorides were prepared and the solvolysis rates were determined in 80% (v/v) aqueous acetone at 45 °C. The effects of $-R$ substituents at respective positions were treated on the basis of the equation, $\log k/k_0 = \rho_i\sigma_i + \rho_\pi{}^+\sigma_\pi{}^+ = \rho(C_{ij}\sigma_i + q_r^+{}_{ij}\sigma_\pi{}^+)$. The position dependency of the inductive effect was given by $C_{ij}(=\rho_i/\rho_{i,4\alpha})$; $C_{3\alpha}=1.37$, $C_{4\alpha}=1.00$, $C_{5\alpha}=0.75$, $C_{6\alpha}=0.57$, and $C_{7\alpha}=0.72$. The C_{ij} values appear to be correlated with Dewar's simplified field function $1/r_{ij}$. The position dependency of *Pi*-electronic effect given by the ratio $\rho_\pi{}^+/\rho_{i,4\alpha}=q_{r.ij}^+$ was consistent with the prediction from the MO indices, such as Forsyth's $\Delta q_{ij}(\mathrm{ArCH_2}^+)$ parameters. The same treatment was applied also to three other naphthalene reactivities, detritiation, pK_a of α-naphthoic acids and pK_a of naphthylammonium ions. The linear $\rho_i-\rho_i$ relation holds among these reactions, suggesting a reaction-independent scheme of the inductive transmission. The $q_{r.ij}^+$ values vary at conjugate positions with reaction but not at non-conjugate positions irrespective of reactions. The results are discussed in comparison with those of relevant treatments.

We have found that the effects of substituents at the A ring positions of the α-naphthyl derivatives were successfully correlated with the following LArSR Eq. giving $\rho=-5.12$, $r=1.04$.[1]

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

This indicates that the substituent parameters, σ^0 and $\Delta\bar{\sigma}_R{}^+$, which were derived from the benzene system, are valid also for both 3α and 4α series in the naphthalene system. A more fundamental separation of the substituent effects into inductive and π-electronic effects was also examined by means of the equation

$$\log k/k_0 = \rho_i\sigma_i + \rho_\pi{}^+\sigma_\pi{}^+ \tag{2}$$

using inductive and π-electronic substituent parameters, σ_i and $\sigma_\pi{}^+$. Application to the 3α and 4α series gave excellent correlations, indicating that the parameters derived from the benzene system are valid again for the α-naphthyl A ring system. It seems that the substituent effects are given by a certain blend of unique substituent parameters, σ_i and σ_π, characteristic of only substituents and independent of parent hydrocarbons. The blend depends remarkably upon reactions and characteristically upon substituent positions as well as parent hydrocarbons. In this study a 3α/4α inductive ratio of 1.37 was observed, which is slightly larger than the 1.17 *meta*/*para* inductive ratio. The difference might not be unreasonable since the parent hydrocarbons differ.

Our interest in the analysis of substituent effects led us to carry out further studies on the naphthalene B ring positions. LSFE treatment of aromatic reactivities beyond the original benzene system enables us to accomplish the following objectives. The generality of the σ_i and especially $\sigma_\pi{}^+$ parameters can be tested most critically. If they are physically meaningful quantities characteristic of the substituent, they should be applied to any aromatic systems (naphthalene in the present case) as well as the benzene system, independent of different resonance requirement of the reactions. The study provides evidence to clarify the ambiguity in the scale of inductive parameters and subsequently in the definition of π-electronic parameters. The parametric analysis of the apparent substituent effect into the two basic components from different aromatic positions may shed light on the mode of operation of substituent effects.

The present paper is concerned with the treatment based on Eq. (2) of the substituent effects in the solvolysis of substituted 1-(1-naphthylethyl) chlorides in 80% aq. acetone, and also in other types of reactions of α-naphthyl derivatives; detritiation of α-tritionaphthalenes in $\mathrm{CF_3COOH}$ studied by Eaborn's group,[2–4] dissociation of α-naphthoic acids in 50% aq. EtOH,[5] and of α-naphthylammonium ions in $\mathrm{H_2O}$.[6]

Experimental

Materials. Preparation of 5-, 6-, and 7-substituted 1-naphthoic acids was carried out by the standard method with slight modifications. The positions of substituents at substituted 1-acetylnaphthalenes were confirmed by the NMR splitting pattern of the *peri*-hydrogen relative to that of the acetyl group.

1-Acetyl-5-bromonaphthalene: 1-Naphthoic acid was prepared by the acid hydrolysis ($\mathrm{H_2SO_4}$: AcOH: $\mathrm{H_2O}$=1 : 1 : 1)[7] of 1-naphthonitrile (bp 123—126 °C/4 mmHg) obtained from 1-bromonaphthalene with CuCN in DMF.[8] The crude acid (mp 156—159 °C; lit, mp 160 °C[9]) was brominated according to the direction of Short.[9] Recrystallization from AcOH gave (average yields 60%) 5-bromo-1-naphthoic acid, mp 263—264 °C; lit, mp 262 °C,[10] 256—256.5 °C,[8,11] 258—259 °C.[12] Purification was carried out by further recrystallization from MeOH–AcOH, mp 264—265 °C.[13]

5-Bromo-1-naphthoic acid was converted into the corresponding methyl ketone by the application of Bowman's method.[14] 5-Bromo-1-naphthoic acid was chlorinated with $\mathrm{SOCl_2}$ to give 5-bromo-1-naphthoyl chloride; mp 85—86 °C from hexane–benzene; lit,[11] mp 84—84.5 °C. A dry benzene solution (*ca.* 300 ml) of the above chloride (70 g) was added to an excess of diethylethoxymagnesio-malonate (0.6 mol) in benzene with cooling. The mixture was refluxed for 4 h, decomposed with dil. $\mathrm{H_2SO_4}$, and extracted with benzene. The crude acylmalonate was refluxed for 2 h with propionic acid (180 g) and $\mathrm{H_2SO_4}$ (50 drops). Dil. $\mathrm{H_2SO_4}$ was then

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added slowly, refluxing being continued for 22 hr. After addition of AcONa, 1-acetyl-5-bromonaphthalene was distilled to give pale yellow liquid, bp 179—182 °C/7 mmHg, which solidified soon on being left to stand (average yield, 73%); mp 55.5—56.5 °C from ligroin.

1-Acetyl-5-methoxynaphthalene: 5-Bromo-1-nitronaphthalene was prepared following the method of Newman,15) by the bromination of 1-nitronaphthalene; mp 119—122 °C from $EtOH–CHCl_3$, (63% yield); lit, mp 118—122 °C,15) 121 °C,16) 122 °C.10,17) 5-Bromo-1-nitronaphthalene was reduced with iron powder in aq. EtOH–HCl, 4 hr, giving 5-bromo-1-naphthylamine on distillation at 180—185 °C/7 mmHg (lit,18) bp 156—158 °C/1.5 mmHg) which solidified on being left to stand, mp 69—71 °C (92% yield); lit, mp 69.5—71 °C18) 69 °C,10,17) 64—69 °C.15) 5-Bromo-1-naphthylamine hydrochloride was diazotized in aq. AcOH solution of HCl, decomposed by dropwise addition to a boiling 40% aq. H_2SO_4, and extracted with benzene. The alkaline extract on acidification gave 5-bromo-1-naphthol in 40% yield, mp 142 °C from hexane–benzene, lit,10,19) mp 137 °C. Alternate process, the conversion of 5-bromo-1-naphthylamine through 5-cyano-1-naphthylamine into 5-cyano-1-naphthol, appears to be more successful. 5-Bromo-1-naphthylamine (130 g) was converted with CuCN (53 g) and DMF (150 ml) into 5-cyano-1-naphthylamine in 70% yield; bp 205—210 °C/6 mmHg, mp 141.5—142 °C (from aq. EtOH); lit,20) mp 140 °C. 5-Cyano-1-naphthol was prepared quantitatively by the diazonium method.20) The diazotized mixture of 5-cyano-1-naphthylamine (39 g) in AcOH (300 ml) and 40% aq. H_2SO_4 (400 ml) with aq. $NaNO_2$ (16 g) solution was filtered and decomposed by dropwise addition to a boiling 40% aq. H_2SO_4 solution during a period of 1 h. After being boiled for further 1.5 hr, the solid product was collected, washed, and dried (38 g). Alkaline extract from the benzene solution gave on acidification practically pure 5-cyano-1-naphthol, mp 207—210 °C. Further recrystallization from MeOH gave mp 214—215 °C; lit,20) mp 209.5 °C.

The 5-cyano-1-naphthol was hydrolyzed in aq. KOH solution. On acidification, 5-hydroxy-1-naphthoic acid was obtained. The aq. alkaline solution of the crude acid was methylated with Me_2SO_4 to give 5-methoxy-1-naphthoic acid (35 g); mp 234—235.5 °C from EtOH; lit, mp 232.5 °C,20) 230—232 °C.12) 5-Methoxy-1-naphthoic acid (28 g) was converted into 5-methoxy-1-naphthoyl chloride (24 g, mp 78—81 °C from ligroin; lit,21) mp 80—81 °C) and then to 1-acetylmethoxynaphthalene (bp 160—175 °C/7 mmHg), in the same way as the preparation of 5-bromo-1-naphthyl derivative. The yellow distillate (15 g) solidified on standing; mp 88—89 °C from ligroin.

1-Acetyl-5-ethylnaphthalene: 1-Bromo-5-ethylnaphthalene (22 g) was prepared by the Wolff-Kishner reduction22) of 1-acetyl-5-bromonaphthalene (35 g) by a method similar to that for 1-ethylnaphthalene;1) bp 130—150 °C/5 mmHg; main fraction 144—145 °C/5 mmHg. The distillate was converted without purification into 1-cyano-5-ethylnaphthalene with CuCN in DMF and then into 5-ethyl-1-naphthoic acid, using alkaline and acid hydrolysis; recrystallized. from 70% aq. EtOH, mp 150—153 °C. 1-Acetyl-5-ethylnaphthalene was synthesized from the acid by the method described for 5-bromo-1-derivative in 75% yield from the corresponding naphthoyl chloride; bp 157—160 °C/5 mmHg, mp 35.5—36 °C from hexane.

1-Acetyl-5-chloronaphthalene: 1-Chloro-5-cyanonaphthalene was synthesized from the diazonium solution of 5-cyano-1-naphthylamine. The diazotized solution of 5-cyano-1-naphthylamine (40 g) in AcOH (400 ml) and aq. HCl (concd. HCl, 100 ml) was poured into the freshly-prepared CuCl23) in concd. HCl (130 ml) with cooling, and allowed to stand two days at room temperature. The precipitates were dissolved in benzene, treated with alkaline solution and the solvent was evaporated. The crude 1-chloro-5-cyanonaphthalene (33 g) obtained was hydrolyzed by refluxing with AcOH (200 ml), H_2SO_4 (100 ml), and H_2O (100 ml) for 18 h. The acid obtained was purified by distillation of the methyl ester (27 g); bp 171—172 °C/10 mmHg (mp 63—64 °C); lit,24) bp 130 °C/2 mmHg (mp 42 °C), mp 65—66 °C; and followed by recrystallization of the regenerated 5-chloro-1-naphthoic acid (from EtOH), mp 254—255 °C; lit, mp 246—247 °C,11,12) 245 °C.24) The acid (15 g) was similarly converted into the corresponding methyl ketone *via* the naphthoyl chloride; lit,11) mp 68—69 °C. Recrystallization from hexane gave 1-acetyl-5-chloronaphthalene (9 g), mp 69.5—70 °C.

1-Acetyl-6-methoxynaphthalene: 6-Methoxy-1-naphthoic acid was prepared by the reaction of furoic acid and anisole with $AlCl_3$.25) The acid obtained was purified by distillation of the methyl ester; methyl 6-methoxy-1-naphthoate (25 g), bp 180—186 °C/7—8 mmHg. After alkaline hydrolysis, 6-methoxy-1-naphthoic acid was recrystallized from benzene, mp 191.5—192 °C; lit, mp 180—180.5 °C,25) 179—180 °C.12) The acid (19 g) was converted into the corresponding methyl ketone (10 g), distilled at 156—159 °C/4 mmHg. Recrystallization from ligroin yielded 1-acetyl-6-methoxynaphthalene, mp 66—66.5 °C; lit,26) mp 64—65 °C.

1-Acetyl-6-chloronaphthalene: 6-Chloro-1-naphthoic acid was prepared by the condensation of furoic acid and chlorobenzene with $AlCl_3$.25) The product contaminated with 7-chloro-1-isomer24) was recrystallized from benzene (67 g), mp 193—194 °C (lit,25) mp 188—189 °C), and esterified with MeOH and concd. H_2SO_4. Vacuum distillation at 167—170 °C/4 mmHg (65 g) and repeated recrystallization from MeOH gave methyl 6-chloro-1-naphthoate (30 g) melting at 66.5—67 °C; lit, mp 66—66.5 °C,24) 68—69 °C.25) Alkaline hydrolysis yielded pure 6-chloro-1-naphthoic acid (28 g), mp 221—222 °C, lit,12) mp 216—216.5 °C. The acid (20 g) was converted in the usual way into 1-acetyl-6-chloronaphthalene, being distilled at 155—156 °C/3 mmHg (14 g).

1-Acetyl-6-methylnaphthalene: 6-Methyl-1-naphthoic acid was derived by Price's method;25) mp 182.5—183 °C from benzene; lit, mp 178—179 °C,12) 176.5—177 °C.25) 1-Acetyl-6-methylnaphthalene was derived from the corresponding acid and purified by repeated fractional distillation, bp 143—146 °C/4 mmHg.

1-Acetyl-7-methoxynaphthalene: 2-Acetylaminonaphthalene (mp 134.5—135 °C from benzene; lit,27,28) mp 131—132 °C) was acetylated by the application of Brown's procedure,28) with Ac_2O in CS_2 in the presence of $AlCl_3$, and the products were recrystallized twice from 50% aq. EtOH in average yield of 47%, mp 147.5—148 °C; lit, mp 149—150 °C,27) 151 °C.28) 1-Acetyl-7-acetylaminonaphthalene (40 g) was hydrolyzed in aq. EtOH in the presence of H_2SO_4 in average yield of 90%, and recrystallized from aq. MeOH, mp 111—112 °C; lit, mp 110—111 °C,28) 108.5—110 °C.27,29)

1-Acetyl-7-aminonaphthalene (25 g) was diazotized in the usual manner in a solution of H_2SO_4 (45 ml)–H_2O (200 ml) in AcOH (100 ml), and decomposed with aq. H_2SO_4. The product was dissolved into benzene, filtered, and evaporated to give practically pure 1-acetyl-7-hydroxynaphthalene (23 g), mp 150—152 °C. Recrystallization from benzene–ligroin raised the mp to 152.5—153.5 °C; lit,27,30) mp 149—150 °C. The usual methylation with Me_2SO_4 gave 1-acetyl-7-methoxynaphthalene, bp 160—162 °C/5 mmHg, as a colorless liquid in 80% yield; mp 63.5—64 °C from hexane–benzene; lit,27) mp 63 °C.

1-Acetyl-7-chloronaphthalene: Diazotization of 1-acetyl-7-

aminonaphthalene (22 g) in aq. HCl was carried out in the usual manner. The filtered diazonium chloride solution was poured into the ice-cooled freshly-prepared CuCl[23] in HCl (100 ml). Benzene was added to the mixture with vigorous stirring and left to stand at room temperature for 2 days. The benzene layer was separated, filtered, and washed with aq. alkali and water, and crude 1-acetyl-7-chloronaphthalene was distilled at 160—172 °C/5 mmHg, which was solidified soon (12 g) and recrystallized, mp 65—65.5 °C from hexane; lit,[28] mp 64—65 °C (bp 158—160 °C/4 mmHg).

1-Acetyl-7-cyanonaphthalene: The diazonium chloride solution of 1-acetyl-7-aminonaphthalene (50 g) was poured into an aq. solution of CuCN (40 g), NaCN (20 g), and KCN (50 g) with cooling and stirring. After being left to stand overnight, brown precipitates were collected, washed with aq. alkali and water, and dried. Yellow 1-acetyl-7-cyanonaphthalene was distilled at 197—205 °C/5—6 mmHg (23 g); mp 124—125 °C from 95% EtOH.

The cyanide (10 g) was hydrolyzed with the solution of AcOH (100 ml), H_2SO_4 (50 ml), and water (50 ml) for 27 hr to give 8-acetyl-2-naphthoic acid (10 g); mp 235.5—236 °C from 80% aq. EtOH. Found: C, 72.62; H, 4.58%. Calcd for $C_{13}H_{10}O_3$: C, 72.89; H, 4.71%.

1-Acetyl-7-methylthionaphthalene: The diazonium chloride solution of 1-acetyl-7-aminonaphthalene (16 g) was poured into the cooled solution of potassium ethoxyxanthate (30 g) in water (200 ml). After being left to stand overnight, solution was added to aq. KOH (30 g) solution. The mixture was hydrolyzed, made alkaline with 30 g KOH, and methylated with Me_2SO_4. Extraction with benzene, washing with aq. alkali and water, and evaporation of benzene gave crude 1-acetyl-7-methylthionaphthalene which was distilled at 180—205 °C/8 mmHg as yellow viscous liquid (9 g); the product solidified was recrystallized from 80% aq. EtOH, mp 63.5—64.5 °C.

1-Acetyl-7-bromonaphthalene: 2-Bromonaphthalene, bp 130—132 °C/8 mmHg, mp 56—57 °C (lit, bp 122—127 °C/4.5 mmHg, mp 54—56 °C,[31] 56—56.5 °C[28]) prepared from a commercial 2-naphthylamine-1-sulfonic acid,[31] was acetylated according to the method of Girdler *et al.*,[32] using AcCl and $AlCl_3$ in nitrobenzene. The acetylated product distilled at bp 183 °C/9 mmHg was extracted with hot petroleum ether to give a product of mp 62 °C(A). The remaining oily product was purified by column chromatography on Al_2O_3 using hexane–benzene as an eluent. The first and the second fractions gave impure product (mp 70—90 °C from ligroin or hexane), which was repeatedly recrystallized from hexane to give 2-acetyl-6-bromonaphthalene, mp 104.5—105 °C; lit, mp 104—105 °C,[20] 100.5 °C[32] The mother-liquor gave a substance melting at *ca.* 50 °C, which combined with the product (A) was purified by repeated recrystallization from ligroin to give 1-acetyl-7-bromonaphthalene, mp 60—63 °C; lit, mp 63—64 °C,[28] 62—63 °C.[32]

Alcohols and chlorides were prepared according to the reported method.[1] The physical properties and the elemental analytical data of the ketones, alcohols, and chlorides are

Table 1. Physical constants and analytical data of 5-, 6-, and 7-substituted 1-acetylnaphthalenes

Subst.	Mp or (bp)	Carbon		Hydrogen		Other	
		Found	Calcd	Found	Calcd	Found	Calcd
5-MeO-α	88—89°C	78.43	77.98	6.01	6.04		
5-Et-α	35.5—36°C	84.90	84.81	6.90	7.12		
5-Cl-α	69.5—70°C	70.39	70.43	4.72	4.43	17.20	17.32(Cl)
5-Br-α	55.5—56.5°C	58.00	57.86	3.52	3.64	32.40	32.08(Br)
5-CN-α	90—91°C	79.60	79.98	4.38	4.65	6.98	7.17(N)
6-MeO-α	66—66.5°C	77.78	77.98	6.03	6.04		
6-Me-α	(143—146°C/4mmHg)	84.63	84.75	6.50	6.57		
6-Cl-α	(155—156°C/3mmHg)	70.17	70.43	4.22	4.43	17.65	17.32(Cl)
7-MeO-α	63.5—64°C[a]	77.79	77.98	6.07	6.04		
7-MeS-α	63.5—64.5°C	71.99	72.19	5.68	5.59	14.87	14.82(S)
7-Cl-α	65—65.5°C[a]	70.34	70.43	4.43	4.43	17.20	17.32(Cl)
7-Br-α	60—63°C[a]	57.86	57.86	3.62	3.64	31.82	32.08(Br)
7-CN-α	124—125°C	79.95	79.98	4.71	4.65	7.29	7.17(N)

a) For mp in the literature, see Experimental.

Table 2. Physical constants and analytical data of 5-, 6-, and 7-substituted 1-(1-naphthylethanols)[a]

Subst.	Mp	Carbon		Hydrogen		Other	
		Found	Calcd	Found	Calcd	Found	Calcd
5-Et-α	86—87°C	84.01	83.96	8.00	8.05		
5-Cl-α	63—63.5°C	69.92	69.74	5.48	5.37		
5-Br-α	89°C	57.58	57.39	4.29	4.42	31.60	31.82(Br)
6-MeO-α	67—67.5°C	77.09	77.20	6.81	6.98		
6-Me-α	60.5°C	83.69	83.83	7.34	7.58		
6-Cl-α	82—82.5°C	69.82	69.74	5.16	5.36	17.42	17.15(Cl)
7-MeO-α	37—38°C	76.97	77.20	7.08	6.98		
7-MeS-α	37—38°C	71.80	71.52	6.19	6.46		
7-Cl-α	72—73°C	69.65	69.74	5.14	5.37	16.96	17.15(Cl)

a) 5-MeO-α, liq.; it was chlorinated without further purification. 5-CN-α, mp 88.5—90 °C. H-α, mp 65.5—66 °C, bp 133—136 °C/3 mmHg.

Table 3. Physical properties and analytical data of 5-, 6-, and 7-substituted 1-(1-naphthylethyl) chlorides[a)]

Subst.	Mp or (bp)	Carbon		Hydrogen		Chlorine	
		Found	Calcd	Found	Calcd	Found	Calcd
5-MeO-α	39.5—40.5°C	70.35	70.75	5.87	5.94	16.17	16.06
5-Cl-α	62—64°C	64.12	64.03	4.39	4.48	31.39	31.50
5-Br-α	70—71°C	53.42	53.47	3.51	3.74		
6-MeO-α	47—48°C	70.75	70.75	5.80	5.94	16.27	16.06
6-Me-α	34.5—35°C	75.47	76.28	6.15	6.40	17.59	17.32
6-Cl-α	37—37.5°C	63.96	64.03	4.32	4.48	31.92	31.50
7-MeS-α	37—38°C	66.21	65.95	5.48	5.53	14.74	14.97
7-Cl-α	(154—157°C/1mmHg)	64.30	64.03	4.52	4.48	31.42	31.50
7-CN-α	80—82°C	72.44	72.39	4.70	4.67	16.18	16.44

a) 5-CN-α, mp 83—84 °C. 7-MeO-α, liq.; a slightly colored sample was employed for kinetic runs without purification. 7-Br-α, bp 145—147 °C/0.7 mmHg. H-α, bp 131—131.5 °C/5 mmHg.

Table 4. Rate constants of substituted 1-(1-naphthylethyl) chlorides in 80% (v/v) aq. acetone

Series	Subst.	Temp. (°C)	$k_1\times10^5$ (s^{-1})	Series	Subst.	Temp. (°C)	$k_1\times10^5$ (s^{-1})
5α[a)]	MeO	45	33.0	7α[c)]	MeO[d)]	25	43.2
		25	3.13			15	14.4
	Et	45	17.7			0	2.23
		25	1.67		MeS	35	27.5
	Cl	45	0.820			25	8.90
	Br	65	6.30			15	2.59
		45	0.692		Cl	65	17.9
	CN	85	8.38			45	2.12
		75	3.54		Br	65	12.9
		65	1.28			45	1.56
6α[b)]	MeO	45	16.0		CN	85	10.3
	Me	45	20.7			75	3.99
	Cl	45	1.54				

For respective series, a slightly different rate constant for the parent 1-(1-naphthylethyl) chloride was obtained; a) $k_1=12.7\times10^{-5}$, b) $k_1=12.1\times10^{-5}$, c) $k_1=11.1\times10^{-5}$. Relative rates (Table 5) were calculated by use of the corresponding k_1 value. d) slightly colored sample solutions were employed.

given in Tables 1, 2, and 3, respectively.

Solvent and Kinetics. The solvent 80% (v/v) aqueous acetone was prepared by mixing one volume of water with 4 of acetone. Different batches of aqueous acetone which gave only slightly differing rate constants (Table 4) were used without calibration for each series of rate measurements. Solvolysis was carried out at a concentration of *ca.* 0.02 mol/l.[1)] All the runs followed first order kinetics covering over 60—90% reaction within experimental error of *ca.* ±1%, and the rate constants from duplicated runs agreed within ±2% or better. The rate constants obtained at various temperatures are listed in Table 4. Almost all the rate data were based on least squares calculation with at least 10 points covering 2 half lives; those for 7-CN-α were based on initial 5 points (*ca.* 50% reaction) since the rate drifted down slightly with time.

Results and Discussion

The values of log k/k_0 for the solvolysis of substituted chlorides studied in 80% (v/v) aq. acetone at 45 °C are given in Table 5, which also includes the data for 3α and 4α derivatives.[1)] Log k/k_0 varies widely with respect to not only substituent changes but also changes of substituent position. The reactivities of MeO group at the conjugate positions are evidently higher than those at non-conjugate one, and those in the B ring positions are fairly lower than those in the A ring, the lowest being at 5α position; 4α>7α>5α>6α>3α. Schreiber and Byers found a similar sequence in the solvolysis of the methoxy-substituted 1-naphthylmethyl bromides in 80% aq. acetone and in acetic acid.[33)] The effects of Cl substituent at all positions are consistently negative and follow the sequence, 4α>7α>6α>5α>3α, which differs slightly from that of the MeO substituent. The different sequence between both substituents reflects delicately the different blends of the contribution of their *I* and *Pi* effects from respective positions.

The logarithmic relative rates for the present solvolysis at 45 °C are plotted in Fig. 1 against those for the detritiation of substituted 1-tritionaphthalenes in CF_3-COOH at 70 °C.[2)] The linear relation suggests that the contributions of the *Pi* effect relative to the *I* effect from corresponding substituents at respective positions are very close to each other in both reactions. The deviations of MeO derivative from the correlation might result from the decreased rate of the detritiation due to the special interaction of the substituent with the acidic solvent.[34)] From the slope of the plot (0.80), the ρ value for the detritiation can be estimated to be −6.3 (least squares calculation, $R=0.998$, $n=11$). This value is consistent with the ρ value (−6.4) obtained from 3α and

Table 5. Log k/k_0 values of substituted 1-(1-naphthylethyl) chlorides in 80% (V/V) aq. acetone at 45 °C

Series	Subst.	log k/k_0	E_a (kcal/mol)	log A
3α[a]	MeO	−0.570		
	Cl	−2.241*	24.8	10.9
	Br	−2.213*	24.2	10.5
	CN	−2.852*	24.0	9.7
4α[a]	MeO	3.98*		
	Me	1.475*	20.3	11.5
	Et	1.391*	21.0	11.9
	Cl	−0.658		
	Br	−0.784		
	CN	−3.51*	23.8	8.9
5α	MeO	0.415	22.2	11.8
	Et	0.144	22.2	11.5
	Cl	−1.190		
	Br	−1.264	23.6	11.0
	CN	−1.91*	22.6	9.7
6α	MeO	0.121		
	Me	0.233		
	Cl	−0.895		
7α	MeO	1.48*	19.2	10.7
	MeS	0.862*	20.9	11.2
	Cl	−0.719	22.8	11.0
	Br	−0.852	22.6	10.7
	CN	−1.84*	23.6	10.4

*) Values were obtained by extrapolation from other temperatures. a) Ref. 1.

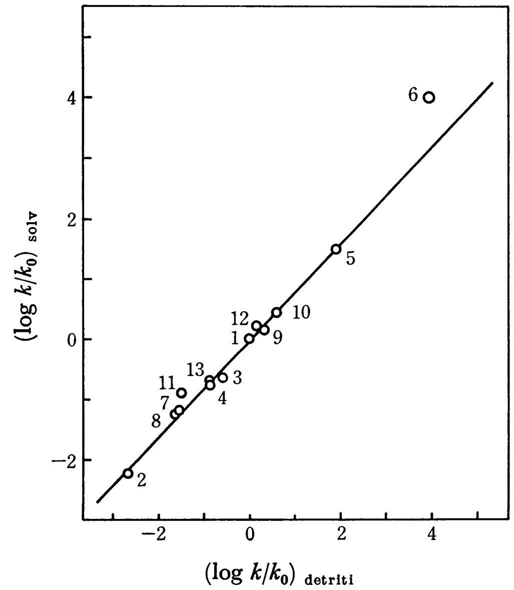


Fig. 1. LFER between the solvolysis and the detritiation rates (slope, 0.80). The points are identified as follows: (1) H-α, (2) 3-Cl-α, (3) 4-Cl-α, (4) 4-Br-α, (5) 4-Me-α, (6) 4-MeO-α, (7) 5-Cl-α, (8) 5-Br-α, (9) 5-Me-α, (10) 5-MeO-α, (11) 6-Cl-α, (12) 6-Me-α, (13) 7-Cl-α.

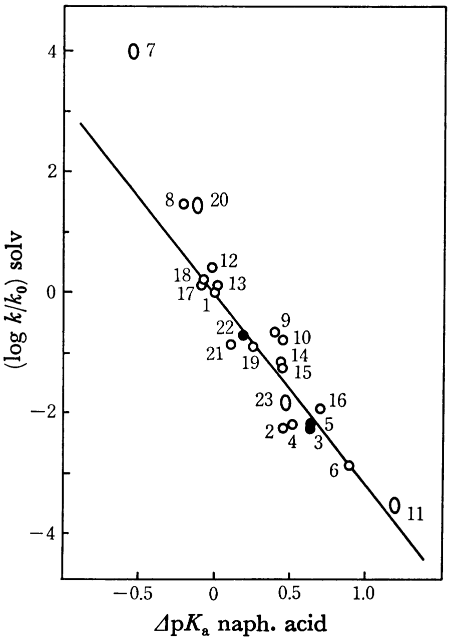


Fig. 2. Total plot of the solvolysis log k/k_0 against ΔpK_a for naphthoic acids (● corrected value for ΔpK_a was employed).
The points are identified as follows: (1) H-α, (2) 3-Cl-α, (3) corrected 3-Cl-α, (4) 3-Br-α (5) corrected 3-Br-α, (6) 3-CN-α, (7) 4-MeO-α, (8) 4-Me-α, (9) 4-Cl-α, (10) 4-Br-α, (11) 4-CN-α, (12) 5-MeO-α, (13) 5-Et-α, (14) 5-Cl-α, (15) 5-Br-α, (16) 5-CN-α, (17) 6-MeO-α, (18) 6-Me-α, (19) 6-Cl-α, (20) 7-MeO-α, (21) 7-Br-α, (22) corrected 7-Cl-α, (23) 7-CN-α.

4α derivatives by the application of Eq. (1) ($r=1.13$, $R=0.997$, $s=\pm0.14$, $n=7$). Logarithms of relative rates of the present solvolysis are plotted in Fig. 2 against ΔpK_a of the corresponding substituted 1-naphthoic acids in 50% aq. EtOH.[5,35] In contrast with the plot in Fig. 1, the correlation is not linear, but appears to be quite analogous to that observed in the case of benzene derivatives against the σ-constants. This is reasonable since the pK_a's of naphthoic acids could be regarded as the essentially unexalted σ-type reactivity.

According to the LArSR assumption,[1] such a plot for an electrophilic resonance reaction against σ may be expected only for conjugatively electron releasing (−R) substituents at the conjugate position to give the substantial upward deviations, the extents of which depend upon their resonance contribution, as observed in the benzene reactivities. The correlation line may be drawn through the origin and the points for CN derivatives for which no exaltation of resonance might be expected. The weakly conjugating groups at the less effective conjugate position lie more closely to the correlation line. With respect to the σ^+ type reactivities, on the other hand, the theory predicts for any kinds of substituents to give no downward deviations from the correlation line. The figure seems to be satisfactory for most substituents except 3α- and 7α-halogen substituents. Unfavorable dispositions of 3α- and 7α-halogens may probably be due to the improper pK_a values for the corresponding naphthoic acids. This is suggested by the following facts. Such deviations of 3α- and 7α-halogen groups were not observed in similar logarithmic plots of the present data against pK_a's of naphthylamines[6] and also those against log k/k_0 of the hydrolysis of naphthoic esters.[36,37] The calibrated points on this basis (closed circles, Fig. 2) fall in fact near the correlation line determined by non- or less conjugative derivatives. It is apparent that all the substituents at the non-conjugate 3 and 6 positions as well as the $+R$ substituents at any position fall on the correlation line for the unexalted substituent effect. The exalted contribution of substituents at any conjugate positions follows the usual order of $\Delta\bar{\sigma}_R{}^+$ values, MeO>Me>Cl, Br, as seen in the benzene reactivities, and that the enhancement of a $-R$ substituent, for example, the most effective MeO group, becomes less extensive by the positional change in the order, 4α>7α>5α>3α, 6α. This is essentially valid also for the other $-R$ substituents. The exaltation of the substituent effects in the present electrophilic reactivities is observed only for the $-R$ class substituents at the conjugate position, but not for $+R$ class substituents even at the conjugate position.

The results are in line with the general features of the substituent effects observed in the Hammett-type treatment of the benzene reactivities, especially with those characteristic of the electrophilic σ^+-type reactivities in the benzene system.[38]

From a survey of the naphthalene reactivity data in the literature, including copious ones, the reaction dependence of the substituent effect can not be overlooked.

The Hammett-type description of the naphthalene reactivities requires several sets of substituents constants such as σ_{ij}, $\sigma_{ij}{}^+$, and $\sigma_{ij}{}^-$. As seen in the benzene case, however, each set of substituent constants should be applied within the limit of closely related classes of reactivities. This is clearly illustrated by a comparison of the plots in Figs. 1 and 2. The results suggest that the exalted-resonance type electrophilic naphthalene reactivities can be treated in the same way as that for benzene by means of the equation

$$\log k_{ij}/k_0 = \rho(\sigma_{ij} + r_{ij}^+ \Delta\bar{\sigma}_{R.ij}^+) \qquad (1')$$

where the subscripts i and j represent the respective naphthalene positions to which are attached substituents (i) and the reacting side-chain (j=α in the present case). The exalted resonance contribution of substituents at effectively conjugative positions (4α,5α,7α) can be given by the second term in Eq. (1′). For all $+R$ substituents and $-R$ ones at weak conjugate positions (3α, 6α), the second term should be zero. The values of $\Delta\bar{\sigma}_{R.ij}^+$ may be defined by the differences of the apparent substituent constants between any two reference reactions in the same way as in the definition of $\Delta\bar{\sigma}_R{}^+$ in the benzene system. The treatment is applicable not only to the effect of substituents in the A ring,[1] but also might be applicable to that of substituents at all positions in the B ring, if the standard set of naphthalene σ values for respective substituents at respective positions, σ_{ij}, or more preferably the naphthalene $\sigma_{ij}{}^0$ parameters are determined. In this treatment, both σ_{ij} and $\Delta\bar{\sigma}_{R.ij}^+$ are assumed to be the parameters characteristic of a substituent as well as constants of respective naphthalene positions. The r_{ij} should then be given as a constant of a given reaction and independent of substituent positions. This treatment will be most convenient for practical use. However, a fundamental set is not immediately available nor sufficient data to verify its general applicability.

For the present purpose, to determine the position dependency of inductive and π-electronic components of substituent effects, the LSFE treatment (2) using σ_i and $\sigma_\pi{}^+$ constants appears to be more reasonable. Accordingly, we employed Eq. (2) statistically for each naphthalene position with respect to only conjugatively electron releasing ($-R$) substituents. The correlational parameters obtained by the method of least squares are given in Table 6 and substituent constants, σ_i and $\sigma_\pi{}^+$, in Table 8. The reliability of statistical ρ_i and $\rho_\pi{}^+$ parameters is strongly dependent upon the number of substituents involved as well as the variation of electronic nature of substituents. Although the limited rate data in our study restrict the precision of fit with which the parameters ρ_i and $\rho_\pi{}^+$ are determined, respective series involves at least one of each representative type of $-R$ substituents, alkoxy, halogen, and hydrogen, and covers an extensive change of reactivity.

It is seen from Table 6 that most correlations are excellent (R>0.999) and the substituent effects of $-R$ substituents at each position in the present naphthalene system can be correlated quite successfully by means of Eq. (2). The same treatment can be applied also to the effects of $-R$ substituents in other naphthalene reactivities; detritiation of substituted α-tritionaphthalenes[2] and dissociation of substituted α-naphthylammonium ions[6] and of substituted α-naphthoic acids.[5,35] The results for these reactivities are given in Table 7. In the case of detritiation, the methoxy group was not included in the calculation because of the special interaction with the acidic solvent, CF_3COOH; only methyl and halogens can be treated as ordinary substituents. Eaborn stated that the kinetic data of halogen substituents at 70 °C are of probable 15% errors due to experimental difficulties.[3] One unpreferable feature resulting from the statistical application to less sufficient data appears as the positive $\rho_\pi{}^+$ value for 6α series, to which we can not give any physical significance; probably the ρ_i and $\rho_\pi{}^+$ values for 6α series in this reaction is not reliable (see Table 7). The correlations for the amine series (R>0.997) appear to be more reliable than those for the acid series.

TABLE 6. CORRELATIONAL PARAMETERS FOR THE PRESENT SOLVOLYSIS DATA WITH RESPECT TO $-R$ SUBSTITUENTS

$$\log k/k_0 = \rho_i\sigma_i + \rho_\pi{}^+\sigma_\pi{}^+ + \delta$$

Series	ρ_i	$\rho_\pi{}^+$	δ	R[a)]	±s[b)]	n[c)]
3α[d)]	−6.96	−2.56	0.00	0.999	0.01	4(MeO, Cl, Br, H)
4α[d)]	−5.09	−17.6	−0.06	0.999	0.07	6(MeO, Me, Et, Cl, Br, H)
5α	−3.82	−4.40	−0.17	0.988	0.17	5(MeO, Et, Cl, Br, H)
6α	−2.90	−2.43	−0.04	0.997	0.07	4(MeO, Me, Cl, H)
7α	−3.66	−7.74	−0.01	0.999	0.03	5(MeO, MeS, Cl, Br, H)

a) Correlation coefficient. b) Standard deviation. c) Number of substituents involved in the calculation. d) Previous results; Ref. 1.

TABLE 7. CORRELATIONAL PARAMETERS FOR THE DATA OF α-NAPHTHYL REACTIVITIES[a)]

Reaction	Series	ρ_i	ρ_π^+	δ	R	±s	n
Detriti.[2)]	3α	−7.81	−1.31				3(Me, Cl, H)
	4α	−5.87	−23.4	−0.09	0.996	0.14	5(Me, F, Cl, Br, H)
	5α	−4.83	−3.12	−0.07	0.997	0.10	5(Me, F, Cl, Br, H)
	6α	(−4.11)[b)]	(+0.83)[b)]				3(Me, Cl, H)
	7α	−3.28	−4.01				3(Me, Cl, H)
Amine[6)]	3α	3.48	0.24	0.07	0.997	0.06	6(OH, MeO, Me, Cl, Br, H)
	4α	(2.50)[c)]	(2.41)[d)]				2(Br, H)
	5α	1.81	1.03	0.01	0.997	0.05	4(NH_2, OH, Cl, H)
	6α	1.45	0.93	0.00	0.999	0.02	4(OH, MeO, Cl, H)
	7α	1.60	1.67	0.02	0.999	0.03	4(OH, MeO, Cl, H)
Acid[5,35)]	3α	1.48	0.61	0.02	0.995	0.04	5(OH, Me, Cl, Br, H)
		1.90[e)]	0.88[e)]	0.04[e)]	0.997[e)]	0.04[e)]	5(OH, Me, Cl,[e)] Br,[e)] H)
	4α	1.38	3.08	0.06	0.991	0.09	8(NH_2, OH, MeO, Me, F, Cl, Br, H)
	5α	1.16	0.98	0.08	0.971	0.08	7(NH_2, OH, MeO, Me, Cl, Br, H)
	6α	0.87	0.92	0.02	0.996	0.02	6(OH, MeO, Me, Cl, Br, H)
	7α	0.50	0.69	−0.02	0.993	0.02	5(OH, MeO, Me, Br, H)
		0.74[f)]	0.86[f)]	−0.01[f)]	0.998	0.01[f)]	5(OH, MeO, Me, Cl,[f)] H)

a) Symbols are the same as those in Table 6. b) Less reliable value because of positive ρ_π^+ value. c) Estimated value from the interpolation of the $\rho_i-\rho_i$ plot. See text. d) Estimated value. See Table 11, footnote. e) Corrected ΔpK_a values were employed; Cl(0.64) and Br(0.64). f) Corrected ΔpK_a value was employed; Cl (0.19).

TABLE 8. SUBSTITUENT PARAMETERS[a)]

Subst.	σ_i	σ_π^+
NH_2	0.06	−0.42
OH	0.19	−0.34
MeO	0.185	−0.281
MeS	0.368	−0.285
Me	−0.045	−0.078
Et	−0.045	−0.069
H	0.000	0.000
F	0.363	−0.118
Cl	0.348	−0.070
Br	0.337	−0.054

a) Values taken from Ref. 38.

Figure 3 shows the linear relations of the sets of ρ_i's for the detritiation (A), the dissociations of amines (B), and acids (C) with the corresponding ρ_i values obtained from the present solvolysis. The linear ρ_i—ρ_i relationship holds. The deviations of 6α and 7α in the plot A may arise from the inaccuracy of ρ_i values due to insufficient number of data in the detritiation. Deviations of 3α and 7α in C might be attributed to the unreasonable pK_a values.

The dissociation of naphthoic acids can reasonably be expected to be a representative σ class reactivity. The pK_a of substituted α-naphthylammonium ions should be a typical nucleophilic reactivity, that is, the resonance exaltation of $+R$ substituents at conjugate positions are significant, while the effect of the $-R$ substituents in this set could be regarded as the unexalted class even for those at conjugate positions. Both the present solvolysis and the detritiation should belong to the electrophilic reactivity. Evidently the linear ρ_i—ρ_i relationship is generally valid in various types of reactions (Fig. 3); between reactions not only of similar contributions but also of distinctly different contributions of the π-electronic effects.

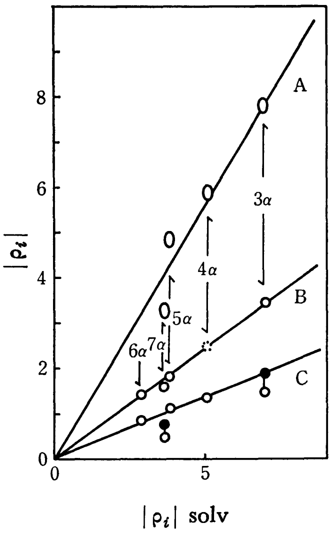


Fig. 3. $\rho_i-\rho_i$ plots.
A: the detritiation, B: the dissociation of naphthylammonium ions ($\rho_{i,4\alpha}$ can be interpolated from B line), C: the dissociation of naphthoic acids (● corrected value was employed).

In view of the positional consistency of the inductive components, it appears to be convenient to express Eq. (2) as follows.

$$\log k/k_0 = \rho(C_{ij}\sigma_i + q^+_{r,ij}\sigma_\pi^+) \quad (3)$$

where i and j represent the naphthalene ring positions bearing a substituent and a reaction site, respectively. C_{ij} is the positional constant concerning the transmission of the inductive effects. The $q^+_{r,ij}$ is the characteristic variable of reactions as well as of substituted positions, giving a measure of the π-electronic interaction of substituents at respective positions with a reaction site. The

ρ value in Eq. (3) should be identical to $\rho_{i,4\alpha}$ (-5.09 for the solvolysis) by definition.

The reference set of C_{ij} can be determined from the ratios of the ρ_i values for the present solvolysis data, since they provide the relatively precise correlations and cover a more sufficient range of reactivity changes. The $\rho_{i,4\alpha}$ value is taken as a standard, as referred to the definition of σ_i scale for benzene derivatives. The values of C_{ij} obtained are as follows. $C_{3\alpha}=1.37$, $C_{4\alpha}\equiv 1.00$, $C_{5\alpha}=0.75$, $C_{6\alpha}=0.57$, and $C_{7\alpha}=0.72$.

In order to interpret the total substituent effects in the naphthalene reactivities, various correlational equations have been developed by various workers. Dewar and Grisdale have treated the dissociation of α-naphthoic acids in terms of the equation[5]

$$\sigma_{\mathrm{ij}} = 1/r_{\mathrm{ij}}F + q_{\mathrm{ij}}M \qquad (4)$$

The field effect is simply assumed to be proportionally transmitted with the reciprocal of the simplified distance between ring carbons, which is taken into account in the first term. The second term represents the mesomeric effect, whose position dependency is assumed to be proportional to the NBMO charge of each naphthalene position.

The same type of approach was developed to interpret the substituent effects on the detritiation of α- and β-tritionaphthalenes:[2,3,39]

$$\sigma^{\mathrm{W}}_{\mathrm{ij}} = 1/r_{\mathrm{ij}}F + q^{\mathrm{W}}_{\mathrm{ij}}M^+ \qquad (5)$$

The main improvement lies in the employment of the other set of M^+ constants instead of M in Eq. (4). In these approaches, the transmission schemes of both *I* and *Pi* effects are restricted by *a priori* assumptions based upon simplified consideration. The transmission schemes were assumed to be reaction-independent. However, all these treatments were applied only to a single set of reactivities, and no definite evidence of the generality has yet been offered. Though a precise comparison may not be possible, it appears that these correlations are of considerably poorer quality than the present results. The present study does not lie on the same line of approach but aims at a purely empirical determination of the transmission schemes of *I* and *Pi* effects by means of Eq. (2). Taft and his co-workers developed the latter line of approach, not based on an *a priori* transmission scheme.[40] Their treatment is based on the assumption that the effects of substituents at respective positions can be given by the statistical blends of the terms proportional to their σ_{I} and $\sigma_{\mathrm{R}}{}^0$ parameters, as represented by

$$\log k/k_0 = \rho_{\mathrm{I,ij}}\sigma_{\mathrm{I}} + \rho_{\mathrm{R,ij}}\sigma_{\mathrm{R}}{}^0 \qquad (6)$$

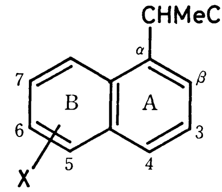
The transmission schemes of the inductive and resonance effects were thus determined as the relative $\rho_{\mathrm{I,ij}}$ and $\rho_{\mathrm{R,ij}}$ values, by means of the statistical application of Eq. (6) for all the substituents, both $+R$ and $-R$ classes, at respective naphthalene positions. However, it should be noted that Eq. (6) can only be applied within the limited range of the unexalted σ^0- or at most σ-type reactivities, as noted by Taft. Otherwise the correlation of the reactivities at the conjugate position would not be so reliable. A similar treatment was also employed for the dissociation of naphthoic acids by Swain and Lupton, in terms of their F and R parameters.[41] The same limitation discussed above applies to this treatment.

Dewar's treatment and its modifications assume that the so-called inductive polar effect of dipolar substituents is mainly controlled by the field effect. Such a field effect is ordinarily taken into account as a first approximation by certain functions of the distances, r_{ij}; $1/r_{\mathrm{ij}}$ or $\cos\theta/r_{\mathrm{ij}}{}^2$ for a special case.[5,35] It is of interest to compare the empirical C_{ij} values with familiar functions of distance accounting for the transmission of electrostatic interaction across space. The relevant parameter values are listed in Table 9. Most of the theoretical parameters indicate roughly the same trend and do not differ significantly from the characteristic order of the C_{ij} values, $C_{3\alpha}>C_{4\alpha}>C_{5\alpha},C_{7\alpha}>C_{6\alpha}$, in which the most striking feature is $C_{5\alpha}\simeq C_{7\alpha}$. As far as the α-naphthyl system is concerned, however, the simplest Dewar function, the dependence on $1/r_{\mathrm{ij}}$, appears to be the best in various field-functions, explaining completely the characteristic order as well as the magnitude of C_{ij}'s. The more sophisticated one does not appear to provide any improvement in the parallelism with the empirical C_{ij}. It is apparent that any orientational factor (function of θ or angular dependence of the field effect of dipolar substituents) is of little practical consequence. The effect, if operative at all, is relatively unimportant at least in the α-naphthyl reactivities.

TABLE 9. COMPARISON BETWEEN C_{ij} VALUES AND VARISOU FUNCTIONS OF DISTANCE

Series	C_{ij}	Ratio of $1/r$[a]	Ratio of $1/R'$[b]	Ratio of $(\cos\theta/R^2)$[c]
3α	1.37	1.15	1.15	1.11
4α	1.00	1.00	1.00	1.00
5α	0.75	0.75	0.87	0.71
6α	0.57	0.67	0.85	0.72
7α	0.72	0.75	1.00	0.58

a) r is distance between ring carbons; Refs. 5 and 35. b) R' is distance between ring carbon and reaction center; Ref. 40 ($1/r_{\mathrm{rX}}$ for $\gamma=1$). c) R is distance between center of substituent dipole and reaction center; Ref. 35.



It might be concluded as follows. (1) The positional dependence of the inductive contribution can be given by the ratio of ρ_i parameters, *i.e.*, by $C_{\mathrm{ij}}=\rho_i/\rho_{i,4\alpha}$, and remains generally a constant in the naphthalene system, independent of reactions, or more precisely, of the varied contributions of the *Pi* effects in any types of reactions. (2) Dewar's simplest field function $1/r_{\mathrm{ij}}$ may be applicable, to a practically useful approximation, generally as the transmission factor of the *I* effects in the naphthalene reactivities. The results provide in part an evidence justifying the validity of the description of the substituent effects in the naphthalene system by means of Eq. (2).

TABLE 10. COMPARISON BETWEEN THE SOLVOLYSIS ρ_π^+ AND VARIOUS THEORETICAL VALUES

Series	ρ_π^+	q_r^{+} a)	q_{ij} b)	π_{ij} c)	π'_{rX} d)	q_{ij}^{W} e)	$\Delta q_{ij}(\mathrm{ArH}^+)$ f)	$\Delta q_{ij}(\mathrm{ArCH_2}^+)$ g)
3α	−2.56	0.5	0.000	0.018	0.000	0.000	0.006	(0.010)
4α	−17.6	3.5	0.200	−0.139	0.180	0.364	0.228	(0.207)
5α	−4.40	0.9	0.050	−0.023	0.045	0.091	0.082	(0.078)
6α	−2.43	0.5	0.000	0.007	0.000	0.000	0.046	(0.046)
7α	−7.74	1.5	0.059	−0.033	0.062	0.091	0.112	(0.104)

a) Value in Eq. (3), $\rho_\pi^+/\rho_{i,4\alpha}$. b) Dewar's formal charge; Refs. 5and 43. c) Atom-atom polarizability; Refs. 5 and 35. d) Bond-atom polarizability, $\pi_{\mathrm{Br},i}$ in Ref. 40. e) Eaborn's parameter; Ref. 3. f) Forsyth's regional charge difference; Ref. 44. g) Approximate value; Ref. 45.

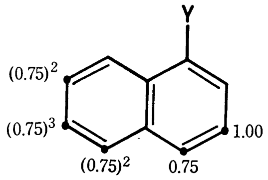


Chart 1. C_{ij} values are approximately represented as power dependence; bond fall off model.

Another instructive feature illustrated in Chart 1, where C_{ij} values are given as a power dependence upon numbers of intervening bonds to a good approximation, is of interest. It suggests that successive polarization of intervening bonds also plays an important role in the contribution of the σ-inductive effect, C_{ij}. A transmission factor per one carbon–carbon bond appears to be 0.75, when C_{ij} values are compared with each other in the naphthalene A or B ring. However, although the number of intervening C–C bond between the carbons i and j is equal for 4α, 5α, and 7α derivatives (through the most effective route), C_{ij} for 5α or 7α is 0.75 times smaller than that for 4α. This gap between rings A and B might reflect the effect of the branched ring-carbon at 9 or 10 position, at which the transmission route is separated into two ways. An explanation in terms of such branched carbons can also be applied to the fact that the ratio $C_{3\alpha}/C_{4\alpha}$ is slightly larger than C_{meta}/C_{para}, since two similar transmission routes are possible from *para* position to a reaction site in the benzene system.

Success in the separation of the contribution of the position-dependent *I* effects from the total electronic effects may provide sufficient reliability for a discussion on the remaining *Pi* effects, if the assumption of the additivity of the two effects is valid. The set of ρ_π^+ for the solvolysis (Table 6) shows that the contributions of the electron donative *Pi* effect of substituents at any conjugate position are evidently more effective than those from substituents at non-conjugate positions, just as the HMO theory predicts. The magnitude of ρ_π^+'s for the conjugate ones is appreciably different; the resulting order of the effectiveness is $3\alpha \simeq 6\alpha < 5\alpha < 7\alpha < 4\alpha$. Since the identical sequence is also found for other electrophilic reactivities such as the sets of ρ_π^+'s for the detritiation and the dissociation of amines (Table 7), it can be concluded that the sequence generally holds for $-R$ substituents in electrophilic reactivities and is inherent to the parent naphthalene π-electron system. This has been recently confirmed for $+R$ substituents in nucleophilic reactivities such as the substituent chemical shifts of OH protons of naphthols in a DMSO solution.[42]

The set of ρ_π^+'s empirically derived from the solvolysis could reasonably be compared with various sets of theoretical indices for the parent naphthalene or related hydrocarbons. The MO parameters of interest in connection with the transmission coefficient are listed in Table 10. As far as conjugate positions are concerned, the correspondence of ρ_π^+ with any HMO indices appears to be good to a rough approximation, but not necessarily complete, since small but definite electron donative *Pi* contributions are observed in the empirical set for non-conjugate 3 and 6 positions. Forsyth proposed a new set of theoretical index based on CNDO/2 approximations, $\Delta q_{ij}(\mathrm{ArH}^+)$ or $\Delta q_{ij}(\mathrm{ArCH_2}^+)$, in which the numerical values are derived from the difference of the regional charges at i'th carbon between a transition state and an initial state model.[44] The plot of the solvolysis ρ_π^+ *vs* $\Delta q_{ij}(\mathrm{ArCH_2}^+)$[45] seems to be satisfactorily linear for all positions well within the limit of approximation (Fig. 4).

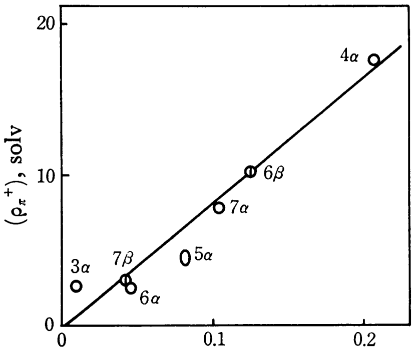


Fig. 4. The plot of solvolysis ρ_π^+ *vs.* $\Delta q_{ij}(\mathrm{ArCH_2}^+)$.[45] (Data for 6β and 7β will be seen in a next paper).

This index can take account for not only the presence of electron donative contributions at non-conjugate positions, but also the relative magnitudes of ρ_π^+'s at conjugate ones. The good coincidence between the empirical and theoretical coefficients gives another evidence verifying the description of the substituent effects in the naphthalene system in terms of the *I* and *Pi* effects by means of Eq. (3).

The results of all four different reactions indicate that the π-electronic components are dependent not only upon the substituent positions but also upon reactions even at a given conjugate position. The most intuitive parameter illustrating such a reaction dependency of the *Pi* effects is the $q_{r,ij}^+$ value in Eq. (3), which is equivalent to the *r* value for the *para* position of benzene system in Eq. (1). The values are calculated as $\rho_\pi^+/\rho_{i,4\alpha}$ and summarized in Table 11.

TABLE 11. COMPARISON OF $q_{r,ij}$ VALUES FOR SOME ELECTROPHILIC α-NAPHTHYL REACTIVITIES

Series	Reaction[a)]			
	Solv.	Detriti.	Acid	Amine
3α	0.5	0.2	0.4* (0.6)[b)]	0.1[c)]
4α	3.5	4.0	2.2	1.0[c, d)]
5α	0.9	0.6	0.7	0.4[c)]
6α	0.5		0.7	0.4[c)]
7α	1.5	0.7*	0.5*(0.6*)[b)]	0.7[c)]

*) Value is less reliable since certain discrepancies are observed in the ρ_i—ρ_i plot in Fig. 3. a) See Table 7. b) Corrected ΔpK_a value was employed. c) Secondary value based on the estimated $\rho_{i,4\alpha}$ of 2.50. d) From ΔpK_a of 4-Br-α, $\rho_{\pi,4\alpha}^{+}$ was estimated as 2.41, using the parameter of Br in Table 8.

Although the crudeness of data does not permit a precise discussion, the results appear to suggest the following. The characteristic order of the $q^+_{r,ij}$ for the conjugate positions, 4α>7α>5α, obtained in the present solvolysis can be observed also in other reactivity sets. The $q^+_{r,ij}$ for any B ring position is much smaller and at most half as large as that for the 4α position. These are in qualitative agreement with the scheme of π-electronic transmission expected from MO indices mentioned above. However, the $q^+_{r,ij}$ is evidently reaction-dependent, in contrast to the reaction-independent C_{ij} value for the inductive contribution, and that for the conjugate position varies from reaction to reaction depending upon the reactivity classes or the amount of charge at the site delocalized through π-electronic interaction. It should be noted that the value for a given conjugate position, especially that for 4α position, shows practically the same dependency upon reactions as the q_r^+ (and in the analogous way to the *r* value) for the same reactions of *para* substituted benzene derivatives. In the reaction of smaller electron demand such as the dissociation of naphthoic acids and naphthylamines, the $q^+_{r,ij}$ only for 4α is significant but those for 7 and 5 positions diminish to a value comparable to that for non-conjugate positions. Concerning the $q^+_{r,ij}$'s for non-conjugate positions (Table 11), although the number of substituents and of reactions examined are limited, it would be reasonable to consider that the $q^+_{r,ij}$ for the non-conjugate position remains practically constant in spite of the variation of reaction (*e.g.*, $q^+_{r,3\alpha}=0.4\pm0.3$ and $q^+_{r,6\alpha}=0.5\pm0.2$). This is in contrast to the behavior of the $q^+_{r,ij}$ for conjugate positions but in line with the general reaction-independency of σ_m values observed in benzene reactivities.[38)]

Finally, the $q^+_{r,ij}$ values for the σ^0-class reactivity (*i.e.*, $q^0_{r,ij}$) may reasonably be expected to be close to the least exalted $q^+_{r,ij}$ values obtained for the pK_a of naphthylammonium ions and probably very close to 0.5 for all positions except 1.0 for 4α position, as far as the $-R$ substituents are concerned. A typical $+R$ cyano substituent at any position in Fig. 2 essentially satisfies the correlation determined by 3α and 6α substituents. This suggests that the exaltation of π-electronic effect of the $+R$ group even at strongly conjugative positions does not occur in the σ^+-type electrophilic reactivity of the naphthalene in the same way as in the benzene system.[38)] In fact, the apparent σ_{ij} values of the CN group in the present solvolysis can be calculated as a good approximation with the above $q^0_{r,ij}$ for σ^0-class reactivity (combined with C_{ij} values) but not with the set of $q^+_{r,ij}$ values for the solvolysis. It is apparent that the dual q_r values, $q^+_{r,ij}$ and $q^-_{r,ij}$, should generally be required each for $-R$ and $+R$ class substituents. The σ^0 class reactivity may thus be defined as the reactivity which shows minimal exaltation of both $-R$ and $+R$ resonance; *i.e.*,

$$q^+_{r,ij} = q^-_{r,ij} = q^0_{r,ij}.$$

From the results, we can figure out the general pattern of the transmission of the substituent effect in the naphthalene system. The substituent effect in the naphthalene system can be separable as a useful approximation into the reaction-independent inductive contribution and the reaction-dependent *pi*-electronic contributions from $+R$ and $-R$ substituents by means of the equation

$$\bar{\sigma}_{ij} = (\log k/k_0)/\rho = C_{ij}\sigma_i + q^+_{r,ij}\sigma_\pi{}^+ + q^-_{r,ij}\sigma_\pi{}^- \qquad (3')$$

The last term applies to the effect of $-R$ substituents. The C_{ij} is generally independent of reactions. The $q_{r,ij}$ for non-conjugate positions also remains to be $q^0_{r,ij}$ regardless of reaction. The reaction dependency of the apparent substituent constants $\bar{\sigma}_{ij}$ is attributable to the changes of the $q^+_{r,ij}$ and/or $q^-_{r,ij}$ for the conjugate positions with reactions. The characteristic ratio $q^+_{r,ij}/q^-_{r,ij}$ reflects the nature of the reaction center at the transition state.[46)]

Dewar's *FM* assumption is in line with the present statistical results at least with respect to the inductive transmission scheme. However, with respect to the *pi*-electronic transmission scheme it appears to be inconsistent with our conclusion, in two points. According to the present analysis there is no reaction-independent general-scheme of the *pi*-effect transmission, as Dewar assumed to be given by a fixed set of NBMO q_{ij} coefficients.[5)] Even if it is valid as a first approximation, the application will be limited to some very narrow range of reactivity class. Use of Eaborn's $q_{ij}{}^w$ scheme as in Eq. (5) for the electrophilic σ^+-type reaction gave better results.[2)] The different reaction-dependency of the *pi*-effect transmission scheme for the $+R$ and $-R$ substituents was not taken into account in the *FM* treatment. The better fit for the σ^+-type reactivities by the use of $q_{ij}{}^w$ in place of q_{ij} is consistent with our observation, since the values of $q_{ij}{}^w$ are approximately 2-fold of q_{ij}, respectively for conjugate positions. However, in such highly electrophilic reactivities, the unexalted *pi*-effect transmission scheme (the $q^0_{r,ij}$ set) was evidently retained for the $+R$ substituents even at a strongly conjugative position. Incorporated application of the M^+ parameters which were derived from σ^+ constant in Eq. (5), instead of M from σ, is reasonably expected to improve the situation,[39)] since the higher ratio of $q_{ij}{}^+/q_{ij}{}^-$ required for electrophilic reactivities may partly be adjusted by the exalted $-R/+R$ resonance contribution ratio of the σ^+ constants.[47)] The authors however do not agree to the use of multiple sets of resonance parameters.[46)]

Taft suggested that there is no universal set of resonance parameters (providing the parameter $\bar{\sigma}_R$ is defined by $\bar{\sigma}_p-\sigma_I$) and that at least four fundamental sets of the resonance parameters, $\sigma_{R,}{}^0$ σ_R, $\sigma_R{}^+$, and $\sigma_R{}^-$, should be required for different reactivity classes.[48] Consequently in the case of $-R$ exalted-resonance reactivities, such as the present solvolysis in the naphthalene system, the σ_R^+ should be employed instead of σ_R^0 in Eq. (6) as the most suitable set for the substituents at strongly conjugative position. However, σ_R^0 should be still utilized for the substituents at non-conjugative 3α and 6α positions. There appears however to be no definite rule for the choice of the most proper set of the parameters for the substituents at intermediate or moderately strong conjugate 5α and 7α positions. The best parameter could only be chosen as to give a best fit correlation. Presumably such $\bar{\rho}_I$ and $\bar{\rho}_R$ values could not be compared with each other within the same series or between different sets of reactivities.

The success in describing the substituent effects in the naphthalene beyond the benzene derivatives provides strong support for the possibility that a unique set of σ_i and σ_π^+ substituent constants can be utilized practically as universal substituent constants.

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