Theoretical Study on the Mechanism of the Aromatic Substitution[1]

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As is well known, the mechanism of aromatic substitution may be regarded as one of the most typical problems to which the quantum mechanical theory has been applied with success. Since 1940, a number of notable theoretical papers on this subject have already been published by several authors[2-8]. In these papers, some quantum mechanical concepts useful for interpreting chemical reactivity of the aromatic molecule have been introduced. They are such concepts as π-electron density, free valency, localization energy, frontier electron density, etc.[9] By means of them, one has succeeded in explaining the orientation rule observed with some aromatic substitution reactions. It seems hasty, however, to consider that all the problems in this field have been settled completely. In fact, one can easily find some facts which can hardly be interpreted by any theory presented hitherto. For instance, the facts that the aliphatic hydrocarbon like methane is generally less susceptible to the electrophilic substitution than the aromatic hydrocarbon is, and that the silver cation is difficult to cause the substitution reaction with benzene while the nitronium cation is well known as a typical reagent for it, are not thought to be explained satisfactorily by the previous theories.

In the present paper, it is undertaken to study the mechanism of the aromatic substitution with reference to the relative heights of energy levels of the reagent to those of the aromatic molecule. From the consideration of these energy levels, it is concluded that a large electron transfer necessarily occurs from the aromatic molecule towards the reagent and in the reverse direction for the electrophilic and the nucleophilic substitution, respectively. On the basis of this electron transfer mechanism, conditions necessary for causing the aromatic substitution are reasonably introduced. It is shown, moreover, that the orientation in the aromatic substitution can properly be predicted by the free valency values evaluated with the aromatic cation, the neutral molecule and the anion for the electrophilic, the radical and the nucleophilic substitution, respectively.

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[1] Preliminary reports on this work have been published in *J. Chem. Phys.*, **22**, 563 (1954) and *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 933 (1954).

[2] T. Ri and H. Eyring, *J. Chem. Phys.*, **8**, 433 (1940).

[3] G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).

[4] M. J. S. Dewar, *J. Chem. Soc.*, **1949**, 463.

[5] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, **A191**, 39; **A192**, 16 (1947).

[6] K. Fukui, T. Yonezawa and H. Shingu, *J. Chem. Phys.*, **20**, 722 (1952); K. Fukui, T. Yonezawa and C. Nagata, This Bulletin, **27**, 423 (1954).

[7] R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

[8] On this problem various excellent reviews have already been published. Some of them are as follows:
(a) C. A. Coulson, *Research*, **4**, 307 (1951).
(b) K. Higasi, *Monograph Ser. Research Institute of Applied Electricity, Hokkaido University*, **No. 4**, 307 (1951).
(c) R. D. Brown, *Quart. Revs.*, **6**, 63 (1952).

[9] Some of these concepts are in intimate relations to one another. This problem has been discussed by Baba and also by Fukui et al. (cf. H. Baba, This Bulletin, **30**, 147, 154 (1957); K. Fukui, T. Yonezawa and C. Nagata, *J. Chem. Phys.*, **26**, 831 (1957)).

Determination of Energy Level Diagrams of Some Reagents and Aromatic Molecules

According to the authors' method described in the previous papers⁽10⁾, the highest occupied (H) and the lowest vacant (V) orbital of a certain molecule can be determined by the aid of the experimental data on the ionization potential and the near ultraviolet absorption spectrum. The same method was applied to the determination of orbital energies of the neutral molecules and radicals considered in the present paper. Concerning electrophilic reagents, such as the nitronium (NO_2^+), chlorine (Cl^+), bromine (Br^+), iodine (I^+), and hydrogen cations⁽11⁾, the lowest vacant orbital was set equal to the ionization potential of the corresponding neutral molecule or atom. On the other hand, the highest occupied orbital of the nucleophilic reagent, such as hydroxyl (OH^-) or chlorine (Cl^-) anion, was estimated from the electron affinity of the corresponding neutral radical or atom. The results thus obtained are shown in Fig. 1, where energy levels of the silver cation (Ag^+) and the iodine molecule are also given for the purpose of comparison. It is worthy of notice that both of them can form the stable charge transfer complex with the aromatic molecule⁽12-14⁾ but are difficult to cause the substitution reaction.

Consideration of the Reaction Mechanism from Energy Level Diagrams⁽15⁾

First of all, let us consider the electrophilic substitution. It is evident from Fig. 1 that the lowest vacant orbital (hereafter abbreviated to V) of the typical electrophilic reagent lies definitely below the highest occupied orbital (hereafter abbreviated to H) of the aromatic molecule which is susceptible to the substitution reaction. On the other hand, the V orbitals of the silver cation and the iodine molecule, which can not act as the electrophilic reagent for the substitution, are apparently higher than the H orbitals of the aromatic molecules. This remarkable fact suggests that it may be necessary for the occurrence of the electrophilic substitution that the V orbital of the reagent is considerably lower than the H orbital of the aromatic molecule. Under this assumption, moreover, the fact that the simple aliphatic hydrocarbon like methane is attacked with difficulty by the electrophilic reagent can readily be understood. As is shown in Fig. 1, the H orbital of methane which exists at -13.0 eV. is clearly lower than or almost equal to the V orbitals for most electrophilic reagents. In this case, therefore, it is difficult to fulfil the necessary condition for causing the electrophilic substitution.

The above-mentioned fact probably gives an interesting suggestion concerning the mechanism of the electrophilic substitution. According to Mulliken's theory relevant to the intermolecular charge transfer phenomenon, the electron transfer occurs to some extent from a donor towards an acceptor when these two components approach each other⁽14⁾. For example, in the case of the molecular complex between benzene (electron donor) and iodine (electron acceptor), the magnitude of this electron transfer was estimated by Mulliken to be about 3%. On the basis of the molecular energy level diagrams shown in Fig. 1, this intermolecular charge transfer phenomenon can approximately be represented by the interaction of the H orbital of the electron donor with the V orbital of the electron acceptor. The simple LCMO treatment on this interaction leads to a qualitative conclusion that the magnitude of the electron transfer increases as the V orbital becomes lower or the H orbital higher if the resonance integral between these two orbitals remains almost constant. In fact, in the

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10) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954); S. Nagakura, ibid., **23**, 1441 (1955); J. Tanaka, S. Nagakura and M. Kobayashi, ibid., **24**, 311 (1956).

11) The reagent ion in solution is undoubtedly stabilized by the orientation of surrounding solvent molecules. In the present state of the study, however, it is difficult to make quantitative discussion on the solvation energy of the ion under actual conditions of reaction. Therefore, the effect of the solvent upon the orbital energies of the ion was not taken into account in the present treatment.

12) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

13) L. J. Andrews and R. M. Keefer, ibid., **71**, 3644 (1949); **72**, 3113 (1950).

14) R. S. Mulliken, ibid., **72**, 600 (1950); **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

15) The description in this chapter is an extention of the basic idea mentioned in the preliminary papers published in 1954⁽¹⁾. The present authors' view on the importance of the electron transfer in the aromatic substitution is based on the energy level diagrams of the reagent and the aromatic molecule, which are determined by the use of the experimental data on the ionization potential and the near ultraviolet absorption spectrum. On the other hand, Fukui et al. have discussed a similar problem from the purely theoretical point of view and derived the equations representing the dependence of the electron density on the reagent upon the Coulomb and resonance integrals (K. Fukui, T. Yonezawa and C. Nagata, *J. Chem. Phys.*, **27**, 1247 (1957).

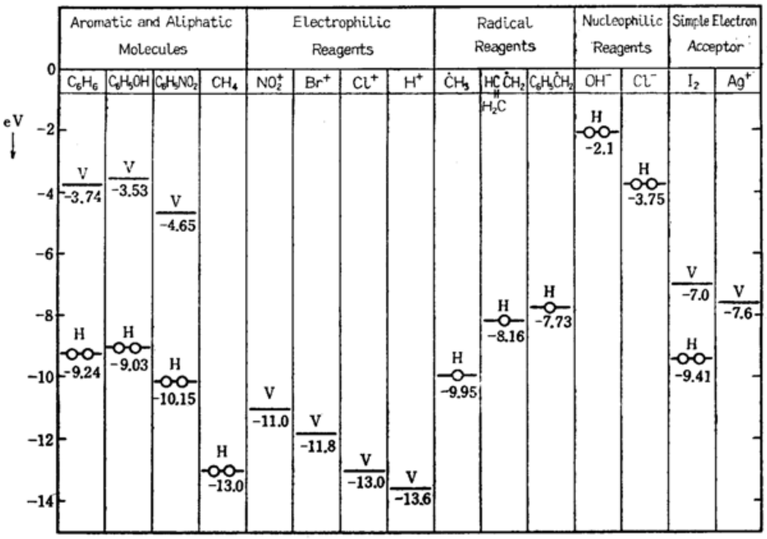

Fig. 1. Energy level diagrams for some reagents, and aromatic and aliphatic molecules.

The ionization potentials necessary for determining these diagrams were taken from the following references:

Benzene: W. C. Price and R. W. Wood, *J. Chem. Phys.*, **3**, 439 (1935).

Phenol and nitrobenzene: J. D. Morrison and A. J. C. Nicholson, ibid., **20**, 1221 (1952) and private communication from Dr. Morrison.

Iodine: J. D. Morrison, ibid., **19**, 1305 (1951).

Methane: R. E. Hornig, ibid., **16**, 105 (1948).

Nitrogen dioxide: E. C. G. Stueckelberg and H. D. Smyth, *Phys. Rev.*, **36**, 478 (1930).

Hydrogen, chlorine, bromine and silver atoms: Landolt-Börnstein, "Physikalische-Chemische Tabellen", 6-Auflage, I Band, 1. Teil, Springer-Verlag, Berlin (1951), p. 211.

Methyl, allyl and phenyl radicals: F. P. Lossing, K. U. Ingold and I. H. S. Henderson, *J. Chem. Phys.*, **22**, 621 (1954).

Electron affinities for hydroxyl group and chlorine atom are taken from Landolt-Börnstein, "Physikalische-Chemische Tabellen", 6-Auflage, I Band, 1. Teil, Springer-Verlag, Berlin (1951).

case of the iodine complex with triethylamine whose H orbital is much higher than that of benzene[16], the extent of the electron transfer certainly exceeds 50% as is revealed from the big dipole moment (11.3D)[17].

Applying the above consideration on the electron transfer to the system consisting of the aromatic molecule and the electrophilic reagent, one may be led to the conclusion that there necessarily occurs an extremely large electron transfer from the former towards the latter, because in this system the V orbital of the reagent is extraordinarily low and even lower than the H orbital of the aromatic molecule as mentioned above. This means that the electrophilic substitution proceeds passing through a stage at which the reagent cation robs almost one electron from the aromatic molecule and consequently the former changes nearly to the neutral radical and the latter nearly to the cation. On the present study of situation, it is difficult to ascertain whether or not this stage corresponds to the so-called transition state, namely the highest point in the potential energy curve for the reaction. According to our opinion, however, it is probably just before the transition state assumed by Wheland[2]. In other words, the above-mentioned large electron transfer may be accompanied by changes of the hybridizations and geometrical configurations in both the reagent and the aromatic molecule, and then a new σ bond may be formed between the former and a carbon atom of the latter

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[16] The ionization potential of triethylamine was determined as 7.50 eV. by Watanabe (K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957), whereas the ionization potential of benzene is 9.24 eV.

[17] S. Nagakura, *J. Am. Chem. Soc.*, **80**, 520 (1958); H. Tsubomura and S. Nagakura, *J. Chem, Phys.*, **27**, 819 (1957).

(Wheland's activated complex, type II)[18]. This view is schematically shown in Fig. 2. In this figure, stages B and C correspond to the electron transfer state and Wheland's transition state, type II, respectively.

Spectrophotometric studies by Reid[19] and also by Gold and Tye[20] show that the aromatic carbonium ion $(ArH)^+$ can be formed by the interaction of the aromatic molecule with proton under suitable conditions. This kind of ion, which is called $b\pi$, $h\sigma$ inner complex and σ-complex by Mulliken[7] and by Brown[21], respectively, may be thought to take a structure similar to that of Wheland's activated complex, type II. Hence, the present theory may be said to clarify the necessary conditions for forming the inner complex.

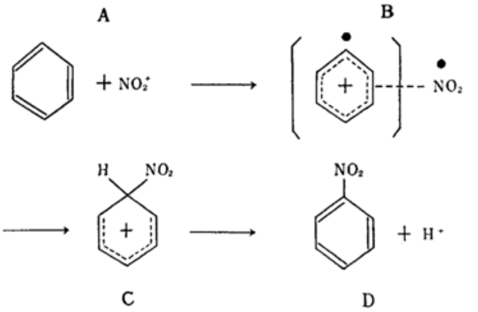

Fig. 2. Schematic diagram depicting the process of the substitution reaction between benzene and nitronium cation.

Let us now turn to the nucleophilic substitution. As is clearly seen from Fig. 1, the H orbital of the nucleophilic reagent is generally very high and may be regarded as comparable to the V orbital of the aromatic molecule. It is inferred from this that in this case a large electron transfer occurs from the reagent towards the aromatic molecule, and consequently the reaction takes place passing through the state in which the reagent becomes a nearly neutral radical and the aromatic molecule becomes an anion.

On the other hand, in the case of the radical substitution one may not expect such a large electron transfer as in the case of the heterolytic substitution, because unpaired electron levels of most radicals lie in an intermediate position between the H and the V orbitals of the aromatic molecule[22]. Thus in our opinion, the distinction between the heterolytic (electrophilic and nucleophilic) and homolytic (radical) substitutions is made in terms of the magnitude of the electron transfer between the reagent and the aromatic molecule. Furthermore, it is sure that in the electrophilic and the nucleophilic substitutions the directions of electron transfer are opposite to each other.

The present theory seems to have intimate relations with that presented by Weiss[23]. In 1946, Weiss emphasizes almost intuitively the importance of the electron transfer in many kinds of organic reactions. However, the grounds for his insistence concerning the aromatic substitution seem to be indefinite. The present theory has an advantage in that the necessity of a large electron transfer is reasonably concluded from the consideration of energy level diagrams of the reagent and the aromatic molecule.

Now, some consideration will be taken of the orientation in the aromatic substitution reaction, namely, the relative rate of substitution on various positions of the aromatic molecule. According to the present authors' view, in the heterolytic substitution the electron transfer takes place and consequently the reagent ion may be thought to attack the substrate as the radical. In other words, after the occurrence of the electron transfer, the mechanism of the heterolytic substitution may be regarded as similar to that of the homolytic substitution. Moreover, as is

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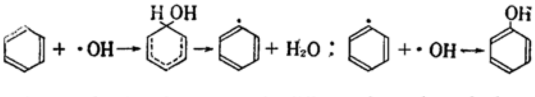
[18] The authors wish to express their sincere thanks to Professor Mulliken at Chicago and Professor Coulson at Oxford for their kindness in giving helpful suggestions on this respect. According to the present authors' opinion, Wheland's transition state, type II, corresponds to a basin in the potential energy curve for the substitution reaction.

[19] C. Reid, *J. Am. Chem. Soc.*, **76**, 3264 (1954).

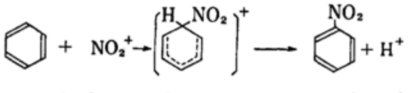
[20] V. Gold and F. L. Tye, *J. Chem. Soc.*, **1952**, 2184.

[21] H. C. Brown and J. D. Brady, *J. Am. Chem. Soc.*, **74**, 3570 (1952).

[22] It is doubtful if the radical and the nucleophilic substitution proceed completely parallel to the electrophilic substitution. For example, the substitution of the hydroxyl radical for the hydrogen atom of benzene is considered to take place through the following procedures (G. Stein and J. Weiss, *J. Chem. Soc.*, **1949**, 3245):



This mechanism is apparently different from that of the electrophilic substitution such as



However, both reactions pass commonly through Wheland's type II transition state where the attacked point is clearly determined. Therefore, it seems reasonable to consider that concerning the orientation rule parallel treatment can be applied to the three types of aromatic substitution reactions.

[23] J. Weiss, *Trans. Faraday Soc.*, **42**, 116 (1946).

well known, in the homolytic substitution the concept of free valency is very useful for explaining the orientation rule[8a,24,25]. Hence, it is quite natural to consider that the orientation in the electrophilic and nucleophilic substitutions can be predicted on the basis of the free valency value of the aromatic cation and of the anion, respectively.

Calculation of the Free Valency and Consideration of the Results

Free valency of the r-th atom(F_r) can be evaluated with the aid of the following equation:

$$F_r = F_{\max} - \sum_s p_{rs}$$

where $F_{\max}$ is the maximum value of the total π bond order of the carbon atom and estimated at $\sqrt{3}$[24], and p_{rs} is the π bond order of the r-s bond, where s denotes the adjacent atom to the r-th one. The value of p_{rs} can be calculated by the aid of the following equation:

$$p_{rs} = \sum_i n_i C_{ri} C_{si}$$

Here C_{ri} is the coefficient of the r-th atomic orbital in the i-th molecular orbital and n_i is the number of π-electron occupying it. The calculation of C_{ri} was made on the basis of the usual LCAO method under the assumption of orthogonality between adjacent $2p\pi$ atomic orbitals. Moreover, it was assumed that one electron is removed from the highest occupied orbital and is added to the lowest vacant one for the cation and the anion, respectively. In molecules containing hetero-atoms, evaluated values of free valency are rather sensitive to the assignment of the Coulomb and resonance integrals[26]. In the present calculation, the Coulomb integral for the hetero-atom was estimated with reference to its electronegativity and the resonance integral was set proportional to the corresponding overlap integral. By employing the self-consistent procedure which was certified to be useful for calculating the electron density for various molecules such as acetamide[27], tropolone[28], furan, pyrrole and thiophene[29], it was proved that the dependence of free valency upon the assignment of the Coulomb integral decreases considerably. The C_{ri} values for aniline, nitrobenzene, benzaldehyde and chlorobenzene were evaluated by the use of this iterative procedure. The C_{ri} values for phenol were calculated by Tsubomura[30]. The free valency values finally obtained in the present study are given in Tables I—III. In these tables, observed orientation rules are also given for the purpose of comparison.

It is seen from these tables that free valency values calculated for the aromatic cation, neutral molecule and anion can explain without contradiction the orientation observed with the electrophilic, radical and nucleophilic substitutions, respectively. Especially, it is worth notice that the free valency values calculated for the cations of the so-called *o*-, *p*-directing monosubstituted benzene molecules generally decrease in the order of $p > o > m$. This order is in complete accordance with the experimental results on the electrophilic substitution.

It is known that in some monosubstituted benzene molecules such as toluene[31] and styrene the radical substitution takes place in the side chain. In the case of styrene, this fact is coincident with the theoretical conclusion as is shown in Table II. The free valency of the carbon atom in the substituent group of benzaldehyde is also great compared with that of each atom in the benzene ring. This predicts the possibility that this molecule may be attacked on the carbon atom of the substituent group by the radical reagent.

The only exception in which the order of the free valency values does not agree with that of the observed reactivities in various positions is the case of radical substitution of biphenyl. In this case, free valencies decrease in the order of $2 > 4 > 3$, while the 4-position is most reactive from the experimental point of view. This descrepancy may be due to steric hindrance in the 2-position.

Such a satisfactory agreement between theoretical and experimental results as is seen from Tables I—III seems to support our view that at some stage of the heterolytic substitution reaction a large electron transfer takes place between the aromatic

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[24] H. H. Greenwood, ibid., **48**, 677 (1952).
[25] F. H. Burkitt, C. A. Coulson and H. C. Longuet-Higgins, ibid., **47**, 553 (1951).
[26] C. M. Moser, *J. Chem. Soc.*, **1953**, 1073.
[27] S. Nagakura, This Bulletin, **25**, 164 (1952).
[28] Y. Kurita and M. Kubo, ibid., **24**, 13 (1951).
[29] S. Nagakura and T. Hosoya, ibid., **25**, 179 (1952).

[30] The authors wish to express their thanks to Dr Tsubomura for his kindness in giving them information on these values.
[31] J. H. Merz and W. A. Waters, *J. Chem. Soc.*, **1949**, 2427.

TABLE I. FREE VALENCY VALUES CALCULATED WITH VARIOUS AROMATIC CATIONS

Parent molecule	Free valency			Orientation	
				Theoretical	Experimental
	o	m	p		
Toluene	0.502	0.454	0.697	$p>o>m$	$p>o>m$
Aniline	0.494	0.395	0.495	$p>o>m$	$p>o>m$
Phenol	0.497	0.431	0.622	$p>o>m$	$p>o>m$
Chlorobenzene	0.472	0.405	0.488	$p>o>m$	$p>o>m$
Nitrobenzene	0.694	0.884	0.472	$m>o>p$	$m>o>p$
	o	m	p		
Styrene	0.502	0.407	0.518	$\beta>\alpha>p>o>m$	β
	α	β			
	0.517	1.055			
	α	β			
Naphthalene	0.545	0.447		$\alpha>\beta$	$\alpha>\beta$
	2	3	4		
Biphenyl	0.500	0.409	0.523	$4>2>3$	$4>2>3$
	1	2	3		
Phenanthrene	0.376	0.06	0.541	$9>4>3>1>2$	9
	4	9			
	0.768	0.814			

The experimental results given in this table are taken from the following references:

C. K. Ingold, "Structure and Mechanism in Organic Chemistry", G. Bell and Sons, Ltd., London (1953).

F. Bell, J. Kenyon and P. H. Robinson, *J. Chem. Soc.*, **1926**, 1239.

G. M. Badger, "The Structures and Reactions of the Aromatic Compounds", Cambridge University Press, London (1954).

TABLE II. FFEE VALENCY VALUES CALCULATED WITH VARIOUS AROMATIC MOLECULES

Molecule	Free valency					Orientation	
						Theoretical	Experimental
	o	m	p				
Toluene	0.412	0.398	0.402			$o>p>m$	$o>p>m$
Aniline	0.433	0.396	0.415			$o>p>m$	—
Phenol	0.400	0.387	0.396			$o>p>m$	$o>p>m$
Chlorobenzene	0.420	0.389	0.409			$o>p>m$	$o>p>m$
Nitrobenzene	0.444	0.428	0.472			$p>o>m$	$p>o>m$
	o	m	p	α	β		
Benzaldehyde	0.438	0.396	0.457	0.870[a)]	—	$\alpha>p>o>m$	—
Styrene	0.448	0.396	0.412	0.412	0.821	$\beta>o>\alpha=p>m$	β
	2	3	4				
Biphenyl	0.437	0.396	0.412			$2>4>3$	$4>2>3$

The experimental results given in this table are taken from the following references:

D. H. Hey and G. H. Williams, *Discussions Faraday Soc.*, **14**, 216 (1953).

J. I. G. Gadogan, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, **1954**, 794.

O. Simamura and T. Migita, This Bulletin, **27**, 228 (1954).

O. Simamura and T. Inukai, ibid., **28**, 444 (1955).

T. Suehiro, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **72**, 301 (1951). (The experimental result on phenol referred to above is taken from this paper which is concerned with anisole).

a) This value was evaluated under the assumption that the π bond order for the C=O bond may be obtained with the aid of the same equation as for the C=C bond.

TABLE III. FREE VALENCY VALUES CALCULATED WITH NITROBENZENE AND CHLOROBENZENE ANIONS

Parent molecules	Free valency			Orientation	
				Theoretical	Experimental[a]
	o	*m*	*p*		
Nitrobenzene	0.436	0.427	0.448	$p > o > m$	$p > o > m$
Chlorobenzene	0.669	0.648	0.409	$o > m > p$	$o > m > p$

The experimental results given in this table are taken from the following reference: J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 273 (1951).

a) The orientation rules for nitrobenzene and chlorobenzene were deduced from the experimental results on dinitrobenzene and chloronitrobenzene, respectively, because it is difficult to replace a hydrogen atom of benzene directly by nucleophilic reagents such as Cl^- and OH^-.

TABLE IV. THE RELATIVE RATES OF RADICAL SUBSTITUTIONS IN *o*-, *m*- AND *p*-POSITIONS OF NITROBENZENE AND BENZOIC ACID

Molecule	Radical	Relative rate (%)		
		o	*m*	*p*
Nitrobenzene	OH[a]	35.5	29.0	35.5
Nitrobenzene	C_6H_5[b]	43.1	7.50	49.4
Benzoic acid	OH[c]	40.0	40.0	20.0
Benzoic acid	OH[d]	29.4	11.8	58.9
Benzoic acid ester	C_6H_5[e]	44.1	8.30	47.5

a) H. Loebl, G. Stein and J. Weiss, *J. Chem. Soc.*, **1950**, 2704.
b) D. H. Hey and G. H. Williams, *Discussions Faraday Soc.*, **14**, 216 (1953).
c) H. G. C. Bates, M. G. Evans and N. Uri, *Nature*, **166**, 869 (1950).
d) H. Loebl, G. Stein and J. Weiss, *J. Chem. Soc.*, **1951**, 405.
e) O. Simamura, T. Inukai and T. Migita, unpublished data.

molecule and the reagent, and consequently the orientation in the substitution can be determined by free valency values of the aromatic cation, neutral molecule and anion for the electrophilic, radical and nucleophilic substitutions, respectively.

Finally it may be necessary to add a note on the reaction between the OH radical and the aromatic molecule. According to the measurement by Robertson[32], the ionization potential of the OH radical is determined as 13.75 eV. This means that the energy of its unpaired electron orbital is fairly low and a large electron transfer from the aromatic molecule may be expected for this radical as well as for the electrophilic reagent. From this it is inferred that the orientation rule for this radical becomes somewhat similar to that for the electrophilic reagent. In this respect, it seems interesting that in the radical substitution of nitrobenzene and of benzoic acid, the ratio of *m*-derivative to *o*- or *p*-derivative is conspicuously greater for the hydroxyl radical than for the phenyl radical (cf. Table IV). One of possible explanations for this is presumably that the hydroxyl radical partly possesses the characteristic of the electrophilic reagent.

Summary

The mechanism of the aromatic substitution was studied on the basis of the energy level diagrams determined for both the aromatic molecule and the reagent. From the consideration of the relative heights of the highest occupied and lowest vacant orbitals of the former to those of the latter, it was deduced that a large electron transfer occurs at some stage of the reaction from the aromatic molecule towards the reagent for the electrophilic substitution and in the reverse direction for the nucleophilic substitution.

In connection with this electron transfer mechanism, it was expected that the orientation rule observed with the aromatic substitution can be explained by free valency values of the aromatic cation,

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[32] A. G. B. Robertson, *Trans. Faraday Soc.*, **48**, 228 (1952).

neutral molecule and anion for the electrophilic, radical and nucleophilic substitutions respectively. It was shown that this expectation is fully satisfied for various aromatic substitutions.

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