Reaction of Ib with Performic Acid.[17]—A 25.5-mg. portion of Ib (8.3 × 10^{-5} mole) was mixed with 0.2 ml. (4 × 10^{-3} mole) of 90% formic acid and 0.05 ml. (4.4 × 10^{-4} mole) of 30% hydrogen peroxide. The mixture was warmed 3 hr. at 40–50°, then refluxed with 5 ml. of 3 *N* potassium hydroxide for 1.5 hr. The alkaline hydrolysate was neutralized with hydrochloric acid, then extracted repeatedly with ether. The combined ether extracts were dried over sodium sulfate and evaporated *in vacuo*. The recovered product consisted of 15.0 mg. of liquid; its infrared spectrum had only a small OH peak (2.75 μ), but had absorption 2.8–3.3, 3.6–3.8, and 10.6 μ indicating free carboxylic acid, and a small C≡C peak at 4.54 μ; there was no maximum at 10.46 μ. These cleavage products were converted to methyl esters by treatment with diazomethane and were subjected to g.l.c. analyses. Nonanedioic acid (55%) was identified among the products. β-Hydroxydecanedioic acid (*ca.* 7%) was tentatively identified on the basis of equivalent chain length.[41] Short-chain acids were present that were not readily identified by equivalent chain length, but no hexanoic acid was found.

Attempted Dehydration of Ib with Toluenesulfonic Acid.[34]—Ib (12.3 mg.) and *p*-toluenesulfonic acid (5 mg.) were refluxed 15 min. in 1 ml. of benzene under a nitrogen atmosphere. The mixture was shaken with sodium bicarbonate solution, dried over sodium sulfate, and evaporated *in vacuo*. The recovered product (8.4 mg.) showed ultraviolet maxima at 194, 226, 271 ($E^{1\%}_{1\,\mathrm{cm}}$ 845), and 280 mμ (inflection.) It had an infrared maximum at 10.2, but had none at 2.75 (OH) or 10.46 μ (conjugated enyne). The product did not form a maleic anhydride adduct and appeared to be quite unstable. It was not further characterized.

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A Free-Electron Model for Kinetic Substituent Effects[1]

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A qualitative treatment of the distribution of electron density in a three-nucleus, four-electron system is developed using the free-electron method. The method is shown to be inappropriate to stable systems, but appropriate to systems with highly polarizable electron groups, such as transition states.

The free-electron (electron-gas) method is a conceptually simple approximation which has been applied with signal success to the spectroscopic problems of polyenes[2] but not, to our knowledge, to problems in chemical reactivity. The analytic simplicity of the free-electron wave functions encouraged us to develop the qualitative model for kinetic substituent effects presented here, with a view toward quantitative extensions in the future.

A linear system composed of three nuclei, A, B and C, can be regarded as a one-dimensional potential box (Figure 1). If the three nuclei are of equal electronegativity and are assumed to lie at such a separation that the overlap of their positive fields results in a nearly constant electrical field out to, say, half a bond length beyond A on the one end and C on the other,[2] then the potential box will be flat over this distance and rise to infinity at either end. If four electrons are added to the system, as in a hydrogen bond or in the transition states for proton-transfer or nucleophilic-displacement reactions, they can be regarded as particles enclosed in this potential box and will occupy the first two particles-in-the-box[3] energy levels for a box of this size. Since we are interested in the electron-density distribution for this system, we require the squares of the first two wave functions of the system; these are shown in Figure 1. The lowest wave function is a simple sine function and the next is its first harmonic.[4] To find the electron-density function for the system we have only to superimpose these functions for the individual energy levels (Figure 2).

In order to apply this model to the prediction of substituent effects, we consider the perturbation on this electron distribution induced by a change in the electrical character of one of the nuclei. Organic chemists usually discuss substituent effects in terms of "electron withdrawal from X" and "electron release to X." For our purposes we will consider the former to represent an increase in the effective electronegativity of X and the latter a decrease in the effective electronegativity of X; in the absence of strong conjugation effects this will be a good approximation.

Center-Atom Substituent Effects.—Figure 3 shows the potential box corresponding to a system in which the effective electronegativity of B has been increased ("electron withdrawal from B"), represented in the model by a dip in the potential in the neighborhood of B. The qualitative nature of the perturbed electron-density distribution can be deduced by considering that the more favorable potential in the vicinity of B will cause a drift of electrons toward B from both sides of the box; since the total number of electrons remains four, the increase in density about B must occur with a corresponding decrease in density about A and C.

The opposite situation, a higher potential near B than near A or C, thus a decrease in the effective electronegativity of B ("electron release to B"), by

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[1] Supported in part by the Atomic Energy Commission under Contract No. AT(301)-905 and the National Institutes of Health under Research Grant No. RG-3711.

[2] H. Kuhn, *Progr. Chem. Org. Nat. Prod.*, **16**, 169 (1958); **17**, 404 (1959). See earlier and more exact treatments of σ-electrons: J. R. Arnold, *J. Chem. Phys.*, **22**, 757 (1954); **24**, 181 (1956); A. A. Frost, *ibid.*, **25**, 1150 (1956); G. M. Barrow, *ibid.*, **26**, 558 (1957); **28**, 485 (1958).

[3] L. Pauling and E. B. Wilson, Jr., "Introduction to Quantum Mechanics," McGraw-Hill Book Co., Inc., New York, N. Y., 1935, p. 95 ff.

[4] Wave functions of the same general form are obtained by an MO method [*e.g.*, C. G. Swain, R. A. Wiles, and R. F. W. Bader, *J. Am. Chem. Soc.*, **83**, 1945 (1961)]; hence, the free-electron approximation in no way affects the generality of our results.

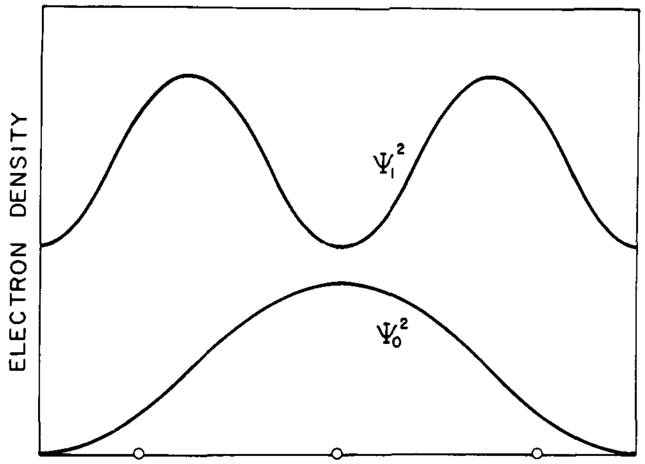

Figure 1.—Electron densities for the two lowest energy levels for a three-atom system.

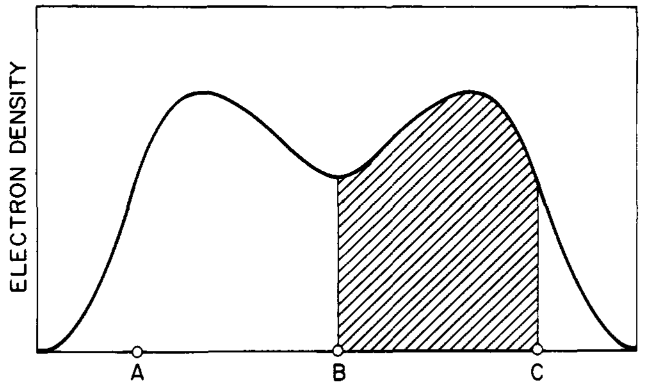

Figure 2. —Total electron-density distribution for a four-electron, three-nucleus system; A, B, and C all of equal electronegativity.

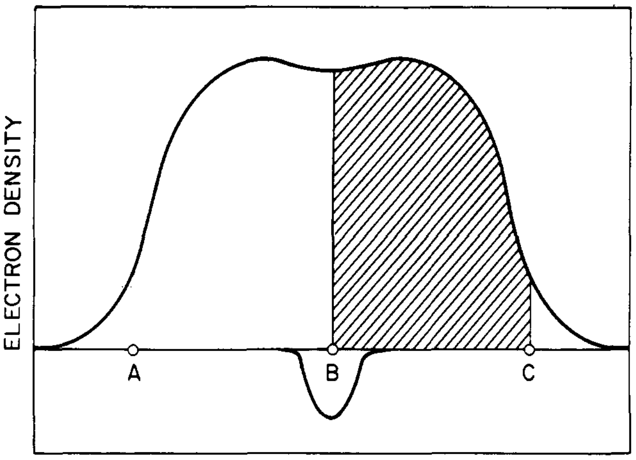

Figure 3.—Perturbed electron-density distribution for increased electronegativity of B ("electron withdrawal from B").

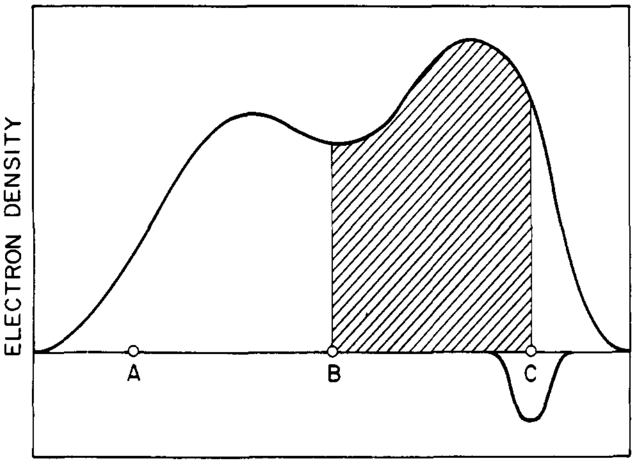

Figure 4.—Perturbed electron-density distribution for increased electronegativity of C ("electron withdrawal from C").

the same reasoning as above, will result in an electron-density distribution in which migration of electron density away from B toward the extremities of the system has occurred.

End-Atom Substituent Effects.—The symmetry of the system allows a consideration of the effects at either A or C to suffice for both. Figure 4 shows the resultant electron-density distribution for an increase in the electronegativity of C ("electron withdrawal from C"). There is an electron drift toward the center of greater electronegativity at the expense of the rest of the system. A corresponding degree of "electron release to C" will result in the mirror image of the distribution of Figure 4.

Comparison with Experimental Results. Hydrogen Bonds.—Since hydrogen bonds may be treated quantum mechanically as three-nucleus, four-electron systems,[5] it is of interest to determine whether our model accurately reproduces their behavior. Figures 2 and 4 represent the prediction of hydrogen-bond behavior with hydrogen-bonding bases of different strengths (C) with an acid of constant structure (A–B where B is now a proton). If we assume that the total electron density between two nuclei is a measure of the strength of the bond uniting the two nuclei, then the area under the electron-density curve and between the nuclei in the figures gives an indication of the bond strengths. In particular, the total electron density between C and B (shaded areas) is greater in Figure 4 than in Figure 2. Since a greater electronegativity for C (Figure 4) corresponds to a lowered basicity for C, the model predicts that hydrogen bonds will increase in strength, the weaker the hydrogen-bonding base. Since this is contrary to fact,[5,6] we conclude that our model does not apply to normal, stable hydrogen bonds. A reason for this result is advanced under "Scope of the Model" below.

Nucleophilic-Displacement Transition States.—Hydrogen-transfer reactions such as the enolization of ketones are special cases of nucleophilic displacement which might be thought to bear a special analogy in chemical behavior to hydrogen-bonding systems. If the results of Figures 2 and 4 are applied to ketone enolization, the prediction is reached that the weaker the catalyzing base, the stronger the base–proton bond in the transition state will be, *i.e.*, the more protonated will be the base. This is in accord with the reacting-bond rule[7] and is true for ketone enolization by two criteria of the degree of proton transfer.[8] In like manner, the proton is more tightly bound to more acidic ketones as measured by the magnitude of their Brønsted catalysis law slopes.[8] Thus the model is in

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(5) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, pp. 236–238.

(6) J. E. Gordon, *J. Org. Chem.*, **26**, 738 (1961).

(7) C. G. Swain and E. R. Thornton, *J. Am. Chem. Soc.*, **84**, 817 (1962).

(8) C. G. Swain and A. S. Rosenberg, *ibid.*, **83**, 2154 (1961); C. G. Swain and R. L. Schowen, paper in process.

excellent agreement with a variety of data for hydrogen-transfer reactions and appears accurately to reproduce the chemical behavior of these transition states.

Comparison is also possible with end-atom effects in other nucleophilic displacements; examples were given in the paper on the reacting-bond rule.[7]

In addition, the model shows a decrease in BC strength with an increase in AB strength and *vice versa;* this is just the "alternating effect" of the reacting-bond rule.

Our earlier attempts at theoretical justification of the rule were limited to bond-dissociating or bond-associating reactions involving two atoms (two electrons and two nuclei) only.[7]

Figure 3 shows that electron withdrawal from the center atom of a nucleophilic-displacement transition state should result in the strengthening of the bonds to both entering and leaving groups, while conversely electron release to the center atom should weaken both bonds. Again the model is in exact agreement with the reacting-bond rule; examples of isotope effects and other data following the rule were given previously.[7]

Furthermore, the model predicts (Figure 3) that electron withdrawal at the center atom should produce an accumulation of negative charge on the center atom whereas electron release to the center atom should result in a loss of reacting-electron density and thus an increase in positive charge on B. If the Hammett reaction constant ρ is taken as a measure of the charge on B, then nucleophilic displacements on benzyl compounds fit the model very well. These reactions display curved Hammett plots generally possessing a minimum; thus relatively electron-releasing substituents produce a negative ρ (B relatively low in electron density) while relatively electron-withdrawing substituents produce a positive ρ (B relatively high in electron density).

We conclude that the model represents the substituent effects in hydrogen-transfer and other nucleophilic-displacement transition states in considerable detail.

Scope of the Model.—The reason for the failure of the model to account for normal, stable hydrogen-bond behavior in spite of its good success in reproducing substituent effects in transition states lies in an assumption made in constructing the figures: that the electron cloud is sufficiently polarizable and the nuclei sufficiently far apart that the electron shift due to changes in nuclear electronegativity greatly outweighs the increased or decreased nuclear repulsions arising from the same variation. Note that the nuclei were assumed to remain stationary in constructing all the figures.

This assumption is very poor for hydrogen bonds, where one pair of electrons is nearly localized in the lone-pair orbital of the base and the other is involved in a strong σ-bond. However, in transition states for nucleophilic displacement where the internuclear distances are abnormally long and where the electron cloud is especially polarizable, the assumption is apparently nearly enough true to produce excellent agreement with experiment.

The agreement of this model with the reacting-bond rule suggests that the success of the reacting bond rule may be due to (a) the high polarizability of the electron cloud in the transition states to which it was applied and (b) the relative constancy of the transition-state internuclear distances with the structural variations considered. If, in the future, cases arise which fail to follow the reacting-bond rule they should be examined for violation of one of these restrictions.

The Nitro Group as an *ortho* Participant in the Dissociation of Iodobenzene Dichloride

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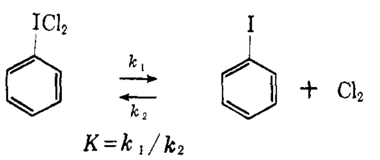
Evidence is presented that an *o*-NO_2 substituent participates as an internal nucleophile in promoting the dissociation of iodobenzene dichloride in acetic acid while the *o*-CN group does not. The capacities of the *o*-NO_2 and *o*-$COOCH_3$ groups to enhance the dichloride dissociation rate are comparable in magnitude.

The rate of dissociation of iodobenzene dichloride (eq. 1) in a polar solvent such as acetic acid is subject to marked rate enhancement when certain substituents which are nucleophilic in nature are located *ortho* to the reaction center.[1] Presumably these *ortho* substituents promote the reaction by releasing electrons to the iodine atom as it undergoes positive polarization in the activation process. Of all the *ortho* substituents investigated, those which contribute most to reactivity of the dichloride are the carbomethoxy and structurally closely related groups.[2,3] In fact *o*-carbomethoxyiodobenzene dichloride equilibrates with its components in acetic acid too rapidly to permit even a semiquantitative investigation of the reaction rate by the spectrophotometric method employed in earlier work on $C_6H_5ICl_2$ and its derivatives. Evidence has also been presented that COOR groups participate as internal nucleo-



$K = k_1/k_2$ (1)

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[1] For a recent survey see L. J. Andrews, L. J. Spears, and R. M. Keefer, *J. Am. Chem. Soc.*, **86**, 687 (1964).

[2] L. J. Andrews and R. M. Keefer, *ibid.*, **81**, 4218 (1959).

[3] R. M. Keefer and L. J. Andrews, *ibid.*, **81**, 5329 (1959).