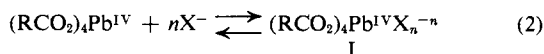
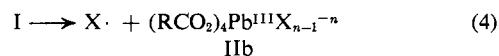
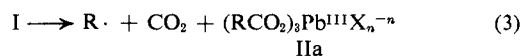


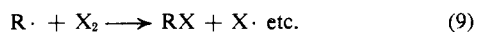
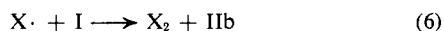
Pre-equilibration:



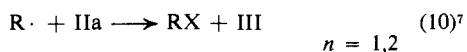
Initiation:



Propagation:



Termination:



tive decarboxylation.<sup>6</sup> The pertinent difference between the mechanism for oxidative decarboxylation and halodecarboxylation is attributable primarily to the complexing of the propagation steps.<sup>8</sup> Ligand transfer oxidation of alkyl radicals by species such as I and II has been delineated earlier.<sup>9</sup> Lead(IV) carboxylates are reasonably stable, and the rapid decomposition in the presence of halide is attributed to the lability of anionic complexes such as I (eq. 3, 4), similar to the catalysis by acetate<sup>10</sup> and bases<sup>11</sup> in oxidative decarboxylations.<sup>6</sup> We consider halogen to be a side product and not an important intermediate<sup>2c</sup> in the halodecarboxylation reaction. Thus, cyclohexyl chloride formed quantitatively from cyclohexanecarboxylic acid in benzene is an unimportant product (~2%) when the same reaction is carried out in the presence of added chlorine (chlorobenzene is the preponderant product). Halogens probably arise<sup>12</sup> by sequence 4, 6, and 8, and disappear by radical chain halogenation of the substrates; they assume greater importance in the order  $\text{Cl} < \text{Br} < \text{I}$ .

(7) Alternative modes of decomposition of IIa and IIb are also possible. The principal reactions in the propagation sequence are (5) and (7).

(8) We do not favor acyl hypohalites by reactions such as 11, 12, or 13 as prime intermediates since they readily form halogen in the



presence of halide [J. Kochi, B. M. Graybill, and M. Kurz, *J. Am. Chem. Soc.*, **86**, 5257 (1964); J. Kochi and R. V. Subramanian, *ibid.*, **87**, 1508 (1965)]. Moreover, the ease of decarboxylation, tertiary > secondary > primary, is contrary to the order found in the Hunsdiecker reaction,<sup>1,2</sup> but it is the same as that in oxidative decarboxylation.<sup>6</sup>

(9) C. H. Bamford, A. Jenkins, and R. Johnston, *Proc. Roy. Soc. (London)*, **A239**, 214 (1957); J. K. Kochi and D. M. Mog, *J. Am. Chem. Soc.*, **87**, 522 (1965).

(10) D. Benson, L. Sutcliffe, and J. Walkley, *ibid.*, **81**, 4488 (1959).

(11) C. A. Grob and A. Weiss, *Helv. Chim. Acta*, **43**, 1340 (1960).

(12) Formation of halogen is facilitated by soluble salts of halides. An alternative route is  $\text{I} + \text{X}^- \rightarrow \text{X}_2 + (\text{RCO}_2)_3\text{Pb}^{\text{III}} + 2\text{RCO}_2^-$  or similar nucleophilic displacements (e.g., eq. 11).<sup>8b</sup>

(13) The author wishes to thank the National Science Foundation for generous support of this work.

Jay K. Kochi<sup>18</sup>

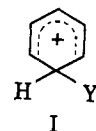
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Received March 18, 1965

## A Correction to the Hückel Localization Energy Approximation of Aromatic Substitution Rates

Sir:

A familiar approach to the problem of predicting relative aromatic substitution rates is to treat the transition state in terms of a structure such as I.



Streitwieser<sup>1</sup> has defined a reaction hydrocarbon constant  $\sigma_r$  based on the linear free-energy relationship

$$\log k_r/k\alpha(\text{C}_{10}\text{H}_8) = \sigma_r\rho^* \quad (1)$$

where  $\rho^* = 1$  for the protonation equilibria of aromatic hydrocarbons in hydrogen fluoride. Other electrophilic substitution rates are used to evaluate  $\sigma_r$  for hydrocarbons for which the protonation equilibrium constant is not available. These  $\sigma_r$  values give fair to good correlations with simple Hückel calculations of the localization energies  $L^+$  and  $L^0$ . The localization energies are defined as the difference in  $\pi$ -energy between the aromatic hydrocarbon and the carbonium ion I.

The equilibrium constants for protonation of aromatic hydrocarbons in hydrogen fluoride are found to give a good correlation with Hückel localization energies including overlap, except for pyrene and perylene,<sup>2</sup> which deviate considerably from the regression line.

A large source of error in either a simple Hückel calculation, or  $\omega$ -type calculation,<sup>3</sup> arises from the difference in charge of the electron core of the reactant and transition state. As one-electron localization energies, the error in neglecting this "core" difference in such calculations is not as likely to cancel for electrophilic and nucleophilic aromatic substitution as in a case such as free-radical addition wherein reactants and transition state have the same charge. If self-consistent field localization energies, which should remove this "core" error, are used, an excellent linear correlation is obtained<sup>4</sup> with the protonation constants in which pyrene and perylene no longer deviate from the line.

The following thermodynamic arguments supply a correction by which the Hückel localization energies may be easily improved without the work of carrying out a self-consistent field calculation.

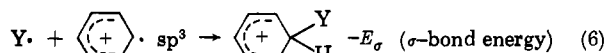
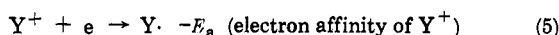
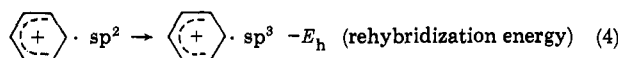
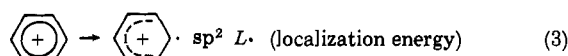
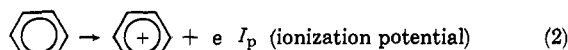
For a given reaction series with the same electrophile in the same solvent  $E_a$  and  $E_s$  will be constant. The variation of  $E_h$  with substrate hydrocarbon is more uncertain but will be considered as nearly constant in this approximation. If then  $\Delta E$  is taken as either equal to or proportional to the activation energy the log of the substitution rate should be a linear function of  $Ip + L\cdot$ .

(1) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 307-350.

(2) K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, pp. 97-99.

(3) A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **82**, 4123 (1960).

(4) A. A. V. Stuart and J. A. Kruizinga, Quantum Chemistry Symposium, Paris, Sept. 1957, p. 229.



$$\Delta E = I_p + L \cdot - E_h - E_a - E_\sigma \quad (8)$$

The more conventional localization energy  $L$ , where  $M$  and  $M^+$  are the total  $\pi$ -energies of the aromatic hydrocarbon and the carbonium ion I, is given by eq. 9 in units of the resonance integral  $\beta$ .

$$L = M - M^+ \quad (9)$$

where  $L \cdot$  is related by

$$L \cdot = (M - m) - M^+ = L - m \quad (10)$$

and  $m$  is the energy of the highest filled molecular orbital.

$$\Delta E = I_p + L - m + \text{constant} \quad (11)$$

If  $L$  and  $m$  are self-consistent field energies then the energy of the highest filled molecular orbital,  $m$ , is equal to the ionization potential and  $E$  is simply a

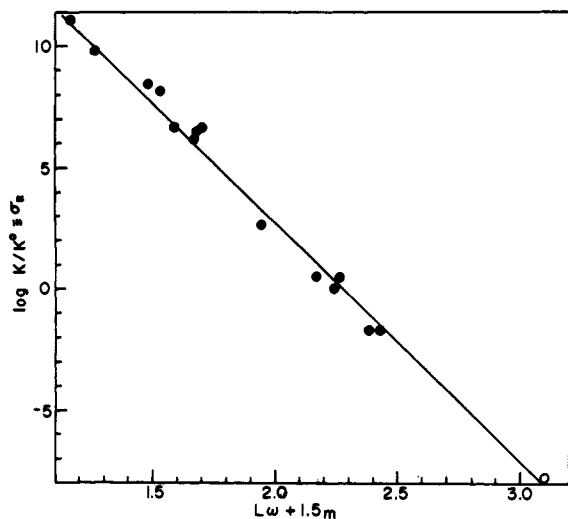


Figure 1. Logarithm of relative equilibrium constants for protonation in HF as a function of  $L^\omega + 1.5m$ , taken from ref. 1.

function of the SCF localization energy  $L$ . In the Hückel approximation, however,  $m$  is not equal to  $I_p$ ; it is, however, linearly related, and from

$$I_p = km\beta + \text{constant} \quad (12)$$

$$\Delta E = L + m(k - 1) + \text{constant} \quad (13)$$

where  $L$  may be  $L^+$  or  $L^\omega$  and  $k$  may be evaluated from the slope of a plot of ionization po-

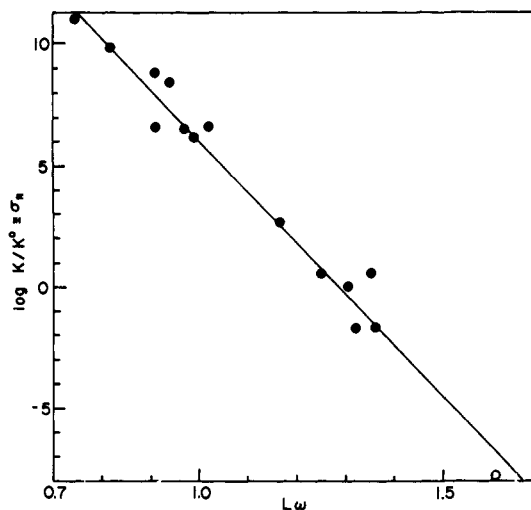


Figure 2. Logarithm of relative equilibrium constants for protonation in HF as function of  $L^\omega$ , taken from ref. 1.

tentials<sup>1</sup> as a function of  $m$ , the highest filled Hückel molecular orbital energies. At the moment a certain arbitrariness is necessary in the value of  $k$  since it depends on the choice of ionization potentials of the hydrocarbons and the value of the resonance integral. The particular value of  $k = 2.5$  results from the ionization potentials of Wacks and Diebler<sup>5</sup> and empirical resonance energies for the hydrocarbons of  $\beta = 0.9$  to 1.0 e.v.

A plot of the log of the equilibrium constant,<sup>1</sup> divided by that for naphthalene, for protonation in hydrogen fluoride of 11 condensed aromatic hydrocarbons, including pyrene and perylene, as a function of  $L^\omega + 1.5m$ <sup>6</sup> has a standard deviation of  $0.4 \sigma_r$  unit (Figure 1). The  $\sigma_r$  value 7.8 of benzene is supplied in Figure 1 as the missing protonation equilibrium constant. A reference plot is given in Figure 2 for basicity as a function of  $L^\omega$  alone; here the standard deviation is  $0.8 \sigma_r$  unit. The  $L^\omega + 1.5m$  function is thus a considerable improvement over other functions. Similarly, the  $L^+ + 1.5m$  function with a standard deviation of  $0.8 \sigma_r$  is an improvement, although not as large, over the  $L^+$  function, standard deviation  $1.0 \sigma_r$ . Furthermore, pyrene and perylene no longer deviate significantly from the  $L^+ + 1.5m$  regression.

(5) M. E. Wacks and V. H. Diebler, *J. Chem. Phys.*, **31**, 1557 (1959).

(6) Values of  $m$  taken from E. Heilbronner and J. W. Murrel, *J. Chem. Soc.*, 2611 (1962).

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### Ionic Strength as a Factor in a Thiocyanate-Induced Reduction of Acidified Trivalent Gallium on Mercury. A Doublet Admittance Peak in Salicylate Media<sup>1</sup>

Sir:

One result of a prior study<sup>2</sup> dealing with the dropping gallium amalgam electrode was the unanticipated find-

(1) This work was made possible by a Frederick G. Cottrell grant-in-aid from the Research Corporation. The author expresses his thanks to Mr. George Frame for assistance with several of the measurements.

(2) W. M. MacNevin and E. D. Moorhead, *J. Am. Chem. Soc.*, **81**, 6382 (1959).