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Mechanism of Hydrogenolysis. I. Effect of Methyl Substituent on the Demethylation Rate of Polymethylbenzenes

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Rates of demethylation of six different polymethylbenzenes have been measured, at 702°C and residence times ranging from 0.5 to 6.0 sec in the presence of five-fold in excess hydrogen, by using toluene as an internal reference. The rates per one equivalent methyl group were: 1.08 for *p*-xylene, 1.73 for *o*-xylene, 1.26 for 4-position of 1,2,4-trimethylbenzene, 1.87 for 2-position of 1,2,4-trimethylbenzene, 1.85 for 1-position of 1,2,4-trimethylbenzene, 1.20 for 1,3,5-trimethylbenzene, 2.22 for 1-position of 1,2,3-trimethylbenzene, 3.25 for 2-position of 1,2,3-trimethylbenzene, 1.5 for 5-position of 1,2,3,5-tetramethylbenzene, 2.1 for 1-position of 1,2,3,5-tetramethylbenzene, and 2.8 for 2-position of 1,2,3,5-tetramethylabenzene, all the figures being expressed against the standard value of 1.00 for toluene. The observed accelerating effect of neighboring methyl groups on the demethylation rates of crowded reactant molecules has been correlated with modified superdelocalizability in *z* direction for radical aromatic substitution. The latter values calculated by the extended Hückel molecular orbital method were: 0.4070, 0.4116, 0.4908, 0.4169, 0.4124, 0.4116, 0.4131, 0.4133, 0.4148, 0.4204, 0.4120, and 0.4029 (toluene) in the order given above. The general parallelism between the observed and the theoretical values may be taken as a support not only of the extention of the concept of superdelocalizability to radical aromatic substitution, but also of our mechanistic interpretation on the key reaction of hydrogenolyses.

Considerable number of kinetic investigations were reported on the thermal hydrogenolytic demethylation of toluene.[1] Observed rates of the hydrogenolysis, $C_6H_5CH_3+H_2\rightarrow C_6H_6+CH_4$, can best be summarized within the specified deviations by $-d(C_6H_5CH_3)/dt=10^{(11.0\pm1.0)-(55\pm5)/\theta}(C_6H_5CH_3)\cdot(H_2)^{0.5}$ mol/*l*·sec over strikingly wide ranges of both temperature and pressure. The following chain mechanism initially proposed by us[2] and later supported by Benson and Shaw,[3] gives reasonable accounts for the observed overall three-halves reaction order as well as the values of Arrhenius kinetic parameters.

$$C_6H_5CH_3 \rightleftharpoons C_6H_5CH_2 + H$$

$$H + C_6H_5CH_3 \rightleftharpoons H_2 + C_6H_5CH_2$$

$$H + C_6H_5CH_3 \xrightarrow{(a)} C_6H_6 + CH_3$$

$$CH_3 + C_6H_5CH_3 \rightleftharpoons CH_4 + C_6H_5CH_2$$

In the above chain scheme, the propagation rate is effectively controlled by reaction (*a*). This reaction can be pictured as a perpendicular approach of hydrogen atom to ring carbon atom to which methyl group is attached. This is followed by elimination of methyl group to complete the reaction. Energetics of the concerted process, quoted by Benson and Shaw as abstraction-elimination reaction,[3] has been successfully treated in our following communication[4] in terms of total electron energies of postulated transition structures using extended Hückel molecular orbital calculations.

The rate measurements were also reported for

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[1] a) H. Matsui, A. Amano and H. Tokuhisa, *Bull. Japan Petrol. Inst.*, **1**, 67 (1959); A. Tsuchiya, A. Hashimoto, H. Tominaga and S. Masamune, *ibid.*, **1**, 73 (1959); S. Masamune, A. Amano and H. Tokuhisa, *Tech. Reports Tohoku Univ.* (Japan), **25(1)**, 27 (1960); J.G. Burr, R.A. Meyer and J.D. Strong, *J. Amer. Chem. Soc.*, **86**, 3846 (1964). b) R. I. Silsby and E. W. Sawyer, *J. Appl. Chem.*, **6**, 347 (1956); W. D. Betts, F. Popper and R. I. Silsby, *ibid.*, **7**, 497 (1957); H. Morii, A. Hashimoto and H. Tominaga, *World Petrol. Congr. Proc. 6th*, Frankfurt, Germany 1963, 131.

[2] A. Amano, H. Tominaga, and H. Tokuhisa, *Bull. Japan Petrol. Inst.*, **7**, 59 (1965).

[3] S. W. Benson and R. Shaw, *J. Chem. Phys.*, **47**, 4052 (1967).

[4] H. Tominaga, H. Arai, T. Kunugi, A. Amano, M. Uchiyama and Y. Sato, This Bulletin, **43**, 3658 (1970).

xylenes,1b,5,6) 1,3,5-trimethylbenzene,6) and 1,2,4-trimethylbenzene.7) The reaction order was again found to be three-halves, indicating the validity of the same chain scheme proposed for toluene.3) There is certain evidence,5,7) however, that the specific rate of demethylation is affected by both number and position of methyl substituents of the reactant molecule. Thus, demethylation of the first methyl group of xylene and trimethylbenzenes was quite definitely easier than that of toluene. Unequal amounts of *o*-, *m*-, and *p*-xylenes were formed from 1,2,4-trimethylbenzene.

In the first part of the present work, effort has been made to evaluate quantitatively the ease with which any particular methyl group is substituted. Experiments are carried out for six different polymethylbenzenes at a fixed temperature of 702.1°C by an internal competitive reaction system. The latter technique assures a fair comparison of the demethylation rates. The value of demethylation rate constant for any given methyl group relative to that of toluene is then correlated with the relevant reactivity index for radical substitution.

Experimental

Commercial reagent grade polymethylbenzenes were used as received. Purities of the reagents as analyzed by gaschromatography were: benzene, >99.9 mol%; toluene, >99.9 mol%; *o*-xylene, 94.2 mol%; *m*-xylene, 97.3 mol%; *p*-xylene, >99.9 mol%; 1,2,3-trimethylbenzene, >99mol%; 1,2,4-trimethylbenzene, 99.7mol%; 1,3,5-trimethylbenzene, 99.8 mol%; 1,2,3,5-tetramethylbenzene, 96.6 mol%. Balancing impurities were consisted of hydrocarbons in the neighboring boiling ranges. Cylinder hydrogen of not less than 99.9 mol% purity was used after a conventional purification.

An all-glass flow apparatus was operated under an atmospheric pressure. Reactant polymethylbenzene was mixed with an adequate amount of toluene, and the mixture was introduced into the apparatus by using a glass syringe. The polymethylbenzene-toluene vapor was then carried into a reaction vessel along with a stream of hydrogen dried over magnesium perchlorate. Rate of hydrogenolysis of any given polymethylbenzene was thus evaluated in relation with that of toluene admixed as a standard reference. The use of the internal competitive reaction technique could afford a sufficiently reliable measure as to the reactivity ratios. In a few runs, where toluene was not a convenient reference because of an interference in the product analyses, 1,3,5-trimethylbenzene was used as a reference material.

The reaction vessel was made of a quartz tubing, 23 mm in inside diameter and 90 mm in length, and was equipped with a thermo-sheath placed along its central axis. The vessel was fitted in an electrically heated aluminum-bronze block furnace, the temperature of which was controlled electronically within ±0.5°C. Temperature profiles of the reaction vessel were determined, during each run while the reaction was taking place, by a movable Pt-Pt·Rh thermocouple in the sheath. Annular space of the vessel was filled with quartz tips, resulting in a free volume of about 10 ml. Reaction temperature and residence time were defined by the method described elsewhere.8) The reaction was carried out at a fixed temperature of 702.1°C, hydrogen-hydrocarbon mole ratio of 5, and residence times ranging from 0.5 to 6.0 sec.

Condensable components of the products were collected in a train of cold traps immersed in liquid nitrogen, and were subjected to the conventional gaschromatographic analysis using dinonylphthalate (3 m) and polyethyleneglycol (3 m) packed columns.

Results

The gaseous products consisted mainly of methane and unreacted hydrogen with trace amounts of ethane, propane, propene, *etc.* The liquid products were compared of lower homologues of reactant polymethylbenzenes. Distributions of the products were in accord with those already reported for trimethylbenzenes.6,7) The hydrogenolyses of polymethylbenzenes should therefore follow the general consecutive scheme: $C_6H_{6-n}(CH_3)_n+H_2\rightarrow C_6H_{7-n}(CH_3)_{n-1}+CH_4$. The relative rate of demethylation per one equivalent methyl group of polymethylbenzenes could thus be obtained directly from the composition of liquid products. The procedure assumes that the first order reaction with respect to polymethylbenzene takes place in an ideal plug flow reactor. It should be noted, however, that the deviations from the ideality do not produce substantial error in the values of reactivity ratio.

Demethylation rates of *o*-xylene and *p*-xylene were measured in relation with that of 1,3,5-trimethyl-

Table 1. Relative demethylation rate, *o*-xylene *vs.* 1,3,5-trimethylbenzene

Conversions (mol%)		Relative rates
o-Xylene	1,3,5-Trimethylbenzene	
2.28	2.39	0.95
4.17	4.47	0.94
7.46	8.05	0.93
11.73	11.62	1.01
		(Av. 0.96)

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5) S. Masamune, M. Uchiyama, and H. Tokuhisa, *Tech. Reports Tohoku Univ.* (Japan), **25**(**1**), 39 (1960); A. Tsuchiya, A. Hashimoto, H. Tominaga and S. Masamune, *Bull. Japan Petrol. Inst.*, **2**, 85 (1960); J. G. Burr and J. D. Strong, *J. Am. Chem. Soc.*, **86**, 5065 (1964).

6) S. E. Shull and A. N. Hixon, *Ind. Eng. Chem., Process Design and Develop.*,**5**, 146 (1966),

7) H. Tominaga, K. Takagi, K. A. Moghul and T. Kunugi, *Kogyo Kagaku Zasshi*, **71**, 48 (1968); H. Tokuhisa, A. Amano, M. Uchiyama and Y. Sato, Preprints for the 21st Annual Meeting of Japan Chem. Soc., Tokyo (1968).

8) A. Amano and M. Uchiyama, *J. Phys. Chem.*, **67**, 1242 (1963).

TABLE 2. RELATIVE DEMETHYLATION RATE, *p*-XYLENE *vs.* 1,3,5-TRIMETHYLBENZENE

Conversions (mol%)		Relative rates
p-Xylene	1,3,5-Trimethylbenzene	
2.02	3.61	0.55
3.76	5.81	0.64
		(Av. 0.60)

benzene by analyzing for toluene and *m*-xylene produced. The results obtained under varying conversion levels are listed in Table 1 and 2. In excellent agreement with previously reported values,[1b,5)] *o*-Xylene is shown 1.6 times as reactive as *p*-xylene.

Demethylation rates of other polymethylbenzenes were measured using toluene as internal referance. The results are listed in Tables 3, 4 and 5. In these instances, either two or three structural isomers were initially formed depending on the number of unequivalent methyl groups in the reactant molecule. Thus, the liquid product from 1,2,4-trimethylbenzene at a conversion level of 2.73 mol% was composed of *o*-xylene (0.64 mol%), *m*-xylene (0.98 mol%), *p*-xylene (1.01 mol%), and toluene (0.10 mol%). The amount of toluene produced from the three xylene isomers by secondary reaction was then corrected based on the reported relative reactivity among these isomers, resulting in the initial isomer distribution of *o*-xylene (21.1 mol%), *m*-xylene (38.7 mol%), and *p*-xylene (40.2 mol%). The values of the initial distribution corrected by the method described above are listed in the second column of Tables 3, 4 and 5. Relative rate to produce any particular isomer was deduced from the overall relative rate and the initial distribution, giving proper consideration of statistical factor if necessary. Thus, for example, relative rate to produce *o*-xylene from 1,2,3-trimethylbenzene was obtained by dividing analytical value by statistical factor of two. The final values of the relative rate are listed in the last column of the tables. A check of the data can be made, for example, by comparing the overall relative rate of 4.98 given in Table 3 with the reported value of 5.0.[7)]

Table 6 lists the results obtained for a mixed feed of toluene and 1,3,5-trimethylbenzene. Summarized in Table 7 are the relative rates of demethylation per one equivalent methyl group based on the averaged value of 3.59 given in Table 6. It should be emphasized at this point that the values of relative rates listed in Table 7 are essentially those for (*a*), and are free from other elementary reactions included in our mechanism.[2)] This is, in fact, one of the advantages of the present experimental method.

TABLE 3. RELATIVE DEMETHYLATION RATE, 1,2,4-TRIMETHYLBENZENE *vs.* TOLUENE

Conversions (mol%)			Relative rates	
1,2,4-Trimethylbenzene		Toluene		
2.73	*m*-Xylene 38.7%	0.53	5.20	*m*-Xylene 2.01
	p-Xylene 40.2%			*p*-Xylene 2.09
	o-Xylene 21.1%			*o*-Xylene 1.10
4.66	*m*-Xylene 36.7%	0.93	5.10	*m*-Xylene 1.88
	p-Xylene 37.9%			*p*-Xylene 1.93
	o-Xylene 25.4%			*o*-Xylene 1.29
7.69	*m*-Xylene 35.6%	1.63	4.72	*m*-Xylene 1.68
	p-Xylene 37.1%			*p*-Xylene 1.76
	o-Xylene 27.3%			*o*-Xylene 1.28
12.65	*m*-Xylene 37.1%	2.72	4.90	*m*-Xylene 1.82
	p-Xylene 36.3%			*p*-Xylene 1.78
	o-Xylene 26.6%			*o*-Xylene 1.30
18.14	*m*-Xylene 37.3%	3.96	4.95	*m*-Xylene 1.84
	p-Xylene 36.0%			*p*-Xylene 1.78
	o-Xylene 26.7%			*o*-Xylene 1.35
			Av. 4.98	*m*-Xylene 1.85
				p-Xylene 1.87
				o-Xylene 1.26

TABLE 4. RELATIVE DEMETHYLATION RATE, 1,2,3-TRIMETHYLBENZENE *vs.* TOLUENE

Conversions (mol%)			Relative rates	
1,2,3-Trimethylbenzene		Toluene		
12.72	*o*-Xylene 57.8%	1.60	8.44	*o*-Xylene 2.44
	m-Xylene 42.2%			*m*-Xylene 3.56
16.19	*o*-Xylene 57.4%	2.24	7.79	*o*-Xylene 2.24
	m-Xylene 42.6%			*m*-Xylene 3.31
20.08	*o*-Xylene 58.1%	3.02	7.31	*o*-Xylene 2.12
	m-Xylene 41.9%			*m*-Xylene 3.07
26.27	*o*-Xylene 57.2%	4.14	7.21	*o*-Xylene 2.06
	m-Xylene 42.8%			*m*-Xylene 3.09
			Av. 7.69	*o*-Xylene 2.22
				m-Xylene 3.25

TABLE 5. RELATIVE DEMETHYLATION RATE, 1,2,3,5-TETRAMETHYLBENZENE *vs.* TOLUENE

Conversions (mol%)			Relative rates	
1,2,3,5-Tetramethylbenzene		Toluene		
22.01	1,3,5-TriMB 34.0%	2.93	8.4	1,3,5-TriMB 2.8
	1,2,4-TriMB 46.1%			1,2,4-TriMB 2.0
	1,2,3-TriMB 19.9%			1,2,3-TriMB 1.6
13.15	1,3,5-TriMB 33.0%	1.62	8.7	1,3,5-TriMB 2.8
	1,2,4-TriMB 49.9%			1,2,4-TriMB 2.2
	1,2,3-TriMB 17.1%			1,2,3-TriMB 1.5
			Av. 8.6	1,3,5-TriMB 2.8
				1,2,4-TriMB 2.1
				1,2,3-TriMB 1.6

Table 6. Relative demethylation rate, 1,3,5-trimethylbenzene *vs.* toluene

Conversion (mol%)		Relative rates
1,3,5-Trimethylbenzene	Toluene	
1.23	0.305	3.98
2.50	0.708	3.56
5.02	1.44	3.55
5.25	1.49	3.56
6.24	1.78	3.59
9.25	2.92	3.28
7.45	2.73	3.60
13.65	4.03	3.57
		(Av. 3.59)

Table 7. Relative rates of demethylation per one equivalent methyl group

Compound	Position of methyl group	Relative reactivity
Toluene	—	1.00 (reference)
o-Xylene	1, 2	1.72
p-Xylene	1, 4	1.08
1,2,4-Trimethylbenzene	1	1.85
1,2,4-Trimethylbenzene	2	1.87
1,2,4-Trimethylbenzene	4	1.26
1,3,5-Trimethylbenzene	1, 3, 5	1.20
1,2,3-Trimethylbenzene	1, 3	2.22
1,2,3-Trimethylbenzene	2	3.25
1,2,3,5-Tetramethylbenzene	1, 3	2.1
1,2,3,5-Tetramethylbenzene	2	2.8
1,2,3,5-Tetramethylbenzene	5	1.5

Discussion

As has been shown by the foregoing experimental results, the rate of reaction *a* is affected by both number and position of methyl substituents in any given reactant molecule. In the word of classical organic chemistry, this is due obviously to a cummulative result of inductive and resonance effects. Such effects should modify electronically the reactivity of methylated carbon atoms in benzene ring toward hydrogen atom attack, reaction (*a*), which in turn controls the rate of the overall hydrogenolysis. Fukui, Yonezawa, and Nagata have successfully introduced an index termed superdelocalizability,[9] in their work calculated by the simple Hückel method, as a measure of the reactivity of aromatic compounds for substitution reactions.

We adopt in the present paper the concept put forward by Fukui *et al.* but using the extended Hückel method. The use of the latter method should be preferred in elucidating the electronic structures of polymethylbenzenes, since *sigma* and *pi* electrons can be treated without arbitrary parametrizations. The modified superdelocalizability radical substitution, $S_p(\mathrm{R})$, defined by the following equation is thus taken as reactivity index.

$$S_p(\mathrm{R}) = \sum_i^{\mathrm{occ}} \{(c_{p_i})^2/\lambda_i\} + \sum_j^{\mathrm{unocc}} \{(c_{p_j})^2/-\lambda_j\}$$

where $\lambda_i = -\varepsilon_i + \alpha_0$, and $\alpha_0 \fallingdotseq (\varepsilon_{\mathrm{no}} + \varepsilon_{\mathrm{lv}})/2$. ε_i and c_{p_i} are eigen value and eigen vector of the *i*th molecular orbital, respectively. The validity of the approximation in estimating the value of α_0 can be tested for the case of toluene hydrogenolysis where the energy level of half-filled orbital of the activated complex was estimated as being −10.439 eV in our follwing paper.[4] This should be compared with −10.426 eV deduced from the energy level of the highest occupied orbital, $\varepsilon_{\mathrm{ho}}$, of −12.491 eV and that of the lowest unoccupied orbital, $\varepsilon_{\mathrm{lv}}$, of −8.361 eV for toluene both listed in Table 8.

Detail of the molecular orbital calculations by the extended Hückel method have been described.[4] The calculations are carried out for ten different polymethylbenzenes based on the following molecular geometries: coplanar skeletal structure;[10] C(ring)-C(ring) distance, 1.40 Å; C(ring)-C(methyl) distance, 1.51 Å; C(ring)-H distance, 1.09 Å; C(methyl)-H distance, 1.09 Å. It is further assumed

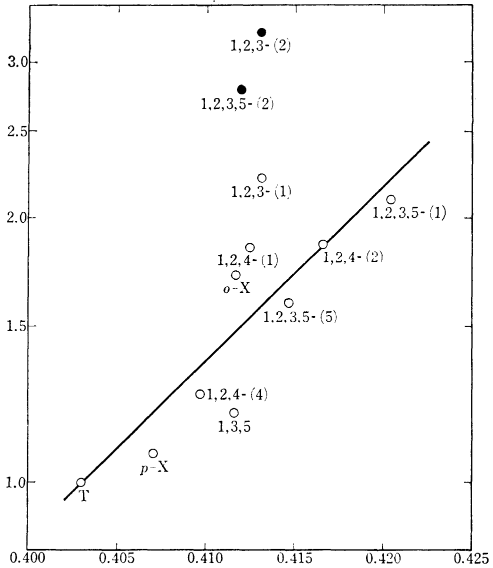

Fig. 1. Correlation between observed relative reactivity and modified superdelocalizability.

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[9] K. Fukui, T. Yonezawa, and C. Nagata, This Bulletin, **27**, 423 (1954); *J. Chem. Phys.*, **27**, 1247 (1957).

[10] G. Furguson and J. M. Robertson, "Advances in Physical Organic Chemistry," Vol. 1, Academic Press, New York (1963), p. 202.

Table 8. Reactivity indices by extended Hückel method

Compound	Energy levels (eV)		Position	Modified superdelocalizability in z direction			Atomic bond population
	ε_{ho}	ε_{lv}		$S_p(\mathrm{R})$	$S_p(\mathrm{E})$	$S_p(\mathrm{N})$	
Toluene	−12.4906	−8.3615	1	0.4029	0.2749	0.5309	0.7744
o-Xylene	−12.3253	−8.2432	1,2	0.4116	0.2987	0.5245	0.7748
m-Xylene	−12.3794	−8.2510	1,3	0.4063	0.2609	0.5517	0.7745
p-Xylene	−12.2094	−8.3625	1,4	0.4070	0.2998	0.5142	0.7712
1,3,5-Trimethylbenzene	−12.3777	−8.0057	1,3,5	0.4116	0.2468	0.5765	0.7746
1,2,3-Trimethylbenzene	−12.3021	−8.0287	1,3	0.4131	0.2828	0.5434	0.7750
1,2,3-Trimethylbenzene	—	—	2	0.4133	0.3208	0.5058	0.7750
1,2,4-Trimethylbenzene	−12.1232	−8.2170	1	0.4124	0.3235	0.5013	0.7716
1,2,4-Trimethylbenzene	—	—	2	0.4169	0.2846	0.5493	0.7750
1,2,4-Trimethylbenzene	—	—	4	0.4098	0.2839	0.5357	0.7713
1,2,4,5-Tetramethylbenzene	−11.9715	−8.1369	1,2,4,5	0.4168	0.3089	0.5248	0.7718
1,2,3,4-Tetramethylbenzene	−12.0974	−8.0212	1,4	0.4126	0.3067	0.5184	0.7719
1,2,3,4-Tetramethylbenzene	—	—	2,3	0.4158	0.3058	0.5257	0.7754
1,2,3,5-Tetramethylbenzene	−12.0826	−8.0031	1,3	0.4204	0.2691	0.5717	0.7752
1,2,3,5-Tetramethylbenzene	—	—	2	0.4120	0.3417	0.4823	0.7719
1,2,3,5-Tetramethylbenzene	—	—	5	0.4148	0.2682	0.5613	0.7714

that the conformation of neighboring methyl groups is such that the separation between two hydrogen atoms should be maximum. Summarized in Table 8 are the values of the modified superdelocalizability in z-direction, namely perpendicular to ring plane, of ring carbons for radical substitution together with eigen values of the highest occupied and the lowest unoccupied orbitals. The values of the modified superdelocalizability for electrophilic and nucleophilic substitutions are also included in Table 8 for comparison.

The observed rates of demethylation per one equivalent methyl group of polymethylbenzenes relative to that of toluene have already been listed in Table 7. These values are plotted in Fig. 1 against the relevent values of modified superdelocalizability. Since the latter quantity should relate primary with the energetics of the critical reaction path, the observed relative rates are expressed by logarithmic scale in Fig. 1.

The linearity shown by empty circles in Fig. 1 serves as an evidence for the extension of Fukui's concept of superdelocalizability which has been largely confined within ionic substitutions.[9] Conversely, if it is assumed that the aromatic reactivity for radical substitution can be properly described by the value of $S_p(\mathrm{R})$, the linearity may be taken as a support of our mechanistic interpretation on the hydrogenolyses and hence the role of reaction (*a*) in the chain scheme.[2,4]

The values of atomic bond population[11] M-[C(ring)-C(methyl)] have also been calculated by the extended Hückel method, and are listed in the last column of Table 8.

$$M[\mathrm{C(ring)}-\mathrm{C(methyl)}] = \sum_p\sum_q N_{pq}$$

$$N_{pq} = 4\sum C_{p_i}C_{q_i}S_{pq}$$

They exhibit no radical correlation what so ever with the observed reactivity ratios. This indicates that the reactivity for aromatic substitution is determined by the dynamic property of the ring carbon atom at whicn the substitution takes place, and not by the static property such as atomic bond population at the bond which is to be broken. The conclusion drawn here is in conformity with our following computational analysis[4] in which hydrogen atom attack has been reckoned as rate-determing step of reaction (*a*).

Deviation from the theory is, however, beyond any conceivable uncertainty for cases marked by filled circles in Fig. 1. They include 2-positions of 1,2,3-trimethylbenzene and 1,2,3,5-tetramethylbenzene where neighboring methyl groups have an effect toward higher reactivity than can be predicted by the theory. The following may possibly be the reasons for the present discrepancy. (1) Slight alternations in the planar conformation of these highly crowded homologues may lead to a significant effect on the values of $S_p(\mathrm{R})$. (2) Structure of transition-state for the hydrogen atom attack toward the 2-positions may be influenced by the presence of neighboring methyl groups.

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[11] R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).