

$$\begin{array}{llll}
 H_{17} = (1/3)S_{\text{ex}}\gamma_{\text{ex}} & \Delta_{17} = (1/3)S_{\text{ex}} & H_{67} = (1/\sqrt{3})S_{\text{ex}}\gamma_{\text{ex}} & \Delta_{67} = (1/\sqrt{3})S_{\text{ex}} \\
 H_{37} = (2/\sqrt{15})S_{\text{ex}}\gamma_{\text{ex}} & \Delta_{37} = (2/\sqrt{15})S_{\text{ex}} & \text{where} & \gamma_{\text{ex}} = \int \phi_i H \phi_t \, dv, \quad S_{\text{ex}} = \int \phi_i \phi_t \, dv \\
 H_{57} = (2/3)S_{\text{ex}}\gamma_{\text{ex}} & \Delta_{57} = (2/3)S_{\text{ex}} & \text{TOKYO, JAPAN} &
 \end{array}$$

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Some Studies in Molecular Orbital Theory. II

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Conjugative and inductive effects in substituted benzenes are scrutinized by means of a second-order perturbation method based on molecular orbital theory including electron interaction but neglecting overlap. It is found that a mixing of the one- and two-electron excited states of benzene and the so-called electron transfer states which arise from the transfer of an electron from the substituent to benzene play an important role in determining the energies of the lower electronic states of substituted benzene. The conjugative and inductive parameters are determined for chlorobenzene, bromobenzene and phenol using the observed ionization potentials and the spectral shifts of the lowest L_b bands in these molecules. The agreement between the computed and observed energies of the lower electronic states in these molecules is satisfactory for the L_a band, not so good for the B_b band.

1. Introduction

In the previous paper,² a general interpretation of the conjugative and inductive effects was given with special reference to the first ionization potentials and the spectral shifts of the O-O bands in substituted aromatic hydrocarbons, particularly halogen-monosubstituted benzenes. Essentially the method was based on an effective one-electron Hamiltonian including overlap integrals but neglecting electron interactions. Although this method should be promising for the semi-quantitative interpretation of electronic spectra in substituted aromatic hydrocarbons, it is desirable to get a more detailed picture of the spectra by taking account of electron interaction.

Recently, Pariser and Parr,^{3a} and Pople^{3b} have put forth a useful idea for evaluation of the effect of electron interaction without rigorous computation of complicated integrals, and showed how their treatment including electron interaction accounts for many detailed features of the electronic spectra of an aromatic hydrocarbon. An important feature of the method consists of expressing the lowest excited states of an aromatic hydrocarbon as combinations of various configurations in which one or more electrons in the ground state have been excited to higher vacant orbitals. The method seems to be useful for discussing the effect of perturbations which are caused by introduction of the substituent, because it appears reasonable to expand the lower electronic states of a substituted hydrocarbon in terms of the corresponding lower states of the unperturbed hydrocarbon neglecting the various higher electronic states. Recently Murrell, *et al.*,⁴ have in fact investigated in just such a manner the effects of conjugation and induction in some substituted

benzenes, and they determined the empirical parameters from the shifts of the lowest $A_{1g} \rightarrow B_{2u}$ transitions.

Mixing of the one- and two-electron excited states of the hydrocarbon and the so-called "electron transfer" states plays an important role in both the electron migration and induction effects. In this paper, discussion will be given of the four main singlet-singlet transitions of substituted benzenes which Platt called L_b , L_a , B_b , and B_a , making use of second-order perturbation theory and configuration interaction; the conjugative and inductive parameters will be determined using the observed ionization potentials and the spectral shifts of the lowest L_b bands.

2. General Consideration of Configurations

The ground state configuration of an alternant hydrocarbon Ψ_0 can be written as an antisymmetrized product (Slater determinant) built up from orthogonal molecular orbitals $\psi_1, \psi_2, \dots, \psi_n$ which are linear combinations of carbon $2p_\pi$ atomic orbitals $\phi_1, \phi_2, \dots, \phi_{2n}$

$$\Psi_0 = \left(\frac{1}{(2n)!} \right)^{1/2} \sum_p (-1)^p \{ (\psi_1\alpha)(\psi_1\beta)(\psi_2\alpha) \dots (\psi_n\beta) \} \quad (1)$$

$$\psi_i = \sum_{\mu=1}^{2n} \chi_{i\mu} \phi_\mu \quad (i = 1, 2, \dots, n) \quad (2)$$

We shall be interested only in the two highest occupied orbitals ψ_i, ψ_j , and the two lowest vacant ones ψ_k, ψ_l , and so we abbreviate the notation for the ground state configuration Ψ_0 as

$$\Psi_0 = |(\psi_i\alpha)(\psi_i\beta)(\psi_j\alpha)(\psi_j\beta)| \quad (3)$$

We write Ψ_i^k for the singlet configurational wave function in which one electron is raised from an occupied orbital ψ_i to a vacant one ψ_k . This singly excited configuration Ψ_i^k will be a sum of two Slater determinants⁵ and is written as

$$\Psi_i^k = 2^{-1/2} \{ |(\psi_i\alpha)(\psi_k\beta)(\psi_j\alpha)(\psi_j\beta)| + |(\psi_i\beta)(\psi_k\alpha)(\psi_j\alpha)(\psi_j\beta)| \} \quad (4)$$

(5) The corresponding triplet wave function is

$${}^3\Psi_i^k = \sqrt{\frac{1}{2}} \{ |(\psi_i\alpha)(\psi_k\beta)(\psi_j\alpha)(\psi_j\beta)| - |(\psi_i\beta)(\psi_k\alpha)(\psi_j\alpha)(\psi_j\beta)| \}$$

but is not considered in this paper.

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(2) Part I of this series, THIS JOURNAL, **81**, 6120 (1959).

(3) (a) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953). (b) J. A. Pople, *Proc. Phys. Soc.*, **A68**, 81 (1955).

(4) (a) J. N. Murrell and H. C. Longuet-Higgins, *ibid.*, **A68**, 329 (1955); (b) J. N. Murrell, *ibid.*, **A69**, 969 (1956); (c) J. N. Murrell and K. L. McEwen, *J. Chem. Phys.*, **25**, 1143 (1956).

The functions for doubly excited configurations Ψ_{ij}^{kl} , which arise from taking electrons from ψ_i and ψ_j and raising them to ψ_k and ψ_l , can be divided into three classes.^{4c} The first kind for example has closed shell structure, and may be expressed as a single Slater determinant

$$\Psi_{ii}^{kk} = |(\psi_{k\alpha})(\psi_{k\beta})(\psi_{j\alpha})(\psi_{j\beta})| \quad (5)$$

The second type of configuration has two orbitals which contain one electron, and the third one has four orbitals containing one electron. Forms of such configurations are shown in Appendix A.

Next we consider the energies of the various excited configurations. The energy of the singly excited configuration Ψ_i^k relative to the energy of the ground state Ψ_0 is⁶

$$E(\Psi_i^k) = F_{kk} - F_{ii} - J_{ik} + 2K_{ik} \quad (10)$$

Here F_{kk} and F_{ii} are the energies of the Hartree-Fock molecular orbitals, chosen to make the following matrix F_{ik} diagonal

$$F_{ik} = I_{ik} + \sum_{j=1}^n \{2(ik|kj) - (ij|kj)\} \quad (11)$$

where

$$I_{ik} = \int \bar{\psi}_i(a) H^{\text{core}}(a) \psi_k(a) dv(a)$$

and the two-electron matrix elements are defined by

$$(ij|kl) = \int \int \bar{\psi}_i(a) \bar{\psi}_k(b) \frac{e^2}{r_{ab}} \psi_j(a) \psi_l(b) dv(a) dv(b) \quad (12)$$

In this notation the Coulomb and exchange integrals in eq. 10 are

$$J_{ik} = (ii|kk), K_{ik} = (ik|ik)$$

Using eq. 10, the energies of the doubly excited configurations relative to the energy of the ground state can be written in terms of the energies of singly excited configuration, the J_{ik} , and the K_{ik} . For example

$$E(\Psi_{ii}^{kl}) = E(\Psi_i^k) + E(\Psi_l^i) + J_{ii} + J_{kl} - J_{ik} - J_{il} + K_{kl} - K_{ik} - K_{il}$$

The reduction of the many-electron integrals between the determinantal wave functions can be made by the usual method,⁷ and we obtain matrix elements between singly excited configurations, between singly excited configurations and the ground state, between doubly excited and singly excited configurations, and between doubly excited configurations and the ground state. For example

$$(\Psi_{ii}^{kl}|\Psi_r^s) = \delta_{sk}\delta_{ri}F_{ii} + \delta_{ri}\{(ki|ls) + (li|ks)\} - \delta_{sk}(ir|il)$$

The complete formulas for diagonal and off-diagonal matrix elements thus obtained are given in Appendix A.

3. Inductive Effect

Before scrutinizing the inductive effect in the lower electronic states of substituted benzenes, let us first consider the lower energy electronic transitions of benzene itself. The molecular orbitals may be taken in their real forms, with atomic orbital coefficients (neglecting overlap) as in eq. 2 of Part I. The states of symmetry B_{2u} ,

B_{1u} and E_{1u} arise from the excitation of an electron from one of the highest occupied (degenerate) orbitals ψ_2 and ψ_3 to one of the lowest vacant (degenerate) orbitals ψ_4 and ψ_5 ; the corresponding spectra are called L_b , L_a , B_b and B_a by Platt,⁸ and α , p , β , and β' by Clar.⁹ Table I gives the relevant information about these states and also some of slightly higher energy, *i.e.*, the states arising from the excitations $\psi_1 \rightarrow \psi_4$, ψ_5 and ψ_2 , $\psi_3 \rightarrow \psi_6$.

TABLE I
THE ELECTRONIC STATES OF BENZENE

Notation	Assignment	Symmetry	Excitation energy (e.v.) ^a	Oscillator strength
$\Psi(L_b)$	$\sqrt{\frac{1}{2}}(\Psi_2^5 - \Psi_3^4)$	B_{2u}	4.89	0.0014
$\Psi(L_a)$	$\sqrt{\frac{1}{2}}(\Psi_2^4 + \Psi_3^5)$	B_{1u}	6.14	0.10
$\Psi(B_b)$	$\sqrt{\frac{1}{2}}(\Psi_2^5 + \Psi_3^4)$	E_{1u}	6.75	0.69
$\Psi(B_a)$	$\sqrt{\frac{1}{2}}(\Psi_2^4 - \Psi_3^5)$			
Hypothetical E_{2g} states			Calcd. energy, ev. ^b	
	$\sqrt{\frac{1}{2}}(\Psi_1^5 + \Psi_3^6)$		8.18	
	$\sqrt{\frac{1}{2}}(\Psi_1^4 + \Psi_2^6)$			
	$\sqrt{\frac{1}{2}}(\Psi_1^5 - \Psi_3^6)$		8.89	
	$\sqrt{\frac{1}{2}}(\Psi_1^4 - \Psi_2^6)$			
	$\sqrt{\frac{1}{2}}(\Psi_{32}^{44} - \Psi_{32}^{54})$		10.36	
	$\sqrt{\frac{1}{2}}(\Psi_{33}^{54} - \Psi_{32}^{55})$			
	Ψ_{33}^{55}		11.40	
	Ψ_{33}^{44}			
	$\sqrt{\frac{1}{2}}(\Psi_{32}^{44} + \Psi_{22}^{54})$		11.49	
	$\sqrt{\frac{1}{2}}(\Psi_{33}^{54} + \Psi_{32}^{55})$			
A_{2g} States	$\sqrt{\frac{1}{2}}(\Psi_{22}^{55} - \Psi_{33}^{44})$		10.69	
A_{1g} States	$\sqrt{\frac{1}{2}}(\Psi_{22}^{55} + \Psi_{33}^{44})$		10.69	

^a H. B. Klevens and J. R. Platt, "Technical Report of Laboratory of Molecular Structure and Spectra," The University of Chicago, 1953-1954, Part I, p. 145. ^b Calculated using the Pariser and Parr method (ref. 3a).

Doubly excited configurations arise from the excitation of two electrons from ψ_2 and ψ_3 to ψ_4 and ψ_5 . In Table I, the lowest energy doubly excited E_{2g} , A_{2g} and A_{1g} configurations are listed; their energies can be computed using suitable resonance and electron repulsion integrals.^{3a} Of course, the possible interactions among the E_{2g} configurations will give rise to slightly different E_{2g} states, and singly excited states also may be slightly depressed by the doubly excited configurations. In this paper, the higher electronic states of benzene will not be discussed in detail because the effect of substitution is the primary concern.

(6) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

(7) E. U. Condon and G. H. Shortley, "The Theory of Atomic Spectra," Cambridge University Press, 1935, p. 169ff.

(8) J. R. Platt, *J. Chem. Phys.*, **17**, 484 (1949).

(9) E. Clar, "Aromatische Kohlenwasserstoffe," Springer, Berlin, 1941.

TABLE II
INDUCTIVE INTERACTIONS BETWEEN THE ELECTRONIC STATES OF MONO-SUBSTITUTED BENZENE

$\Psi(L_b)$	$\Psi(B_b)$	$\sqrt{\frac{1}{2}}(\Psi_{1^4} + \Psi_{2^2})$	$\sqrt{\frac{1}{2}}(\Psi_{1^4} - \Psi_{2^2})$	$\sqrt{\frac{1}{2}}(\Psi_{33^{54}} - \Psi_{32^{55}})$	$\sqrt{\frac{1}{2}}(\Psi_{33^{54}} + \Psi_{32^{55}})$	$\sqrt{\frac{1}{2}}(\Psi_{22^{55}} - \Psi_{33^{44}})$	$\sqrt{\frac{1}{2}}(\Psi_{22^{55}} + \Psi_{33^{44}})$	
$\Psi(L_b)$	$E'(L_b)$	$\frac{1}{3}\delta$	$\frac{1}{3\sqrt{2}}\delta$	0	0	$-\frac{1}{3}\delta$	$\frac{1}{\sqrt{6}}\delta$	0
$\Psi(B_b)$	$\frac{1}{3}\delta$	$E'(B_b)$	0	$-\frac{1}{3\sqrt{2}}\delta$	$\frac{1}{3}\delta$	0	0	$\frac{1}{\sqrt{6}}\delta$
Ψ_0	Ψ_0	$\Psi(L_a)$	$\Psi(B_a)$	$\sqrt{\frac{1}{2}}(\Psi_{1^5} + \Psi_{2^2})$	$\sqrt{\frac{1}{2}}(\Psi_{1^5} - \Psi_{2^2})$	$\Psi_{33^{55}}$		
Ψ_0	$E'(0)$	$\frac{1}{3}\delta$	$-\frac{1}{3}\delta$	$\frac{\sqrt{2}}{3}\delta$	0	0		
$\Psi(L_a)$	$\frac{1}{3}\delta$	$E'(L_a)$	0	0	$\frac{1}{3\sqrt{2}}\delta$	$\frac{1}{3}\delta$		
$\Psi(B_a)$	$-\frac{1}{3}\delta$	0	$E'(B_a)$	$\frac{1}{3\sqrt{2}}\delta$	0	$-\frac{1}{3}\delta$		

As has been mentioned in Part I,² the inductive effect may be ascribed to the fact that the substituent modifies the potential field acting on the π -electrons of the hydrocarbon, *i.e.*, the perturbation on a single electron at the atom attached to the substituent. In the way described in Sec. 3 of Part I, we suppose that a coulomb integral contribution δ_r ($\delta_r\beta$ in Part I) is manifest on the carbon atom r adjacent to the substituent, due to the perturbing potential H_i' acting on electron i at atom r

$$\delta_r = \int \phi_r(i) H_i' \phi_r(i) dv(i) \quad (13)$$

Such portions of diagonal matrix elements on atoms not adjacent to the substituent and the non-diagonal elements $\int \phi_r(i) H_i' \phi_s(i) dv(i)$ are assumed to be negligibly small compared with δ_r .

The matrix elements of $\mathcal{H} (= H_0 + \sum_i H_i')$ between the electronic states listed in Table I can be evaluated from the formulas given in Appendix A, and the matrix elements of H' between the molecular orbitals are determined by the perturbation parameter δ_r and the atomic orbital coefficients $x_{i\mu}$ in eq. 2. In Table II are shown the matrix elements of \mathcal{H} including the inductive perturbation for the various states in mono-substituted benzene. (δ in this table corresponds to δ_1 of definition 13.) It will be observed that the inductive substitution causes the ground state to interact with $\Psi(L_b)$ and $\Psi(B_a)$ states, but not with $\Psi(L_b)$ and $\Psi(B_b)$ states. In addition, only $\Psi(L_b)$ and $\Psi(B_b)$ states interact with the doubly excited configurations $\sqrt{\frac{1}{2}}(\Psi_{22^{55}} \pm \Psi_{33^{44}})$ of A_{2g} and A_{1g} symmetries.

To calculate the energy shifts in the actual bands resulting from the inductive substitution, we may use the second-order perturbation theory

$$\Delta E_m = \int \Psi_0 H' \Psi_0 dv + \sum_k \frac{(m|\mathcal{H}|K)^2}{E_m - E_k} \quad (14)$$

and this formula can be applied to the four main bands in benzene. When we consider energy differences, the first-order terms of eq. 14 cancel, so that the observed shifts should be proportional to δ_2 . The second-order energy changes of the ground state and the four lowest electronic states of mono-substituted benzenes thus computed are shown in Table III. It is seen from this table that the wave length shifts relative to benzene are to

the red for the L_b band; the three L_b , B_b and B_a bands experience blue shifts.

4. Electron Transfer States and Conjugative Effect

When electrons are transferred from the substituent to the hydrocarbon, or from the hydrocarbon to the substituent, there will be interaction between such electron transfer states and the excited states of the hydrocarbon. If we restrict our attention to electron transfer from the substituent to the hydrocarbon (benzene), the energies and the matrix elements of the interactions can be evaluated using the formulas given in Appendix A. For example, the energy of the one-electron transfer configuration Ψ_{ω^1} , which arises from excitation of an electron in the non-bonding orbital ω of the substituent to one of the vacant orbitals ψ_i of benzene, is given by

$$E(\Psi_{\omega^1}) = F_{ii} - F_{\omega\omega} - \int \int \psi_i^2(a) \frac{e^2}{r_{ab}} \omega^2(b) dv(a) dv(b) \quad (15)$$

where F_{ii} and $F_{\omega\omega}$ are the Hartree-Fock parameters or the energies of the self-consistent orbitals ψ_i and ω , and are taken to be equal to the negatives of the electron affinity A of benzene and of the ionization potential I of the substituent, respectively. As the formal neglect of differential overlap between atomic orbitals has been assumed, the interelectronic exchange repulsion integrals involving the orbital ω should vanish and only coulomb type ones such as the last term of eq. 15 need to be considered. These coulomb type repulsion integrals can be expanded as linear combinations of integrals over atomic orbitals of the form^{9,10}

$$\int \int \phi_p^2(a) \frac{e^2}{r_{ab}} \omega^2(b) dv(a) dv(b) \quad (16)$$

These can be evaluated using the uniformly charged sphere approximation^{9a,11} as discussed in Appendix B.

The energies of the two-electron transfer configurations are given in a similar manner, but in those cases both coulomb and exchange electronic repulsion integrals involving the orbitals ψ_2 , ψ_3 , ψ_4 and ψ_5 of benzene need to be evaluated. It will be seen in Appendix B that this is done easily by

(10) See ref. 2.

(11) R. G. Parr, *J. Chem. Phys.*, **20**, 1499 (1952).

TABLE III
COMPUTED SECOND-ORDER ENERGY CHANGES OF THE LOWEST ELECTRONIC STATES OF MONO-SUBSTITUTED BENZENES (UNITS OF δ^2)

	$\psi(1_{1a})$	$\psi(1_{1b})$	$\sqrt{\frac{1}{2}}(\psi_1^4 + \psi_2^6)$	$\sqrt{\frac{1}{2}}(\psi_1^4 - \psi_2^6)$	$\sqrt{\frac{1}{2}}(\psi_{33}^4 + \psi_{22}^6)$	$\sqrt{\frac{1}{2}}(\psi_{33}^4 - \psi_{22}^6)$	$\sqrt{\frac{1}{2}}(\psi_{33}^4 + \psi_{22}^6)$	$\sqrt{\frac{1}{2}}(\psi_{22}^6 + \psi_{33}^4)$	$\sqrt{\frac{1}{2}}(\psi_{22}^6 - \psi_{33}^4)$	Total	Relative to ψ_0
$\Delta E(L_a)$...	-0.0598	-0.0168	-0.0357	...	-0.1292	-0.0674
$\Delta E(B_b)$	-0.0598	-0.0259	-0.0308	-0.0319	-0.0288	+0.0330
	ψ_0	$\psi(1_{1a})$	$\psi(1_{1b})$	$\psi(B_a)$	$\sqrt{\frac{1}{2}}(\psi_1^6 + \psi_2^6)$	$\sqrt{\frac{1}{2}}(\psi_1^6 - \psi_2^6)$	ψ_{33}^4	Total	Relative to ψ_0		
$\Delta E(0)$...	-0.0181	...	-0.0165	-0.0272	-0.0618	0		
$\Delta E(L_a)$	-0.0181	-0.0202	-0.0211	-0.0232	+0.0386		
$\Delta E(B_a)$	-0.0165	-0.0388	...	-0.0241	-0.0464	+0.0154		

making use of the Pariser and Parr approximation. In addition, $E(\Psi_3^4)$ and $E(\Psi_2^6)$ may be assumed to be equal to 5.51 e.v., the mean of the B_{1u} and B_{2u} state energies of benzene, while $E(\Psi_3^5)$ and $E(\Psi_2^4)$ may be taken as 6.75 e.v., the observed energy of the E_{1u} state. The energies of possible electron transfer configurations which interact with the ground state and the four lower electronic states of benzene are listed in Table IV. We thus have taken into account all possible electron transfer configurations except the ones which arise from the excitation $\omega \rightarrow \psi_6$.

Following the procedure of Sec. 2, the matrix elements of the interaction between the electron transfer configurations and the ground state or the lower excited configurations of benzene can be expressed in terms of the exchange integral

$$\gamma_{ex} = \int \phi_r(i)H(i)\omega(i)d\tau(i) \quad (17)$$

where ϕ_r is the atomic orbital of the carbon atom to which the substituent is attached. The results are shown in Table IV. We now can calculate the energy shifts in the actual bands resulting from the conjugative effect, applying the second-order perturbation theory. As has been emphasized in Part I, we must be attentive to the application of the second-order perturbation theory, whenever the energy levels of some electron transfer configurations are close to the levels of the lower excited configurations of benzene. We take this simplified step in order to avoid complicated computations; an example of an unreasonable conclusion resulting from applying this treatment will be discussed later.

5. Method of Empirical Parameter Determination and its Application to Some Mono-substituted Benzenes

It has been emphasized in Part I that the observed displacement of the first ionization potential in substituted benzenes relative to benzene is of practical use for the determination of energy parameters which cannot be calculated non-empirically. To obtain the theoretical expression for the first ionization potential of a substituted benzene, we shall first consider to what extent the electron interaction affects the orbital energies in benzene. The effect of electron interaction seems to be very important for the computations of orbital energies and consequently of the first ionization potentials of conjugated molecules.¹²

Now the interactions which occur between the molecular orbitals are shown in Table V. These are obtained easily from the atomic orbital coefficients of each benzene molecular orbital and the definitions 13 and 17 (see also Appendix of Part I). Because of neglecting differential overlap, the off-diagonal matrix elements do not involve the electron interaction terms. Applying the second-order perturbation theory, the change in the first ionization potential ΔI is given by (see Appendix C)

$$\Delta I \equiv I_B - I_S = \frac{1}{2} \left[\frac{1}{3} \delta + 0.0037\delta^2 + \frac{1}{3(I_X - I_B)} \gamma^2_{ex} \right] \quad (18)$$

(12) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953). See also ref. 6.

TABLE IV
THE ENERGIES OF THE ELECTRON TRANSFER STATES AND THE MATRIX ELEMENTS OF THE RESONANCE INTERACTIONS

State	Energy	Interaction energy with				
		Ψ_a	$\Psi(L_b)$	$\Psi(L_a)$	$\Psi(B_b)$	$\Psi(B_a)$
Ψ_{ω^5}	$I - A - J_{\omega_5}$	$\sqrt{\frac{2}{3}}\gamma_{cx}$	0	$-\sqrt{\frac{1}{6}}\gamma_{cx}$	0	$\sqrt{\frac{1}{6}}\gamma_{cx}$
Ψ_{ω^4}	$I - A - J_{\omega_4}$	0	$\sqrt{\frac{1}{6}}\gamma_{cx}$	0	$-\sqrt{\frac{1}{6}}\gamma_{cx}$	0
$\Psi_{\omega_2^{55}}$	$I - A - 2J_{\omega_5} + J_{\omega_4} + 5.37$	0	$-\sqrt{\frac{1}{6}}\gamma_{cx}$	0	$-\sqrt{\frac{1}{6}}\gamma_{cx}$	0
$\Psi_{\omega_3^{55}}$	$I - A - J_{\omega_5} + 5.80$	0	0	$-\sqrt{\frac{1}{6}}\gamma_{cx}$	0	$\sqrt{\frac{1}{6}}\gamma_{cx}$
$\Psi_{\omega_2^{54}(A)}$	$I - A - J_{\omega_5} + 5.65$	0	0	$-\frac{1}{2\sqrt{3}}\gamma_{cx}$	0	$-\frac{1}{2\sqrt{3}}\gamma_{cx}$
$\Psi_{\omega_3^{54}(A)}$	$I - A - J_{\omega_4} + 4.80$	0	$\frac{1}{2\sqrt{3}}\gamma_{cx}$	0	$-\frac{1}{2\sqrt{3}}\gamma_{cx}$	0
$\Psi_{\omega_2^{54}(B)}$	$I - A - J_{\omega_5} + 5.98$	0	0	$\frac{1}{2}\gamma_{cx}$	0	$\frac{1}{2}\gamma_{cx}$
$\Psi_{\omega_3^{54}(B)}$	$I - A - J_{\omega_4} + 6.98$	0	$\frac{1}{2}\gamma_{cx}$	0	$-\frac{1}{2}\gamma_{cx}$	0

TABLE V

THE MATRIX ELEMENTS OF THE INTERACTIONS BETWEEN THE MOLECULAR ORBITALS IN MONOSUBSTITUTED BENZENE^{a, b}

	ψ_1	ψ_2	ψ_3	ψ_4	ψ_5	ψ_6	ω
ψ_1	$E_1^0\left(+\frac{1}{6}\delta\right)$	0	$\frac{1}{3\sqrt{2}}\delta$	0	$\frac{1}{3\sqrt{2}}\delta$	$\frac{1}{6}\delta$	$\frac{1}{\sqrt{6}}\gamma_{cx}$
ψ_2	0	E_2^0	0	0	0	0	0
ψ_3	$\frac{1}{3\sqrt{2}}\delta$	0	$E_3^0\left(+\frac{1}{3}\delta\right)$	0	$\frac{1}{3}\delta$	$\frac{1}{3\sqrt{2}}\delta$	$\frac{1}{\sqrt{3}}\gamma_{cx}$
ψ_4	0	0	0	E_4^0	0	0	0
ψ_5	$\frac{1}{3\sqrt{2}}\delta$	0	$\frac{1}{3}\delta$	0	$E_5^0\left(+\frac{1}{3}\delta\right)$	$\frac{1}{3\sqrt{2}}\delta$	$\frac{1}{\sqrt{3}}\gamma_{cx}$
ψ_6	$\frac{1}{6}\delta$	0	$\frac{1}{3\sqrt{2}}\delta$	0	$\frac{1}{3\sqrt{2}}\delta$	$E_6^0\left(+\frac{1}{6}\delta\right)$	$\frac{1}{\sqrt{6}}\gamma_{cx}$
ω	$\frac{1}{\sqrt{6}}\gamma_{cx}$	0	$\frac{1}{\sqrt{3}}\gamma_{cx}$	0	$\frac{1}{\sqrt{3}}\gamma_{cx}$	$\frac{1}{\sqrt{6}}\gamma_{cx}$	E_{ω}^0

^a Concerning the values for E_1^0 , see Appendix B. ^b The terms in parentheses correspond to the first-order ones.

where I_B , I_X and I_S are the first ionization potentials of benzene, substituent, and substituted benzene, respectively, and δ and γ_{cx} are as defined earlier. The factor of $1/2$ in eq. 18 has its origin in assumption (4) of Part I, Sec. 3. If an appropriate value is assigned to I_X , ΔI may be expressed in terms of δ and γ_{cx} . The following illustrations will show how these empirical parameters can be determined in some mono-substituted benzenes from the spectral shifts of the L_b bands and eq. 18, and the parameters thus determined then used to predict higher electronic states.

The energies of the possible electron transfer states in chlorobenzene, bromobenzene and phenol listed in Table VI have been calculated from the energy formulas given in Table IV, taking the values of I as equal to the ionization potentials¹³ of HCl (12.74 e.v.), HBr (11.62 e.v.), and H₂O (12.59 e.v.), respectively, and A as -0.54 e.v.¹⁴ J_{ω_5} and J_{ω_4} are computed by making use of the uniformly charged sphere approximation, taking the bond length of benzene to be 1.39 Å. and the length of the bond joining the substituent to the benzene in chlorobenzene, bromobenzene and phenol to be 1.69, 1.86 and 1.40 Å. (assumed),

(13) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

(14) J. A. Pople and N. S. Hush, *Trans. Faraday Soc.*, **51**, 600 (1955).

respectively (see Appendix B). To apply the second-order perturbation theory, the matrix elements of the interactions between the lower electronic states of benzene and the electron transfer states due to the substituent shown in Table IV are needed. Calculated resonance depressions of the ground state and lower electronic states are listed in Table VII. The second-order energy

TABLE VI

CALCULATED ENERGIES OF THE ELECTRON TRANSFER STATES OF CHLOROBENZENE, BROMOBENZENE AND PHENOL (e.v.)

	Chloro- benzene	Bromo- benzene	Phenol
$E(\Psi_{\omega^5})$	8.54	7.65	7.94
$E(\Psi_{\omega^4})$	8.93	7.98	8.47
$E(\Psi_{\omega_2^{55}})$	13.52	12.69	12.78
$E(\Psi_{\omega_3^{55}})$	14.34	13.45	13.74
$E(\Psi_{\omega_2^{54}(A)})$	14.19	13.30	13.59
$E(\Psi_{\omega_3^{54}(A)})$	13.73	12.78	13.27
$E(\Psi_{\omega_2^{54}(B)})$	14.92	13.63	13.92
$E(\Psi_{\omega_3^{54}(B)})$	14.52	14.96	15.45
J_{ω^5}	4.74	4.51	5.19
J_{ω^4}	4.35	4.18	4.66

changes due to the inductive effect, on the other hand, are given in Table III, and the actual spectral shifts of the lower electronic states should be the sum of the two changes.

TABLE VII

DEPRESSIONS OF THE GROUND STATE AND THE LOWER ELECTRONIC STATES OF MONOSUBSTITUTED BENZENES BY THE CONJUGATIVE EFFECT IN UNITS OF γ^2CX

	Chlorobenzene		Bromobenzene		Phenol	
	Relative to $E(0)$		Relative to $E(0)$		Relative to $E(0)$	
$E(0)$	-0.0781	0	-0.0871	0	-0.0876	0
$E(L_b)$	-.0960	-.0179	-.1106	-.0235	-.1014	-.0138
$E(L_a)$	-.1286	-.0505	-.1782	-.0911	-.1578	-.0702
$E(B_b)$	-.1452	-.0671	-.2079	-.1208	-.1660	-.0784
$E(B_a)$	-.1569	-.0788	-.2591	-.1720	-.2110	-.1234

TABLE VIII

ENERGY PARAMETERS AND COMPARISON OF THE OBSERVED AND CALCULATED SPECTRA OF CHLOROBENZENE, BROMOBENZENE AND PHENOL^a (e.v.)

	Benzene	Chlorobenzene		Bromobenzene		Phenol	
		Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.
I_X^b (=HX)	...		12.74		11.62		12.59
δ	...	-0.921		-0.824		-1.555	
γ_{CX}	...	-2.620		-2.390		-3.582	
I^b	9.24	(9.07)	9.07	(8.98)	8.98	(8.50)	8.50
L_b	4.89	(4.71)	4.71	(4.71)	(4.71) ^c	(4.55)	4.55
L_a	6.14	5.81	5.78	5.65	5.77	5.33	5.83
B_b	6.75	6.35	6.54	6.08	6.50	5.82	6.53
B_a		6.22	...	5.78	...	5.20	...

^a The spectral data are taken from H. B. Klevens and J. R. Platt, "Technical Report of Laboratory of Molecular Structure and Spectra," The University of Chicago, 1953-1954, Part one, p. 145. ^b The ionization potential data are taken from K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957). ^c Assumed from the data of H. Sponer and E. Teller, *Rev. Mod. Phys.*, **13**, 75 (1941).

Taking the values of I_X , I and the energy of the $\Psi(L_b)$ state in three substituted benzenes and the corresponding values of benzene, listed in Table VIII, two parameters δ and γ_{CX} are determined by solving simultaneously the equation on spectral shifts of L_b band and eq. 18. The results are shown in Table VIII. It is of interest to examine whether the higher electronic states of these substituted benzenes can be predicted accurately using the parameters thus determined. The spectral shifts of L_a , B_b and B_a bands in these molecules relative to benzene are evaluated readily by utilizing Tables III and VII, and are compared with the observed values. The results are fairly satisfactory for the L_a band, but not so good for the B_b band; *i.e.*, the electronic states $\Psi(B_b)$ and $\Psi(B_a)$ tend to be more depressed than $\Psi(L_b)$ and $\Psi(L_a)$ states. This is attributable to the use of the second-order perturbation method, and will be discussed in the following section.

6. Critical Discussion

It has been shown how the simple wave functions expressing the lower electronic states of benzene can pave the way for the interpretation of the spectral changes produced by the conjugative and inductive substituents. This idea has been initiated by Dewar and Longuet-Higgins and their co-workers. In this paper, a plan for a further step toward improvement of this useful idea has been carried out. The effect of electron interaction has been taken into account under the formal neglect of differential overlap. Although this assumption has been used successfully in the works of Pariser and Parr^{2,15} for the computation of the lower electronic states of aromatic hydrocarbons, circumstances may be slightly different in substituted hydrocarbons. The assumptions that δ

and γ_{CX} are fixed for all interactions may also produce considerable errors, particularly when comparatively weak inductive and conjugative effects are treated.

Here several works done by Goodman and Shull¹⁶ should be cited; they treat the substituted benzene spectra using the perturbation method but not including the higher-order configuration interaction such as a two-electron excitation. It should be noted that the present paper and reference 4c show that the two-electron excited configurations play an important role in the substituted benzene spectra.

Now we should refer to the application of the second-order perturbation method. As has been mentioned already in Part I, this method may introduce significant errors when one or more of the interacting levels are fairly close to the others. In fact, such cases are found in bromobenzene and phenol, in which the $\Psi(B_b)$ and $\Psi(B_a)$ states of benzene and the electron transfer states Ψ_{ω^5} or Ψ_{ω^4} are close. As Table VIII shows the $\Psi(L_a)$ states in both molecules can be predicted with tolerable accuracy for the $\Psi(B_b)$ and $\Psi(B_a)$ states but the agreement is poor. This state of affairs is at its worst in the cases of aniline and iodobenzene. For example, the energies of the Ψ_{ω^5} and Ψ_{ω^4} states are calculated as 5.61 and 6.10 e.v. in aniline and as 6.52 and 6.72 e.v. in iodobenzene. In these molecules, therefore, the second-order perturbation method cannot be applied with suitable accuracy for the computation of the lower electronic states although strong charge transfer spectra should be expected. Some other method should be used in this connection.

Lastly, it may be questioned whether the transfer of electrons from the benzene ring to the sub-

(15) R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).

(16) I. Goodman and H. Shull, *ibid.*, **27**, 1388 (1957); I. Goodman, I. G. Ross and H. Shull, *ibid.*, **26**, 474 (1957).

stituent may be also allowed in some cases. In the molecules we have treated in this paper, such an opposite transfer seems to be energetically unfavorable because the vacant orbital of the substituent is located at a high energy level.

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Appendix A

The functions for doubly excited configuration which forms are not shown in Sec. 2 can be written as

$$\Psi_{ij}^{kk} = 2^{-1/2} \{ |(\psi_i\alpha)(\psi_j\beta)(\psi_k\alpha)(\psi_k\beta)| +$$

$$|(\psi_i\beta)(\psi_j\alpha)(\psi_k\alpha)(\psi_k\beta)| \}$$

$$\Psi_{ii}^{kl} = 2^{-1/2} \{ |(\psi_k\alpha)(\psi_i\beta)(\psi_j\alpha)(\psi_j\beta)| +$$

$$|(\psi_k\beta)(\psi_i\alpha)(\psi_j\alpha)(\psi_j\beta)| \}$$

$$\Psi_{ij}^{kl} (A) = 2^{-1} \{ |(\psi_i\alpha)(\psi_j\beta)(\psi_k\alpha)(\psi_l\beta)| +$$

$$|(\psi_i\beta)(\psi_j\alpha)(\psi_k\beta)(\psi_l\alpha)| -$$

$$|(\psi_i\alpha)(\psi_j\beta)(\psi_k\beta)(\psi_l\alpha)| - |(\psi_i\beta)(\psi_j\alpha)(\psi_k\alpha)(\psi_l\beta)| \}$$

$$\Psi_{ij}^{kl} (B) = 12^{-1/2} \{ 2|(\psi_i\alpha)(\psi_j\alpha)(\psi_k\beta)(\psi_l\beta)| +$$

$$2|(\psi_i\beta)(\psi_j\beta)(\psi_k\alpha)(\psi_l\alpha)| -$$

$$|(\psi_i\alpha)(\psi_j\beta)(\psi_k\alpha)(\psi_l\beta)| - |(\psi_i\beta)(\psi_j\alpha)(\psi_k\beta)(\psi_l\alpha)| -$$

$$|(\psi_i\beta)(\psi_j\alpha)(\psi_k\alpha)(\psi_l\beta)| - |(\psi_i\alpha)(\psi_j\beta)(\psi_k\beta)(\psi_l\alpha)| \}$$

The formulas of the matrix elements between doubly and singly excited configurations, and between those and the ground state are reproduced here together with the energies of these configurations. Mostly they are listed in reference 4c.

$$E(\Psi_{ii}^{kk}) = 2E(\Psi_i^k) + J_{ii} + J_{kk} - 2J_{ik} - 2K_{ik}$$

$$E(\Psi_{ij}^{kk}) = E(\Psi_i^k) + E(\Psi_j^k) + J_{ij} +$$

$$J_{kk} - J_{ik} - J_{jk} + K_{ij} - K_{ik} - K_{jk}$$

$$E(\Psi_{ii}^{kl}) = E(\Psi_i^k) + E(\Psi_i^l) + J_{ii} +$$

$$J_{kl} - J_{ik} - J_{il} + K_{kl} - K_{ik} - K_{il}$$

$$E(\Psi_{ij}^{kl} (A)) = E(\Psi_i^k) + E(\Psi_j^l) + J_{ij} +$$

$$J_{kl} - J_{jk} - J_{il} + K_{ij} + K_{kl} +$$

$$\frac{1}{2}(K_{ik} + K_{il}) - \frac{3}{2}(K_{ik} + K_{jl})$$

$$E(\Psi_{ij}^{kl} (B)) = E(\Psi_i^k) + E(\Psi_j^l) + J_{ij} + J_{kl} - J_{ik} -$$

$$J_{jl} - K_{ij} - K_{kl} - \frac{1}{2}(K_{jk} + K_{il}) - \frac{3}{2}(K_{ik} + K_{il})$$

$$(\Psi_i^k | \mathcal{H} | \Psi_0) = \sqrt{2} F_{ik}$$

$$(\Psi_i^k | \mathcal{H} | \Psi_j^l) = \delta_{ij} F_{kl} - \delta_{kl} F_{ij} + 2(ik|jl) - (ij|kl)$$

$$(\Psi_{ii}^{kk} | \mathcal{H} | \Psi_0) = (ik|ik)$$

$$(\Psi_{ij}^{kk} | \mathcal{H} | \Psi_0) = -\sqrt{2}(ik|jk)$$

$$(\Psi_{ii}^{kl} | \mathcal{H} | \Psi_0) = \sqrt{2}(ik|il)$$

$$(\Psi_{ij}^{kl} (A) | \mathcal{H} | \Psi_0) = (kj|li) - (ki|lj)$$

$$(\Psi_{ij}^{kl} (B) | \mathcal{H} | \Psi_0) = \sqrt{3} \{ (kj|li) - (ki|lj) \}$$

$$(\Psi_{ii}^{kk} | \mathcal{H} | \Psi_r^s) = \sqrt{2} \{ \delta_{ri} \delta_{sk} F_{kl} - \delta_{sk} (ri|ki) + \delta_{ri} (ki|ks) \}$$

$$(\Psi_{ij}^{kk} | \mathcal{H} | \Psi_r^s) = - [\delta_{sk} \delta_{ri} F_{kj} + \delta_{rk} (kj|ks) -$$

$$\delta_{sk} \{ (ki|rj) + (kj|ri) \}]$$

$$(\Psi_{ii}^{kl} | \mathcal{H} | \Psi_r^s) = \delta_{sk} \delta_{ri} F_{il} +$$

$$\delta_{ri} \{ (ki|ls) + (ks|li) \} - \delta_{sk} (ri|li)$$

$$(\Psi_{ij}^{kl} (A) | \mathcal{H} | \Psi_r^s) = -1/\sqrt{2} [\delta_{ri} \delta_{sk} F_{ij} - \delta_{sk} \{ (ri|lj) +$$

$$(rj|li) \} + \delta_{ri} \{ (kj|ls) + (ks|lj) \}]$$

$$(\Psi_{ij}^{kl} (B) | \mathcal{H} | \Psi_r^s) = -\sqrt{3}/2 [\delta_{ri} \delta_{sk} F_{ij} - \delta_{sk} \{ (ri|lj) -$$

$$(rj|li) \} - \delta_{ri} \{ (kj|ls) - (ks|lj) \}]$$

Appendix B

The uniformly charged sphere approximation^{2,10} consists of replacing each charge distribution

$e\bar{\phi}_i(1)\phi_j(1)$ by a pair of tangent uniformly charged non-conducting spheres of diameter

$$R_i = (4.597/Z_i) \times 10^{-8} \text{ cm.} \quad (A)$$

where Z_i is the Slater effective nuclear charge for the π atomic orbital ϕ_i , and the integrals $(ii|jj)$ over atomic orbitals are computed as classical electrostatic repulsions. In practice, the two-center integrals $(ii|jj)$ are computed for the atomic distance r longer than 2.80 Å. by the following formula based on the uniformly charged model

$$(ii|jj) = (7.1975/r) \{ [1 + (1/2r)^2(R_i - R_j)^2]^{-1/2} + [1 + (1/2r)^2(R_i + R_j)^2]^{-1/2} \} \quad (B)$$

and for $r < 2.80$ Å., the $(ii|jj)$ are determined by extrapolating the values evaluated at the longer distances down to $r = 0$. Equation (c) is used for this purpose

$$ar + br^2 = -\frac{1}{2} [(ii|ii) + (jj|jj)] - (ii|jj) \quad (C)$$

where the constants a and b are obtained by integral values computed from eq. B for the two appropriate internuclear distances. The integrals $(ii|ii)$ or $(jj|jj)$ are taken as

$$(ii|ii) = I_i - A_i \quad (D)$$

where I_i and A_i are the valence state ionization potential and electron affinity of the neutral atom i , respectively.¹⁷

The computational results for chloro- and bromobenzene and phenol are

Integral	Chlorobenzene		Bromobenzene		Phenol	
	r (Å.)	Value (e.v.) ^a	r (Å.)	Value (e.v.) ^a	r (Å.)	Value (e.v.) ^a
$(\omega \omega)$		9.87		9.25		11.86
$(\omega 11)$	1.69	6.69	1.86	6.29	1.40	7.54
$(\omega 22)$	2.67	5.13	2.82	4.93	2.42	5.53
$(\omega 33)$	3.96	4.95	4.12	3.44	3.69	3.80
$(\omega 44)$	4.47	3.17	4.64	3.06	4.18	3.37

$${}^a(11|11)_{CC} = 11.22 - 0.69 \text{ e.v.}$$

$$(\omega|\omega)_{Cl\ Cl} = 13.66 - 3.79 \text{ e.v.}$$

$$(\omega|\omega)_{Br\ Br} = 12.43 - 3.68 \text{ e.v.}$$

$$(\omega|\omega)_{OO} = 14.73 - 2.87 \text{ e.v.}$$

Integrals for $r \geq 2.80$ Å. are calculated by eq. B taking $Z_C = 3.25$, $Z_{Cl} = 6.10$, $Z_{Br} = 7.60$ and $Z_O = 4.55$. For $r < 2.80$ Å., the following equations are used

$$(\omega|\omega)_{Cl\ C} = 0.1809r^2 - 2.3811r + 10.20$$

$$(\omega|\omega)_{Br\ C} = 0.1385r^2 - 2.0607r + 9.64$$

$$(\omega|\omega)_{OO} = 0.2679r^2 - 2.9930r + 11.20$$

Then $J_{\omega 5}$ and $J_{\omega 4}$ listed in Table VI are evaluated by

$$J_{\omega 5} = \frac{1}{6} \{ 2(\omega|11) + (\omega|22) + (\omega|33) + 2(\omega|44) \}$$

and

$$J_{\omega 4} = \frac{1}{2} \{ (\omega|22) + (\omega|33) \}$$

Appendix C

Ionization Potentials of Benzene and Substituted Benzene.—The orbital energies of benzene, E_1^0 ,

(17) Cf. R. S. Mulliken, *J. Chem. Phys.*, **2**, 782 (1934).

are expressed as¹¹

$$E_0^0 = H_{11} + 2H_2 + \frac{1}{2}(1\ 1|1\ 1) + \frac{4}{3}(1\ 1|2\ 2) + 2(1\ 1|3\ 3) + \frac{7}{6}(1\ 1|4\ 4)$$

$$\left. \begin{matrix} E_2^0 \\ E_3^0 \end{matrix} \right\} = H_{11} + H_{12} + \frac{1}{2}(1\ 1|1\ 1) + \frac{5}{3}(1\ 1|2\ 2) + 2(1\ 1|3\ 3) + \frac{5}{6}(1\ 1|4\ 4)$$

$$\left. \begin{matrix} E_4^0 \\ E_5^0 \end{matrix} \right\} = H_{11} - H_{12} + \frac{1}{2}(1\ 1|1\ 1) + \frac{7}{3}(1\ 1|2\ 2) + 2(1\ 1|3\ 3) + \frac{7}{6}(1\ 1|4\ 4)$$

$$E_6^0 = H_{11} - 2H_{12} + \frac{1}{2}(1\ 1|1\ 1) + \frac{8}{3}(1\ 1|2\ 2) + 2(1\ 1|3\ 3) + \frac{5}{6}(1\ 1|4\ 4)$$

Under the approximations of formal neglect of differential overlap, electron interaction terms due to the introduction of the substituent will not enter the off-diagonal matrix elements between the molecular orbitals. When the second-order perturbation theory is applied for computing the

orbital energies of a substituted benzene, the energy differences between each orbital of benzene, therefore, have considerably different values according to whether the electron interaction is included or not. Referring to Table V, the difference between the observed first ionization potentials of benzene and a substituted benzene is given by the second-order perturbation theory as follows (the terms H_{11} , $(1\ 1|1\ 1)$, and $(1\ 1|3\ 3)$ cancel)

$$I = I_B - I_S = \frac{1}{2} \left\{ \frac{1}{3} \delta + \frac{\delta^2/18}{-H_{12} + \frac{1}{3}(1\ 1|2\ 2) - \frac{1}{3}(1\ 1|4\ 4)} + \frac{\delta^2/9}{2H_{12} - \frac{2}{3}(1\ 1|2\ 2) - \frac{1}{3}(1\ 1|4\ 4)} + \frac{\delta^2/18}{3H_{12} - (1\ 1|2\ 2)} + \frac{\gamma^2 c_X}{3(I_X - I_B)} \right\}$$

If the Pariser and Parr values are used; *i.e.*, $(1\ 1|2\ 2) = 7.30$, $(1\ 1|4\ 4) = 4.90$ e.v., and the $\pi - \pi$ exchange integral of benzene, H_{12} , is taken as -2.39 e.v. (*cf.* ref. 3a), ΔI becomes eq. 18 of Sec. 5.

TOKYO, JAPAN

[CONTRIBUTION FROM THE RICHARDSON CHEMISTRY DEPARTMENT, TULANE UNIVERSITY, AND THE USDA SOUTHERN REGIONAL RESEARCH LABORATORY]

The Thermal Stabilities and Infrared Spectra of Some Solid Metal Salt Stabilized Diazonium Salts¹

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The chlorides of Fe(III), Zn(II), Cd(II), Sn(IV), Sb(III), Hg(II) and Bi(III) have been used to stabilize *p*-dimethylaminobenzenediazonium chloride. The rates of nitrogen evolution from the solids at elevated temperatures have been studied and the infrared spectra of the solids were recorded. A correlation has been found between the rates of nitrogen evolution and the electronic configurations of the metal ions and the electronegativities of the metal atoms. Possible modes of interaction between diazonium ion and stabilizing agent are discussed. Water in the unit cell makes the solid diazonium salt less stable. Of the principal bands in the infrared spectra the band at 2160 cm.⁻¹ and the out-of-plane wag of ring hydrogen are of greatest interest. This latter band appears as a well split doublet in the case of the two most stable compounds.

Introduction

Of the enormous literature on diazonium salts, in which thermal stabilities of these solid substances are reported, the work of Nesmeyanov, *et al.*,³ covers the greatest variety of diazonium salts and inorganic stabilizing agents. Like all other reports on the stabilities they reported decomposition temperatures which were determined in the manner of melting points. The results clearly indicate an important influence of the metal salt stabilizing agents but comparisons of the results are made difficult as the decompositions occurred under various conditions. It was thought that a study of the rate of decomposition under controllable conditions would offer data more easily interpreted and more reliable.

The infrared spectra of the solids studied are also presented here.

(1) From a doctoral dissertation by Alcuin F. Gremillion.

(2) Monsanto Chemical Company, Lion Oil Division Research, El Dorado, Arkansas.

(3) A. N. Nesmeyanov, K. A. Kocheshkov, V. A. Klimova and N. K. Gipp. *Ber.*, **68B**, 1877 (1935).

Experimental

Preparation of Materials.—All ZnCl₂ stabilized diazonium salts were purchased from the Ringwood Chemical Company, Ringwood, Illinois. The other materials were prepared by stabilizing a saturated aqueous solution of *p*-dimethylaminobenzenediazonium chloride with a saturated aqueous solution of the appropriate metal salt. In the cases of stabilization with SbCl₃ and BiCl₃ the saturated stabilizing solutions were prepared with concentrated hydrochloric acid. Water and concentrated hydrochloric acid solutions of SnCl₄ both gave the same results. The compounds prepared were all precipitated from solution. Each precipitate was filtered, washed with 10% hydrochloric acid, pressed dry and stored *in vacuo* for several days with continuous pumping.

The *p*-dimethylaminobenzenediazonium chloride used in the preparations was obtained by destabilization of its ZnCl₂ stabilized derivative. Hydrogen sulfide was passed into an aqueous solution of the *p*-(CH₃)₂N-C₆H₄-N₂Cl·ZnCl₂·2H₂O until zinc sulfide would no longer precipitate. This required several filtrations of zinc sulfide and reuse of hydrogen sulfide. By passing in nitrogen the excess hydrogen sulfide was purged from the solution until the hydrogen sulfide odor was no longer detectable. The resulting solution was subjected to a vacuum distillation with water being removed until a saturated solution of the destabilized salt was obtained.