were used as in the synthesis of I except that 6 ml. of n-butyraldehyde was used in place of the propionaldehyde. Yellow-orange crystals of the $ZnCl_4{}^{2-}$ salt were obtained in a 70% yield.

Anal. Calcd. for $NiC_{12}H_{28}N_4ZnCl_4$: Ni, 11.9; C, 29.3; H, 5.7; Cl, 28.6. Found: Ni, 12.1; C, 29.3; H, 5.9; Cl, 28.4.

5,5-Dimethyl-6-isopropyl-1,9-diamine-3,7-diazanona-3-ene-nickel(II) Tetrachlorozincate(II) (VII).—Similar conditions and amounts were used as in the synthesis of I except that 6 ml. of isobutyraldehyde was used in place of the propionaldehyde. Yellow crystals of the $ZnCl_4{}^{2-}$ salt were obtained in an 80% yield.

Anal. Calcd. for $NiC_{12}H_{28}N_4ZnCl_4$: Ni, 11.4; C, 29.3; H, 5.7; Cl, 28.6. Found: Ni, 12.1; C, 29.2; H, 5.1; Cl, 28.6.

4,6,6-Trimethyl-1,9-diamine-3,7-diazanona-3-enenickel(II) Tetrachlorozincate(II) (X).—Dry acetone (30 ml.) was added to $Ni(en)_3Cl_2\cdot2H_2O$ (6 g.) in a 100-ml. Carius tube. Anhydrous $ZnCl_2$ (6 g.) was dissolved in dry acetone (40 ml.) and the clear solution added to the tube contents. The color of the reaction mixture changed from mauve, through blue and green, to yellow. The tube was sealed and heated at 100° for 3 hr. during which time orange crystals of the product crystallized on the walls. This crystalline material was collected by filtration and recrystallized once from the minimum amount of hot water, yield 80%.

Anal. Calcd. for $NiC_{10}H_{24}N_4ZnCl_4$: Ni, 12.6; C, 25.8; H, 5.2; Cl, 30.4. Found: Ni, 12.6; C, 25.8; H, 5.2; Cl, 30.3.

3-Methyl-4-ethyl-1,5,8,11-tetraazacyclotrideca-1-enenickel-(II) Tetrachlorozincate(II) (XIV).—Anhydrous $ZnCl_2$ (6 g.) was dissolved in dry methanol (30 ml.) and the solution added to powdered $Ni_3(trien)_3Cl_4\cdot2H_2O$ (5 g.) in a 100-ml. Carius tube. Freshly distilled propionaldehyde (10 ml.) was then added. The tube was heated at 120° for 48 hr., cooled to room temperature, and the contents evaporated to a thick orange gum. Water (50 ml.) was added and the solution boiled several times with fresh amounts of decolorizing charcoal to remove the aldehyde polymers. A clear yellow solution was finally obtained. This was made slightly acid (litmus) with dilute HCl and set aside for slow evaporation. Orange crystals of the $ZnCl_4{}^{2-}$ salt formed as needles, yield 5–10%.

Anal. Calcd. for $NiC_{12}H_{26}N_4ZnCl_4$: Ni, 11.9; C, 29.3; H, 5.3; Cl, 28.8. Found: Ni, 11.8; C, 29.6; H, 5.5; Cl, 28.9.

3-Ethyl-4-propyl-1,5,8,11-tetraazacyclotrideca-1-enenickel-(II) Tetrachlorozincate(II) (XV).—Similar conditions and

amounts were used as in the synthesis of XIV except that 10 ml. of n-butyraldehyde were used instead of the propionaldehyde. Orange crystals of the $ZnCl_4{}^{2-}$ salt were obtained in a 50% yield.

Anal. Calcd. for $NiC_{14}H_{30}N_4ZnCl_4$: Ni, 11.3; C, 32.4; H, 5.8; Cl, 27.2. Found: Ni, 11.3; C, 32.1; H, 5.9; Cl, 27.3.

3,3-Dimethyl-1,5,8,11-tetraazacyclotrideca-1-enenickel(II) Tetrachlorozincate(II) (XVI).—Similar conditions and amounts were used as in the synthesis of XIV except that 10 ml. of isobutyraldehyde were used instead of the propionaldehyde and the heating was continued for 5 days. Yellow crystals of the $ZnCl_4{}^{2-}$ salt were obtained in a 50% yield.

Anal. Calcd. for $NiC_{11}H_{24}N_4ZnCl_4$: Ni, 12.3; C, 27.7; H, 5.1; Cl, 29.6. Found: Ni, 12.1; C, 27.9; H, 5.2; Cl, 29.6.

2,4,4-Trimethyl-1,5,8,11-tetraazacyclotrideca-1-enecopper(II) Perchlorate Monohydrate (XIV).—$Cu(ClO_4)_2\cdot7H_2O$ (dried over concentrated sulfuric acid (39 g., 0.1 mole) was dissolved in dry acetone (300 ml.), and triethylenetetramine (14.6 g., 0.1 mole), diluted with an equal volume of dry acetone, was added slowly. The blue solution was allowed to stand in a stoppered flask at room temperature for about 2 weeks. The acetone was then allowed to evaporate slowly and a blue-purple semicrystalline solid formed. This was dissolved in the minimum amount of boiling water and filtered, and isopropyl alcohol was added to the hot filtrate. On cooling, the bright blue monohydrate perchlorate (30 g., 60%) was deposited from the maroon-colored solution.

Anal. Calcd. for $CuC_{12}H_{28}N_4Cl_2O_9$: Cu, 12.5; C, 28.5; H, 5.6; N, 11.0. Found: Cu, 12.5; C, 28.9; H, 6.0; N, 11.2.

Analyses.—The methods used were similar to those described previously.[5]

Spectra.—The visible and ultraviolet spectra were determined in aqueous solution using a Unicam S.P. 700 recording spectrophotometer. The infrared spectra were determined in mulls, a Perkin-Elmer Model 221 spectrophotometer being used.
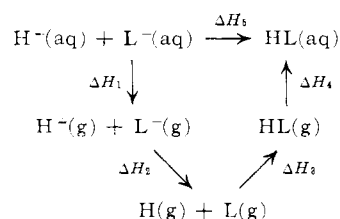

The Use of Basicity and Oxidative Coupling Potential to Obtain Group Electronegativity

BY DARL H. McDANIEL AND AUSTIN YINGST
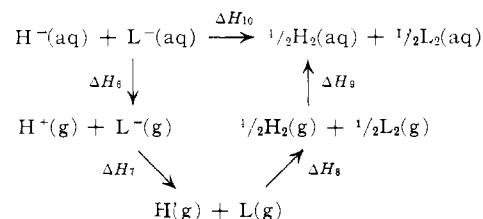
A relationship between basicity, e.m.f. values of oxidative coupling reactions, and Pauling electronegativity values is developed. This relationship provides a vantage point for the interpretation of the Edwards double basicity scale. Use is made of the relationship to calculate a set of group electronegativities.

Thermochemical Analysis.—The factors involved in the dissociation of an acid and in the oxidative coupling of its conjugate base may be analyzed in terms of enthalpy or free energy cycles. In such an analysis similar terms arise in both the dissociation process for the general acid HL and in the oxidative coupling process for L^- producing L_2, as may be noted by inspection of the enthalpy cycles below. For the acid HL the following cycle may be written

$$H^-(aq) + L^-(aq) \xrightarrow{\Delta H_5} HL(aq)$$

$$\Delta H_1 \downarrow \qquad\qquad \uparrow \Delta H_4$$

$$H^-(g) + L^-(g) \qquad HL(g)$$

$$\Delta H_2 \searrow \qquad \swarrow \Delta H_3$$

$$H(g) + L(g)$$

Similarly a cycle may be written for the oxidative coupling of the anion L^-

$$H^-(aq) + L^-(aq) \xrightarrow{\Delta H_{10}} {}^{1}/_2 H_2(aq) + {}^{1}/_2 L_2(aq)$$

$$\Delta H_6 \downarrow \qquad\qquad \uparrow \Delta H_9$$

$$H^+(g) + L^-(g) \qquad {}^{1}/_2 H_2(g) + {}^{1}/_2 L_2(g)$$

$$\Delta H_7 \searrow \qquad \swarrow \Delta H_8$$

$$H(g) + L(g)$$

The steps involving hydrogen are conventionally omitted in the second cycle, but are included here for clarity in comparing oxidative coupling and acidity. From the above cycles one obtains eq. 1 and 2

$$\Delta H_5 = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 \qquad (1)$$

$$\Delta H_{10} = \Delta H_6 + \Delta H_7 + \Delta H_8 + \Delta H_9 \qquad (2)$$

Noting that $\Delta H_1 = \Delta H_6$ and $\Delta H_2 = \Delta H_7$, subtraction of eq. 2 from eq. 1 gives eq. 3.

$$\Delta H_5 - \Delta H_{10} = \Delta H_3 - \Delta H_8 + \Delta H_4 - \Delta H_9 \qquad (3)$$
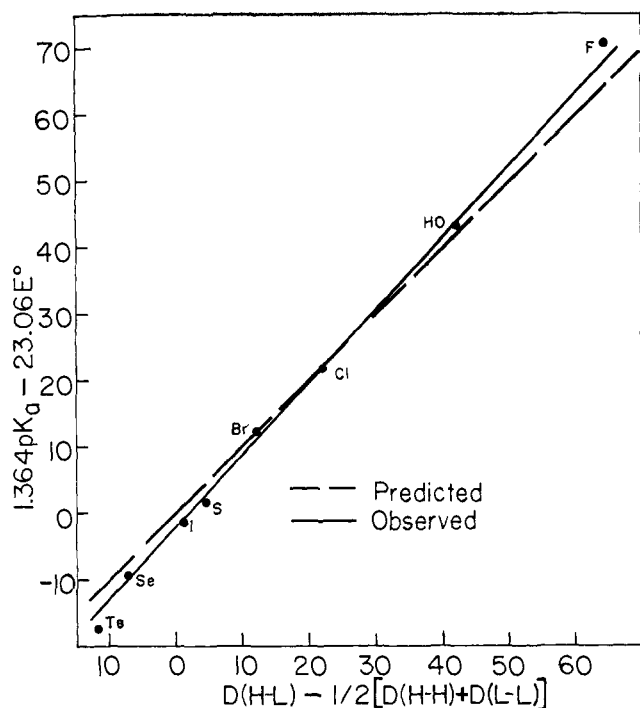
Fig. 1.—Plot of $D(\text{H-L}) - \frac{1}{2}[D(\text{H-H}) + D(\text{L-L})]$ vs. $1.364 \cdot pK_a - 23.06E^0$ (eq. 4).

Fig. 2.—Plot of $(\chi_L - \chi_H)^2$ vs. $0.059pK_a - E^0$ (eq. 6.)

If the solvation terms for neutral molecules (ΔH_4 and ΔH_9) are neglected and the entropy terms for dissociation ($T\Delta S_5$) and oxidative coupling ($T\Delta S_{10}$) are neglected,[1] standard substitutions in eq. 3 yield the following interesting and useful relationship

$$1.364pK_a - 23.06E^0 = D_{HL} - \frac{1}{2}[D_{H_2} + D_{L_2}] \tag{4}$$

where pK_a is the pK_a value of the acid HL at 25°, E^0 is the half-cell electromotive force for the oxidative coupling reaction of L^- (hereafter called the oxidative coupling potential), D_{HL} is the bond energy of HL in kcal./mole, D_{H_2} is the bond energy of H_2 in kcal./mole, D_{L_2} is the bond energy of L_2 in kcal./mole, 1.364 is the numerical value of $2.303RT$ in kcal./mole deg., 23.06 is the numerical value of the volt equivalent in kcal./ abs. v. g. equiv. A plot of eq. 4, using available data,[2] is shown in Fig. 1.

The observed slope of 1.12 is reasonably close to unity, the slope expected from eq. 4. The slight deviation in slope, coupled with the linearity observed, implies that entropy and/or solvation effects are proportional to enthalpy effects in the bond dissociation of the species L_2, H_2, and HL. The linear correlation observed between the parameters expressed appears to be sufficiently good to permit prediction of ionization constants, electrode potentials, or bond dissociation energies when two of these factors are known.

Group Electronegativities.—Pauling[3] has defined an electronegativity scale through eq. 5.

(1) This is equivalent to an assumption that $\Delta S_5 - \Delta S_{10}$ and $\Delta H_4 - \Delta H_9$ are negligible.

(2) (a) Bond energies from M. L. Huggins, *J. Am. Chem. Soc.*, **75**, 4123 (1953); (b) E^0 values from W. M. Latimer, "Oxidation States of the Elements," 2nd Ed., Prentice-Hall, New York, N. Y., 1952; (c) pK_a values from R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959; and from J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants, Part II," The Chemical Society, London, 1958.

(3) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 92.
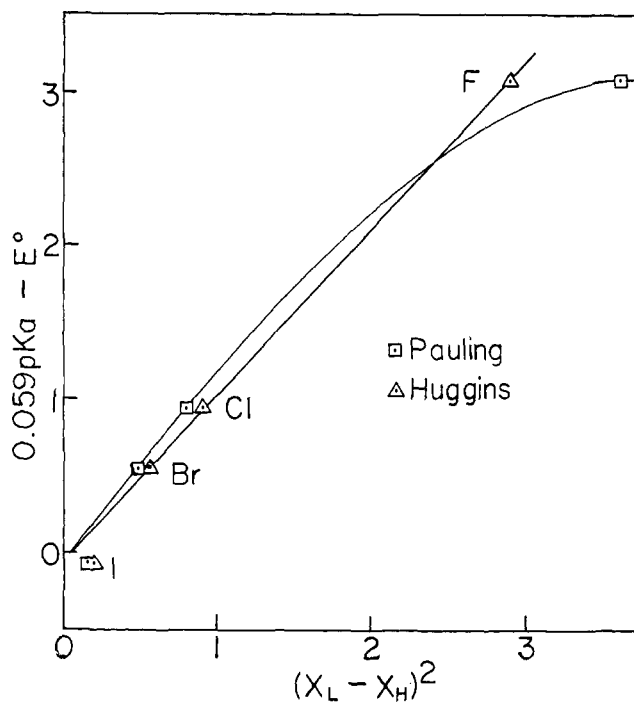
$$23.06(\chi_A - \chi_B)^2 = D(\text{A-B}) - \frac{1}{2}[D(\text{A-A}) + D(\text{B-B})] \tag{5}$$

Appropriate combination of eq. 5 and 4 and division by 23.06 gives

$$0.059pK_a - E^0 = (\chi_L - \chi_H)^2 \tag{6}$$

A plot of this equation is shown in Fig. 2, using electronegativity values of Pauling and of Huggins.[2a] The linear plot obtained using Huggins' values may be taken as support for his assignments. This plot may be combined with pK_a and E^0 data for a species to assign electronegativity values to polyatomic groups which have a positive value for the terms on the left side of eq. 6.

Edwards[4] has pointed out a linear correlation between oxidative coupling potentials and a nucleophilic constant derived by Swain and Scott[5] from kinetic data. Edwards further developed an equation to correlate reactions of electron donors with oxidative coupling potentials and acidities of various donor groups. The donor constants in the Edwards equation, derived from experimental or estimated acidities and oxidative coupling constants, provide the data necessary to evaluate the electronegativity of the donor groups from eq. 6. Values so obtained are given in Table I. For comparative purposes the halogens are included in Table I. The pK_a assignments of Bell[2c] were used for the hydrohalic acids. The electronegativities given in Table I are for the group when the point of attachment of the group is through the last atom indicated in the line formula. Thus the pyridine value of 3.5 is the electronegativity of nitrogen in complexes such as
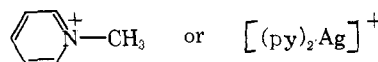
(4) J. O. Edwards, *J. Am. Chem. Soc.*, **76**, 1540 (1954).

(5) C. G. Swain and C. B. Scott, *ibid.*, **75**, 141 (1953).

Table I

Group Electronegativities[a,b]

Group	x	Group	x
F-	4.0[c]	Cl-	3.2[e]
H₂O⁺-	3.8	HS-	3.2[c]
O₂NO-	3.7	NCS-	3.1
⁻O₃SO-	3.7	(CH₃O)₂POS-	3.0
2,4,6-(NO₂)C₆H₂O-	3.6[c]	(C₂H₅O)₂POS-	3.0
ClCH₂(CO)O-	3.6	Br-	2.9[e]
CH₃(CO)O-	3.6	(H₂N)₂⁺CS-	2.8
HO-	3.6		
C₅H₅N⁺-	3.5	⁻S-	2.7
C₆H₅O-	3.5	⁻O₃SS-	2.6
⁻HO₃PO-	3.4[c]	C₂H₅SO₂S-	2.6
HO₂CO-	3.4[c]	CH₃C₆H₄SO₂S-	2.4
H₃N⁺-	3.3	I-	[f]
N₃-	3.3		
NC-	3.3[c,d]		
C₆H₅NH₂⁺-	3.2		
O₂N-	3.2		

[a] Based on χ_H = 2.2. [b] Except as noted, values calculated from ref. 4. [c] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958. [d] R. M. Izatt, J. J. Christensen, R. T. Pack, and R. Bench, *Inorg. Chem.*, 1, 828 (1962). [e] pK_a values from ref. 2c. [f] Not calculatable by this method since $0.059 pK_a - E^0$ is a negative quantity.

The high electronegativity of nitrogen in this state is perhaps not unexpected on the basis of the sp² hybridization and the formal positive charge. The electronegativity of the sp³ nitrogen in an ammine complex is 3.3. The order of electronegativity in the pseudohalogens compared to the halogens is F- > N₃- > NC- > Cl- > NCS- > Br- > I.

Several reservations in the use of eq. 6 for obtaining group electronegativities should be pointed out. First, the atom to which the proton in HL is bound must be the same as that by which L–L coupling occurs. Since the observed pK_a will be an upper limit for the pK_a of L (whether or not the proton is attached through the same atom as that by which coupling occurs) in cases where uncertainty exists regarding the site of protonation the calculated electronegativity values may be taken as an upper limit. Thus SCN⁻ couples through S but protonates at N,[6] hence the value of 3.1 is an upper limit for NCS⁻. The NO₂ group involves proton dissociation from oxygen but N₂O₄ is not coupled through an O–O bond. Second, the L–L bond should be a single bond. The –CN electronegativity may be invalid due to some π-bond character in cyanogen.[7]

(6) C. I. Beard and B. P. Dailey, *J. Chem. Phys.*, 18, 1437 (1950).

Further Interrelationships.—Edwards has correlated many rate and equilibrium data by means of the equation

$$\log (K/K_0) = \alpha E_n + \beta H \qquad (7)$$

where (K/K_0) is a relative rate or equilibrium constant, E_n is a nucleophilic constant based on oxidative coupling potentials, H is a basicity constant based on pK_a values, and α and β are reaction constants determined by the best fit of the data for a particular reaction. Since E_n and H are interrelated through a group electronegativity, eq. 7 may be transformed into one in which the variables are group electronegativity and either E_n or H. Such a transformation may provide a new vantage point from which to interpret the correlations observed. Thus the original Edwards equation for the stability constants of Ag^+ complexes has a β-value of -0.078 which might be interpreted as showing a decrease in stability with an increase in basicity of the ligand. On transformation to an equation involving electronegativity and basicity, it is found that the stability constant increases with increasing basicity and with decreasing electronegativity, as expected for each of these factors independently.[8]

Maurin and Paris[9] observed that the ease of oxidative coupling for mercaptans parallels the acidity of the mercaptans. For the reaction

$$RSH \longrightarrow \tfrac{1}{2}RSSR + \tfrac{1}{2}H_2$$
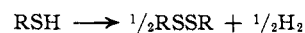
the enthalpy change (ignoring solvation effects) can be calculated from

$$\Delta H = 23.06(\chi_{RS} - \chi_H)^2 \qquad (8)$$

If entropy terms are ignored, then

$$-E^0 = (\chi_{RS} - \chi_H)^2 \qquad (9)$$

Since changes in acidity may be assumed to parallel changes in electronegativity if other factors remain constant, eq. 9 would predict that the mercaptans which undergo oxidative coupling most readily would be the least acidic. This conclusion is exactly the opposite of that reached by Maurin and Paris and indicates the need for further work in this area.

(7) M. F. Hawthorne, G. S. Hammond, and B. M. Graybill, *J. Am. Chem. Soc.*, 77, 486 (1955).
(8) (a) R. J. Bruehlman and F. H. Verhoek, *ibid.*, 70, 1401 (1948); (b) L. G. Van Uitert, W. C. Fernelius, and B. E. Douglas, *ibid.*, 75, 2736 (1953).
(9) J. Maurin and R. A. Paris, *Compt. rend.*, 232, 2428 (1951); *J. chim. phys.*, 48, 30 (1951).