219. *Molecular-orbital Calculations on the Benzoate Ion.*

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Five molecular-orbital calculations on the benzoate ion have given quantitative estimates of the changes in the predictions of physical and chemical properties brought about by the different methods used in these calculations to allow for the presence of the hetero-atoms in the molecule. The calculations now reported give a measure of the dependence of the predictions of bond lengths and chemical reactivity on: (1) Wheland's assumption to determine the value for β carbon–oxygen, namely, that the exchange integral β is proportional to the overlap integral S; (2) the difference of the Coulomb integral α of the carbon atom next to the oxygen atom from the standard α due to an inductive effect on this carbon atom; (3) the inclusion of the overlap integral S in the calculations.

The differences in the predictions of bond lengths are not very large and all occur in the dimensions of the carboxyl group. The presence or absence of an inductive effect on the carbon atom next to the oxygen atom appears to have little influence on the bond lengths predicted. Considerable variation is observed in the predictions of chemical reactivity from these calculations.

THIS paper reports the results of calculations from which there have been obtained some quantitative estimates of the changes in the predictions of chemical and physical properties due to the various methods used in the simple molecular-orbital calculations to allow for the presence of a hetero-atom in a molecule.

The benzoate anion was selected although for some of the predictions of chemical reactivity, particularly for electrophilic substitution (which is generally carried out in acid solution), it would have been preferable to use the acid itself rather than the anion. The experimental data relevant to benzoic acid are not yet available, but from the carbon–oxygen distances in aliphatic acids (cf. Morrison and Robertson, *J.*, 1949, 987) the assumption that the acid possesses an axis of symmetry passing through the carboxyl group and the ring in the plane of the molecule would appear to be unjustified. It did not seem to be justifiable to incur the added complications that would be introduced into the computations in considering the Coulomb terms of the oxygen atoms in the molecule to be different.

The only reported work on molecular-orbital calculations on benzoic acid is that by Wheland and Pauling (*J. Amer. Chem. Soc.*, 1935, **57**, 2080) on benzene derivatives with hetero-atom substituents. They recognised that the Coulomb integral of the hetero-atom would be different from the "standard" carbon Coulomb integral since the electron affinities of hetero-atoms are different from that of carbon. Also they considered that a small inductive effect would be transmitted to the carbon atoms adjacent to the hetero-atoms. Wheland and Pauling did not consider that the values that should be assigned to β carbon–oxygen might be different from the standard value. Variations in the resonance integrals, β_{C-Y} (where Y refers to the hetero-atom) are to be expected (Coulson, *Trans. Faraday Soc.*, 1946, **42**, 106): the importance of these variations in β is greater than has often been supposed (cf. Coulson and De Heer, *J.*, 1952, 483).

Finally, there is the question of the inclusion of the overlap integral, S, between adjacent atomic orbitals. Chirgwin and Coulson (*Proc. Roy. Soc.*, 1950, *A*, **201**, 196) have shown that the inclusion makes no difference in the results of the calculations of the ground state of alternant hydrocarbons, although considerable improvement results in the correlation of calculations and experimental results of the excited states (Mulliken and Rieke, *J. Amer. Chem. Soc.*, 1941, **63**, 1770). Coulson and De Heer (*loc. cit.*) have suggested that the qualitative conclusions regarding the ground state of molecules containing a hetero-atom should not be seriously affected by the inclusion of overlap, but such inclusion is probably essential even in a qualitative discussion of the excited states of molecules that contain a hetero-atom (Chirgwin and Coulson, *loc. cit.*).

Wheland (*J. Amer. Chem. Soc.*, 1942, **64**, 900) included overlap in his calculations on the orienting influence of substituents in aromatic compounds; he explicitly considered variations in the Coulomb integrals brought about by the presence of the hetero-atom and the inductive effect on the neighbouring carbon atoms and also included a variation in the value given to β_{C-H} different from the standard value, but the assumption that he used in deciding on a value for β_{C-H} may not entirely satisfactory (see below).

Five calculations are now discussed. The importance of three assumptions is considered : (1) Wheland's assumption used in order to decide on a value for β_{C-O}; (2) the necessity to consider an inductive effect on the carbon atom next to the oxygen atom; and (3) the inclusion of the overlap integrals. The calculations will be tested by agreement between their predictions of (1) bond lengths and (2) chemical reactivity and the respective experimental values (in so far as these are available).

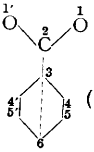
The values chosen for the various parameters (α_{oxygen}, etc.) in these calculations may not be the best possible, and further work on the effect of the variation of the values assigned to these parameters will be reported later.

Wheland's Assumption.—In order to decide on a value for β_{C-Y}, Wheland (*loc. cit.*) assumed that the resonance integral for this bond is proportional to its overlap integral. He defined the symbol

$$\rho_{C-Y} = \beta_{C-Y}/\beta_X = S_{C-Y}/S_X \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where S_{ij} has the usual meaning $\int\phi_i\phi_j d\tau$ (i and j are neighbouring atoms) and S_X refers to the "standard" overlap integral. Since the procedure for determining S_{ij} is straightforward (Mulliken, Rieke, Orloff, and Orloff, *J. Chem. Physics*, 1949, **17**, 2148), the use of Wheland's assumption implies that the value assigned to β_{C-H} can be readily determined.

In the application of this assumption to the present problem certain difficulties arise. Using the recipe of Mulliken *et al.* to determine S_{C-O} (the value of 1·23 Å was used as the length of the carbon–oxygen bond), one finds that $\rho_{C-O} = 0{\cdot}214/0{\cdot}250 = 0{\cdot}856$. Using Wheland's assumption one arrives at the conclusion that the value to be assigned to β_{C-O} is *less than* the value of β_X. However, previous workers have usually assumed that β_{C-O} is *greater than* β_X (Coulson, *Trans. Faraday Soc.*, 1946, **42**, 106; Dewar, *Nature*, 1950, **166**, 790; Brown, *J.*, 1951, 2670). The values assigned have been based on rather crude thermochemical considerations and are to be regarded as tentative. However, it seems probable that these values are of the right order of magnitude and there is certainly the possibility that Wheland's assumption should be modified so that the ratio of the β's is greater than the ratio of the S's.


(I)

In a detailed treatment of the self-consistent field molecular-orbital approximation, Mulliken (*J. Chim. physique*, 1949, **46**, 497, 675) has indicated that for carbon–carbon bonds β/S is approximately constant but that this would not be true for hetero-bonds. The further approximation that Wheland's assumption may not be justified involves no added difficulty in the computations. This can be illustrated by writing the benzoic acid anion as in (I) and considering the secular equation that arises from the wave functions that are symmetrical about the axis of symmetry. Using Wheland's notation as far as possible and remembering that $\gamma_X = \beta_X - S\alpha_X$, we have

$$\begin{vmatrix} \alpha_X + \delta_1\gamma_X - E & \rho_{12}(\beta_X - S_XE) + k\gamma_X & \cdot & \cdot & \cdot & \cdot \\ 2[\rho_{12}(\beta_X - S_XE) + k\gamma_X] & \alpha_X + \delta_2\gamma_X - E & \rho_{23}(\beta_X - S_XE) & \cdot & \cdot & \cdot \\ \cdot & \rho_{23}(\beta_X - S_XE) & \alpha - E & 2(\beta_X - S_XE) & \cdot & \cdot \\ \cdot & \cdot & \beta_X - S_XE & \alpha - E & \beta_X - S_XE & \cdot \\ \cdot & \cdot & \cdot & \beta_X - S_XE & \alpha - E & \beta_X - S_XE \\ \cdot & \cdot & \cdot & \cdot & 2(\beta_X - S_XE) & \alpha - E \end{vmatrix} = 0 \qquad (2)$$

In (2) note has been made that the bond 2–3 is not a "standard" carbon–carbon bond; however, as mentioned above, Wheland's assumption does appear to be justified for such bonds. Equation (2) can readily be transformed into the more useful form (3), where $x = (\alpha - E)/(\beta_X - S_XE)$ and $\mathcal{L} = 1 - S_X\delta$. Equation (4) becomes Wheland's assumption when $k = 0$.

$$\begin{vmatrix} \mathcal{L}_1x + \delta_1 & \rho_{12} + k(1 - S_0x) & \cdot & \cdot & \cdot & \cdot \\ 2[\rho_{12} + k(1 - S_0x)] & \mathcal{L}_2x + \delta_2 & \rho_{23} & \cdot & \cdot & \cdot \\ \cdot & \rho_{23} & x & 2 & \cdot & \cdot \\ \cdot & \cdot & 1 & x & 1 & \cdot \\ \cdot & \cdot & \cdot & 1 & x & 1 \\ \cdot & \cdot & \cdot & \cdot & 2 & x \end{vmatrix} = 0 \qquad (3)$$

Calculations.—A solution for (3) requires a decision on values for δ_1, δ_2, and k. Wheland and Pauling chose the values $\delta_1 = 4$, $\delta_2 = 0{\cdot}8$; the former is twice as large as that used for α_{oxygen} by Brown (*J.*, 1951, 2670). The values $\delta_1 = 2$, $\delta_2 = 0{\cdot}4$ (for both β and γ) will be used in this paper. The value of $k = 0{\cdot}5$ was chosen in order to make the value of $\beta_{\text{C–O}}$ approximately equal to $\sqrt{2}\ \beta_{\text{X}}$ if the overlap integral is neglected (cf. Brown, *loc. cit.*).

In the calculation of ρ_{12}, the choice of structure (C^+, O^- or C, O) for the carbon–oxygen bond makes a formal difference in the calculation of S. However, the numerical difference on calculation from either structure (presumably both make a contribution to the structure of the carbon–oxygen bond) is negligible. The calculation of ρ_{23} was made with the assumption that the $C_{(2)}$–$C_{(3)}$ bond distance is 1·5 Å.

The five calculations now reported are: (I) $\delta_1 = 2$, $\delta_2 = 0{\cdot}5$, $k = 0$ (Wheland's assumption); (II) $\delta_1 = 2$, $\delta_2 = 0{\cdot}4$, $k = 0{\cdot}5$; (III) $\delta_1 = 2$, $\delta_2 = 0$, $k = 0{\cdot}5$ (to assess the importance of the inductive effect $C_{(2)}$); (IV), $\alpha_{\text{O}} = \alpha_{\text{X}} + 2\beta$, $\alpha_{\text{C(2)}} = \alpha_{\text{X}} + 0{\cdot}4\ \beta$, $\beta_{\text{C–O}} = \sqrt{2}\beta$; (V) $\alpha_{\text{C(2)}} = \alpha_{\text{X}}$. In (IV) and (V) $\beta_{2\text{-}3} = \beta_{\text{X}}$. Calculations (IV) and (V) were carried out with neglect of the overlap integral.

The energies of the molecular orbitals for the calculations are listed in Table 1. The energies for calculations (I), (II), and (III) are given in the form $E = E_{\text{X}} + m\gamma_{\text{X}}$ where E_{X} is the energy of an electron in a $2p_z$ orbital in the standard alternant hydrocarbon γ_{X} has its usual meaning, and m is the numerical coefficient found from the secular equation. For calculations (IV) and (V) the form is $E = E_{\text{X}} + k\beta_{\text{X}}$; here k is the numerical coefficient found from the secular equation.

TABLE 1. *Energies of molecular orbitals of benzoic acid anion.*

Calc.:	(I)	(II)	(III)	(IV)	(V)
Symmetry	m (γ)	m (γ)	m (γ)	k (β)	k (β)
S	−4·32278	−4·40318	−4·47274	−2·14569	−2·20127
S	−1·79014	−2·06927	−2·26566	−1·43118	−1·54691
A	−1·33	−1·33	−1·33	−1·0	−1·0
S	−0·21802	−0·71517	−0·84729	−0·56208	−0·66043
A	0·8	0·8	0·8	1·0	1·0
S	0·88678	0·84064	0·83581	1·06775	1·06298
S	1·35261	1·34135	1·34066	2·0	2·0
A	2·0	2·0	2·0	2·0	2·0
S	2·17817	2·59395	2·53173	3·47120	3·34560

Charge density (q_μ) and mobile bonds orders ($p_{\mu\nu}$) can be computed from the formulæ given by Chirgwin and Coulson, but it is possible to recast these formulæ into slightly different but more convenient form. The formulæ (4) and (5) were suggested by R. D. Brown.

$$q_\mu = \sum_{j,\nu} n_j X_{j\mu} X_{j\nu} S_{\mu\nu} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$p_{\mu,\nu} = \tfrac{1}{2}\sum_{j,\rho} n_j (X_{j\mu} X_{j\rho} S_{\nu\rho} + X_{j\nu} X_{j\rho} S_{\mu\rho}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $S_{\mu\nu}$ is the overlap integral between atoms μ and ν, and $X_{j\mu}$, etc., are the coefficients of atom μ in orbital j, the occupied orbitals. In these equations n_j is the number of electrons in the jth orbital. Free valencies (F_μ) were computed from the formula (Burkitt, Coulson, and Longuet-Higgins, *Trans. Faraday Soc.*, 1951, **47**, 553)

$$F_\mu = 1{\cdot}414 - \Sigma p_{\mu\nu} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Localization energies, A, were calculated according to Wheland's method.

Bond Lengths.—Mobile bond orders (p) for the carbon–carbon bonds were converted into bond lengths (x, in Å) (Table 2) by the formula (Coulson, *Proc. Roy. Soc.*, 1939, *A*, **169**, 413) $x = s - (s - d)/[1 + K\ (1 - p)/p]$, where s and d are, respectively, the single- and double-bond distances, taken as 1·540 and 1·340 Å; K is a constant chosen so that the bond order–bond length curve passes through the triple-bond point (1·204 Å). With this condition $K = 0{\cdot}8095$. The length of the carbon–oxygen bond (bond 1–2) was obtained from the standard values of 1·43 and 1·215 Å for the carbon–oxygen single and double bonds, respectively, suggested by Wirtz (*Z. Naturforsch.*, 1947, **2***a*, 264), and the value of the bond order in Å determined from a graph of these standard values against the appropriate bond order, namely, 0 and 0·652, 0·815, 0·823, 0·870, and 0·816 respectively for calculations (I), (II), (III), (IV), and (V). These bond orders are those obtained for a hypothetical C=O molecule under the assumptions of the various calculations. A curve approximating to that for the carbon–carbon bond was drawn between the standard points.

TABLE 2. *Bond orders* (p) *and bond lengths* (in Å).

Calc. :	(I)		(II)		(III)		(IV)		(V)	
Bond	*p*	Å	*p*	Å	*p*	Å	*p*	Å	*p*	Å
1—2	0·485	1·245	0·644	1·237	0·620	1·243	0·602	1·248	0·587	1·245
2—3	0·448	1·440	0·330	1·464	0·323	1·465	0·362	1·458	0·340	1·462
3—4	0·593	1·411	0·639	1·403	0·623	1·406	0·618	1·407	0·625	1·406
4—5	0·688	1·394	0·681	1·395	0·659	1·400	0·677	1·395	0·676	1·395
5—6	0·654	1·400	0·668	1·398	0·706	1·391	0·660	1·400	0·661	1·400

The numerous difficulties associated with the prediction of the lengths of carbon–hetero-atom bonds (see Coulson, *Proc. Roy. Soc.*, 1951, *A*, **207**, 63; *J. Phys. Chem.*, 1952, **56**, 311) suggest that the error in the predictions of these bond lengths may be considerable, certainly more than the usual uncertainty of about 0·02 Å associated with the prediction of bond lengths in alternant hydrocarbons by the simple M.O. procedure (Coulson, Daudel, and Robertson, *Proc. Roy. Soc.*, 1951, *A*, **207**, 306). Even if the standard values suggested by Wirtz are correct, the precise nature of the curve that should connect these points is unknown. The bond lengths assigned to the bond order of the carbon–oxygen bonds are only tentatively suggested, and may well need revision later.

The bonds of the benzene ring (bonds 3–4, 4–5, 5–6) are predicted to be nearly equal in length and all are within about 0·01 Å of the benzene bond length. No appreciable change in the bond distance of the ring appears to have been produced by the presence of the carboxyl group.

$C_{(2)}$–$C_{(3)}$ appears to possess considerable double-bond character, for the predicted bond length is considerably shorter than the 1·54 Å usually assigned to the single-bond length. The value predicted by calculation (I) is 0·018—0·025 Å less than that obtained by the other calculations. The error associated with this prediction may be somewhat larger than usual for here the change in the hybridization of $C_{(2)}$ will cause a change in the bond length–bond order curve (Coulson, "The Atomic Radius of Carbon," Memorial Volume to Victor Henri, Maison Desoer, Liège, 1947—48, p. 15), which has not been explicitly considered here.

All calculations lead to similar values for the carbon–oxygen bond length : inclusion of overlap generally leads to somewhat lower values than if it is neglected, but the differences are probably well within the limit of error inherent in the calculation. The lengths predicted by all the calculations are somewhat shorter (*ca.* 0·015—0·023 Å) than may be found from experiment (Wirtz, *loc. cit.*, suggests that the bond length of the carbon–oxygen bond in the carboxylic acid anion is 1·26 Å), but this is not surprising. The bond lengths of the benzoic acid anion apparently have not been measured; they are being investigated by Mr. S. Block and Professor J. D. H. Donnay in the Crystallographic Laboratory at Johns Hopkins University and will be of interest for comparison with the present calculations.

It is noteworthy that the choice of the bond distance in calculating the value of the overlap integral does not precisely predetermine the value that will be predicted for the bond length. The $C_{(2)}$–$C_{(3)}$ was presumed to be about 1·5 Å in determining S for this bond and by all calculations is predicted to be 0·09—0·10 Å shorter.

The differences in the predicted bond lengths in all five calculations are not very large : they all lead to practically the same values for the ring bonds. The maximum difference in the predicted carbon–oxygen bond length is only 0·03 Å, which is probably within the limits of error inherent in the prediction. The close agreement in bond lengths from calculations (II) and (III) on the one hand and from (IV) and (V) on the other suggests that the inclusion or neglect of an inductive effect on the carbon atom next to the oxygen atom is not of great importance. Coulson and Longuet-Higgins (*Proc. Roy. Soc.*, 1947, *A*, **192**, 16) have shown that for an alternant hydrocarbon $\mathrm{d}p/\mathrm{d}\alpha$ is zero (bond-atom polarizability). Presumably the coefficient for a non-alternant hydrocarbon would still be very small. The difference in the predictions due to the inclusion or neglect of overlap also appears, from these calculations, to be negligible. The most important factor in these calculations causing an appreciable change in the predictions is the value assigned to $\beta_{\text{C–O}}$. This was to be expected from the work of Coulson and De Heer (*loc. cit.*).

Chemical Reactivity.—The data on the calculation of charge density (q), free valence (F), and localization energy for nucleophilic (A_n), electrophilic (A_e), and radical (A_r) substitution reactions are collected in Table 3. Loebl, Stein, and Weiss (*J.*, 1951, 405) found that, on hydroxylation of benzoic acid by free radicals produced by *X*-rays, the hydroxybenzoic acids were formed in the ratio $o : m : p = 5 : 2 : 10$. Dakin and Herter (*J. Biol. Chem.*, 1907, **3**, 419) studied the action of hydrogen peroxide on ammonium benzoate and found that approximately equal amounts of *o*-, *m*-, and *p*-hydroxybenzoic acids were formed. Holleman (*Rec. Trav. chim.*, 1899, **18**, 267) found that nitration of benzoic acid at 30° gave *o*-, *m*-, and *p*-nitrobenzoic acid in the ratio 22 : 76·5 : 1·2. The only data available on the nucleophilic reactions of benzoic acid are not suitable for the present purpose. Barth and Schreder (*Monatsh.*, 1882, **3**, 799) found that fusion of benzoic acid with potassium hydroxide afforded a complete mixture containing about 15% of *p*-hydroxybenzoic acid, some *m*-acid, and only a trace of salicylic acid.

TABLE 3.

Position	q	F	A_e	A_r	A_n	Position	q	F	A_e	A_r	A_n
		Calculation (I)						Calculation (IV)			
4	1·013	0·133	1·881	1·609	1·334	4	0·946	0·119	2·575	2·410	2·244
5	1·102	0·072	1·864	1·864	1·864	5	1·002	0·077	2·656	2·656	2·656
6	0·920	0·107	1·970	1·680	1·389	6	0·955	0·095	2·634	2·466	2·298
		Calculation (II)						Calculation (V)			
4	1·057	0·094	1·871	1·743	1·614	4	0·951	0·114	2·606	2·466	2·325
5	1·102	0·064	1·856	1·856	1·856	5	1·002	0·077	2·648	2·648	2·648
6	0·965	0·077	1·851	1·721	1·591	6	0·961	0·092	2·625	2·484	2·343
		Calculation (III)									
4	0·996	0·132	1·869	1·762	1·655						
5	1·136	0·049	1·857	1·857	1·857						
6	1·024	0·002	1·856	1·748	1·640						

In calculation (I) the predictions from both the values of q and of A_e are in agreement that electrophilic substitution should be in the order $m > o > p$, which agrees qualitatively with the experimental results quoted above. For quantitative comparison with experimental results it is necessary to assign a value to γ_{X} as well as to assume that the localization energies can be used to determine relative rates of reaction at the various free positions of the nucleus. With the choice of $\gamma_{\text{X}} = -34$ kcal. (Dewar, *Trans. Faraday Soc.*, 1946, **42**, 767), and with the assumptions that $\boldsymbol{R}T = 0{\cdot}6$ kcal. and that the relative yield of a particular isomer is directly proportional to its relative reaction rate, and in view of the fact that there are two free *ortho*- and *meta*-, but only one *para*-position available, the A_e values from calculation (I) indicate that the isomers should be formed in the proportions $o : m : p = 24 : 75 : 0{\cdot}3$, in very good agreement with Holleman's results (*loc. cit.*). This agreement is very likely fortuitous: amongst the numerous errors inherent in the calculation, at least two should be mentioned: (1) the value chosen for γ_{X} and (2) the fact that the calculation started initially from a consideration of the anion. As for (1), the value of −34 kcal. for γ_{X} is rather less than that usually chosen to make a suitable fit of calculations with the experimental data of spectra. However, it may well be that the γ_{X} (spectroscopic) and γ_{X} (chemical reaction) are not identical, or, more pertinent, that the γ_{X} (electrophilic reaction), γ_{X} (nucleophilic reaction), and γ_{X} (radical reaction) may all be different. Even small changes in γ_{X} would cause considerable changes in the quantitative predictions of chemical reactivity. The error in (2) is difficult to assess, but it is possibly appreciable.

The predictions of electrophilic substitution from calculations (II) and (III) are not consistent from a consideration of the values of q and A_e and do not seem to be in qualitative agreement with the available experimental data.

If the overlap integral is neglected [as in calculations (IV) and (V)], one finds an order for nucleophilic substitution that is in qualitative agreement with experiment from the q values if an inductive effect is considered on carbon atom 2 but not if this inductive effect is neglected. The values of A_e are in agreement that the order should be $o > p > m$, which is not observed in experiment.

As mentioned on p. 1077, experimental evidence indicates that free-radical substitution of benzoic acid occurs nearly equally well on all three available positions of the benzene nucleus. From calculation (I), the predictions are not consistent from a consideration of the F and A_r values; this inconsistency would be accommodated, following Brown, by the assumption of the "crossing" of the π-energy plots (Brown, *Quart. Reviews*, 1952, **6**, 63). The considerable difference of about 0·26 γ between A_r (*ortho-para*) suggests that, if these predictions are to be made to fit with the experimental data, a value of γ_X (radical) considerably less than -34 kcal. would have to be used. The calculations without overlap are in agreement with calculation (I) that the order of substitution by free radicals should be $o > p > m$ (in these calculations both the F and A_r values are consistent in their predictions) but here again one would have to assign a smaller value than -17 kcal. to β_X (radical) in order to obtain agreement with experiment. In calculations (II) and (III) the A_r values appear to predict substitution that is in qualitative agreement with experiment.

For nucleophilic substitution, the predictions of calculation (I) from the values of q seem to be in better agreement with available experimental evidence than from the values of A_n, though the reverse seems to be true from (II) and (III). Calculations without overlap do not appear to agree with experiment on either basis. Unfortunately the experimental data available do not provide even a good qualitative guide for this type of substitution.

It is of interest that whereas the various calculations made only slightly different predictions as to the bond lengths, yet their predictions of chemical reactivity varied considerably. It seems likely that the latter predictions will prove the more delicate test for deciding which of the calculations most closely agrees with experimental results. Judgment on this point must be reserved until there is some better basis for more quantitative interpretations of the predictions of chemical reactivity.

A few general conclusions can be drawn from these calculations. The first is that inclusion or neglect of an inductive effect on the carbon atom next to the oxygen atom makes no qualitative difference in the predictions of chemical reactivity if the predictions are made from a consideration of the localization energies, but there is a difference in the predictions if these are made from the values of q. Perhaps even more important, it can be seen that, at least in the calculations now reported, the inclusion or neglect of overlap makes a considerable difference in the predictions of chemical reactivity. Previously, good agreement has been obtained between these predictions and experimental results in hetero-molecules from localization energies calculated without overlap. The results of the present calculations lead one to wonder if this agreement would still occur if the overlap integrals had been included in the calculations.

The helpful suggestions and interest shown by Professor C. A. Coulson, F.R.S., are gratefully acknowledged. The work was considerably aided by the advice of the members of the Theoretical Physics Department at King's College and, in particular, the author is indebted to Dr. R. D. Brown.

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[*Received, October* 18*th*, 1952.]