TABLE VIII

HALIDES, CYANIDES AND FERROCYANIDES

No.	Compound[a]	Nicotine, % Calcd.	Nicotine, % Found	Copper, % Calcd.	Copper, % Found	Crystals
1	$2CuCN \cdot RN_2 \cdot HCN$	44.0	43.0	34.5	34.2	Prisms (tricl.)
2	$CuI \cdot RN_2$	46.0	43.2	..	..	Hydrous, irregular
3[b]	$Ag_2 \cdot RN_2 \cdot H_2FeCy_6 2H_2O$	25.9	25.9			

[a] $RN_2 = C_{10}H_{14}N_2$. [b] Calcd., Ag, 34.2; found, Ag, 34.8.

anions formed trinicotinammines; nickelous trinicotinammino thiocyanate was an exception. Bivalent cations (principally limited to copper) combined with bivalent anions usually added 2 moles of ammonia or 1 mole of nicotine; the nicotine double salts usually contained only 1 mole of nicotine, but cupric dinicotine dichromate was an exception. The author prepared only two trinicotinammines of trivalent cations—the trinicotinammino picrates of aluminum and iron. Bivalent cations were often associated with 2 moles of nicotine and up to 6 moles of water.

In general, both types of salts were well crystallized, highly water-insoluble compounds of definite and repeatable composition. Many of them contained definite amounts of water of crystallization; in others this was indefinite or fluctuating. Usually they could be prepared by mixing normal solutions of the required salts in water or in water–ethanol, using the acetates of the desired metals and the sodium or ammonium salts of the desired anions. Manipulations had to be juggled in some cases to avoid the formation of metal hydroxides, or to produce the latter in finely dispersed and reactive form. Sometimes one listed compound was prepared from another, as in Table VI, no. 3 from no. 2; and in Table VII, 3 from 2. Usually the crystals formed immediately, sometimes after a few days at room temperature.

Many of the compounds fluoresced. Some of these were cuprous nicotine thiocyanate (Table I), the cadmium salts of nicotine salicylate (Table II) and thiocyanate, and the zinc salts of nicotine thiocyanate, salicylate and benzoate (Table VII).

In the tables, RN_2 is used as an abbreviation for nicotine, $C_{10}H_{14}N_2$, where R represents $C_{10}H_{14}$, obviously not a definite radical, and N_2 indicates possible chelation of two nitrogens.

EASTERN REGIONAL RESEARCH LABORATORY[5]
PHILADELPHIA 18, PENNA.

---

[5] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

Theory of the Variation of Bond Length with Bond Environment

BY RICHARD P. SMITH[1]

RECEIVED NOVEMBER 5, 1952

Recently a theory of the distribution of electronic charge in aliphatic organic molecules has been published.[2] This theory is particularly useful for calculating the variation of the moment of a C–X (X = halogen or hydrogen) bond with the environment of the bond. Concurrently with the development of this theory and its successful application to several problems, a number of C–X internuclear distances ("bond lengths") in substituted methanes have been accurately determined with the use of microwave spectroscopy. In this paper we propose to show that most of the bond length variations with environment which are observed may be related quantitatively to the bond moment variations calculated with inductive effect theory.

Our theory of bond length variation in saturated molecules is based on the model used in discussing charge distributions.[2] This model has a molecule consisting of touching spheres, each sphere representing an atom and having a radius equal to the covalent bond radius. Spread out over the surface of the sphere representing atom a is an amount of electronic charge equal to the "net charge," ϵ_a, which atom a carries. This net charge "sees" charge Z_a, the effective nuclear charge of atom a, given by

$$Z_a = Z_a^\circ + s_a(\epsilon_a/e) \qquad (1)$$

where e is the negative of the charge of an electron, Z_a° is the effective nuclear charge of atom a when it carries zero net charge, and s_a is 0.30 or 0.35 accordingly as a is or is not hydrogen. Equation (1) is an interpolation of one of Slater's screening rules.[2,3]

Let us now consider an equation holding for Slater approximate atomic orbitals,[3] namely

$$R_a = ((n_a^*)^2/Z_a)a_0 \qquad (2)$$

where a_0 = Bohr radius = 0.53 Å., n_a^* is the "effective quantum number" for atom a, and R_a is the distance from the nucleus for which the electronic density for the shell under consideration is a maximum, and may be considered to be the radius of the atom. From equation (2) we see that, for a given effective quantum number (electron shell), an increase in effective nuclear charge goes along with a decrease in effective radius, and *vice versa*. This may be pictured as a "pulling in" of the electron shell by the increased positive effective nuclear charge.

If we consider molecules from the atomic orbital point of view, which is essentially what we are doing when we use the charged sphere model under discussion, we may expect that equation (2) may have a degree of applicability to molecules; just what this degree is cannot be given a clear-cut theoretical answer, but it must be determined empirically. Let us make the following supposition, to be tested empirically. We suppose that equation (2), when coupled with equation (1), may satisfactorily be used for discussing the *variation* of the *effective radius* of an atom *in a*

---

[1] Junior Fellow, Harvard Society of Fellows, 1951–.

[2] R. P. Smith, T. Ree, J. L. Magee and H. Eyring, THIS JOURNAL, **73**, 2263 (1951).

[3] H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 162–163.

molecule, disregarding the theoretical difficulties which strict interpretations of this idea may encounter. Then the variation of the length of a given type of bond, *e.g.*, C–Cl, will be the sum of the atomic radius variations, and may be discussed in terms of the net charges, which may be calculated from our inductive effect theory, the latter theory being based essentially on the same model. It is the purpose of this paper to show the results of a test of this idea, using accurately measured bond lengths from the recent literature, and charge distributions calculated with the same theory and parameters as used in our first paper on inductive effect theory.[2] We wish to emphasize that we do not consider that equation (2) will hold well for the actual covalent radii of atoms, but that we are merely using it to discuss *small variations.*

Combining equations (1) and (2), and using, from (2)

$$R_a{}^\circ = ((n_a{}^*)^2/Z_a{}^\circ)a_0 \qquad (3)$$

we find

$$R_a = R_a{}^\circ\left(1 - \frac{s_aR_a{}^\circ}{(n_a{}^*)^2a_0}\,\frac{\epsilon_a}{e}\right) \qquad (4)$$

correct to first order in (ϵ_a/e), which is sufficient, as the second term in parentheses in (4) is small as compared with unity. Then

$$R_{ab} = R_a + R_b = R_a{}^\circ + R_b{}^\circ - \frac{s_a(R_a{}^\circ)^2}{(n_a{}^*)^2a_0}\,\frac{\epsilon_a}{e} - \frac{s_b(R_b{}^\circ)^2}{(n_b{}^*)^2a_0}\,\frac{\epsilon_b}{e} \qquad (5)$$

Particularizing equation (5) to C–X bonds, where[2]

$$\epsilon_X = \gamma_{XC} + \beta_{XC}\epsilon_C \qquad (6)$$

where γ_{XC} and β_{XC} are constants for a given C–X bond,[2] we find

$$R_{CX} = A_{CX} - B_{CX}\epsilon_X \qquad (7)$$

where A_{CX} and B_{CX} are constants for a given C–X bond (independent of the environment of the bond). The constant of importance in (7) is B_{CX}, given by

$$B_{CX} = \frac{s_C(R_C{}^\circ)^2}{(n_C{}^*)^2\beta_{XC}ea_0} + \frac{s_X(R_X{}^\circ)^2}{(n_X{}^*)^2ea_0} \qquad (8)$$

for it determines the extent of the variation of R_{CX} with ϵ_X. The value of this constant may be estimated using the appropriate screening constants ($s_C = s_X = 0.35$ except $s_H = 0.30$), the appropriate effective quantum numbers,[3] the values of β_{XC} from reference (2), and the $R_C{}^\circ$ and $R_X{}^\circ$ may be taken to be the Pauling covalent radii,[4] since we need only approximate values of these radii in calculating the B_{CX} constants. The values of the B_{CX} thus obtained, with values of the component parts, are tabulated in Table I for the carbon–hydrogen and carbon–halogen bonds.

TABLE I

THEORETICAL VALUES OF THE B_{CX} OF EQUATION (8)

Bond C–X	β_{XC}[2]	$R_X{}^\circ$(4)	$n_X{}^*$	B_{CX} (Å./10^{-10} e.s.u.)
C–H	0.13	0.30	1	0.167
C–F	.25	.64	2	.096
C–Cl	.71	.99	3	.0437
C-Br	.91	1.14	3.7	.0354
C–I	1.29	1.33	4.0	.0310

$n_C{}^* = 2$; $R_C{}^\circ = 0.77$ Å.

According to our theory, then, if we plot, for a given type of bond (*e.g.*, C–Cl), the value of $(-\epsilon_X)$ against R_{CX}, the result should be a straight line with slope B_{CX}. The theory says nothing about A_{CX}—we are concerned only with bond length *variations.*

Figure 1 shows R_{CX} as a function of $(-\epsilon_X)$ for X = F, Cl and Br, for the substituted methanes. The circles represent experimental values of the bond lengths; the charges are calculated by the procedure outlined in reference 2, with the same parameters as used therein.

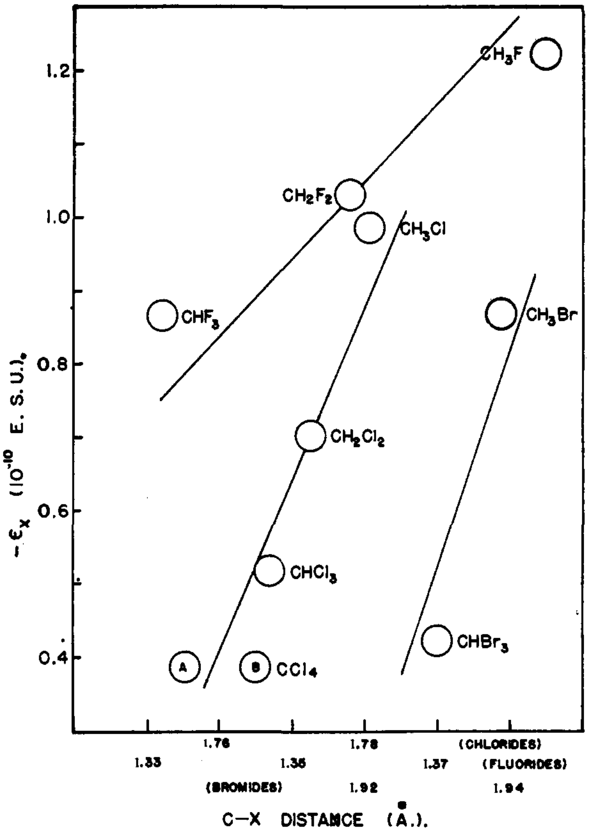

Fig. 1.—Calculated slopes, observed C–X distances plotted against halogen net charges; references for C–X distances: CH_3F[5]; CH_2F_2[6]; CHF_3, $CHCl_3$[7]; CH_3Cl, CH_3Br[8]; CH_2Cl_2[9]; CCl_4[10]; $CHBr_3$.[11]

Except for CCl_4, the experimental values are the best values obtained from microwave spectroscopy. The magnitude of the experimental error involved is uncertain[8]; we have drawn the circles with a

---

(4) L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1940.

(5) O. R. Gilliam, H. D. Edwards and W. Gordy, *Phys. Rev.*, **75**, 1014 (1949).

(6) D. R. Lide, Jr., THIS JOURNAL, **74**, 3548 (1952).

(7) S. N. Ghosh, R. Trambarulo and W. Gordy, *J. Chem. Phys.*, **20**, 605 (1952).

(8) S. L. Miller, L. C. Aamodt, G. Dousmanis, C. H. Townes and J. Kraitchman, *ibid.*, **20**, 1112 (1952).

(9) R. J. Myers and W. D. Gwinn, *ibid.*, **20**, 1420 (1952).

(10) "A" and "B" represent the probable upper and lower limits of the CCl_4 bond length, this not being known accurately, as only electron diffraction results are available. L. O. Brockway, *ibid.*, **41**, 747 (1937), gives 1.755 ± 0.005; C. Finbak and O. Hassel, *Arch. Math. Naturvidenskab*, **45**, No. 3 (1941) give 1.770. Other observers give intermediate values.

(11) Q. Williams, J. J. Cox and W. Gordy, *J. Chem. Phys.*, **20**, 1524 (1952).

diameter of 0.002 Å., which is probably reasonable for the experimental error in most cases.

The straight lines in the accompanying figure have the theoretical slopes, that is, the B_{CX} value of Table I. The intercepts, as mentioned above, are arbitrary. The scales of the three graphs are the same, so that the relative slopes may readily be observed also. The calculated and observed slopes are all approximately the same for each series of halogens, and the relative slopes for the different series are predicted correctly.

The particular molecules included in this study are chosen simply because they are the ones for which accurate bond-length data are available. One other series might be considered: C–H bonds. Here, however, it is found that there is so much variation in the experimental values, due to difficulties encountered in averaging the results for the deuterium isotopes studied, and the results are so sensitive to the methods employed,[8] that it proves impossible to distinguish bond length variations from experimental error and ambiguity for C–H bonds.

We emphasize that, in calculating our theoretical slopes, no "adjustable parameters" have been employed; the constants involved are all carried over directly from the theory of reference (2), which in turn uses only accepted polarizabilities, screening constants, and covalent radii. Hence the results are believed to lend some support both to the theory outlined here and to the theory of reference (2).

CAMBRIDGE, MASS.

Polyphosphoric Acid as a Reagent in Organic Chemistry. IV. Conversion of Aromatic Acids and their Derivatives to Amines[1]

BY H. R. SNYDER, CLAYTON T. ELSTON AND DAVID B. KELLOM

RECEIVED DECEMBER 8, 1952

In a continuation of investigations of the use of polyphosphoric acid as a reagent in organic reactions[2,3] it has been found that aromatic acids can be converted to aryl amines by treatment with hydroxylamine and commercial polyphosphoric acid.[4] The reaction is carried out by heating a mixture of the reactants, with stirring, until rapid evolution of carbon dioxide begins, usually in the range of 150–170°. At such temperatures the reaction normally is complete in five to ten minutes, and the mixture is poured over crushed ice to give an aqueous solution of the amine phosphate.

The yields of crude products obtained from various acids are reported in Table I. In general, acids containing electron-donating substituents were found to give higher yields than those containing electron-withdrawing groups. This is in agreement with the results obtained by Hauser[5] in his studies on the effect of substituents on the Lossen rearrangement. Acids which gave poor yields of amines produced large amounts of dark colored, acid-insoluble material of very indefinite melting point. The two aliphatic acids studied, valeric acid and caprylic acid, failed to yield more than mere traces of the expected amines. Caprylohydroxamic acid likewise failed to yield *n*-heptylamine when subjected to similar conditions.

Many acid derivatives also underwent the reaction (see Table I). However, with the exception of esters, the yields were generally lower than with the corresponding acids themselves. *p*-Chlorobenzamide, N-methyl-*p*-chlorobenzamide and N-methylbenzamide yielded no *p*-chloroaniline or other identifiable product. The reason for this unexpected discrepancy is not known. It is interesting to note that some ketones may be transformed into the corresponding amines by treatment with two moles of hydroxylamine. The first step involves a Beckmann rearrangement[3] to the substituted amide while the second step involves cleavage of this acid derivative to give two moles of amine.

The exact course of the reaction has not been elucidated but it seems likely that a hydroxamic acid is an intermediate. Indeed, hydroxamic acids themselves are smoothly converted to amines in hot polyphosphoric acid. Potassium benzohydroxamate and potassium α-naphthohydroxamate yielded aniline (67%) and α-naphthylamine (73%), respectively. The transformation of *o*-phenylbenzoic acid into phenanthridone and that of salicylic acid into benzoxazolone can be explained by assuming an isocyanate to be an intermediate. Thus it seems likely that the process is a variant of the Lossen reaction.

For most of the reactions the sulfate and hydrochloride of hydroxylamine could be used interchangeably with but little influence on the course of the reaction. However, there were three notable exceptions; hydroxylamine hydrochloride gave markedly better yields with salicylic acid and with benzophenone, but hydroxylamine sulfate was required with *p*,*p*′-dichlorobenzophenone.

Although the method appears to be less generally applicable than the Curtius and Hofmann conversions of acids to amines, it is very attractive within its field of application. Only the simplest apparatus is required and the total reaction time is ten minutes or less. It is more conveniently carried out than the Schmidt reaction, which must be conducted with due regard to the properties of hydrazoic acid.

Experimental

General Method.—To 25–50 g. of polyphosphoric acid was added 5 g. of the carboxylic acid and slightly more than the theoretical amount of hydroxylamine sulfate or hydrochloride. The mixture was stirred mechanically and heated slowly on an oil-bath. When the chloride salt was used hydrogen chloride was evolved from the reaction mixture as the temperature approached 100°. Upon further increase in temperature the reactants gradually entered solution. In the range 150–170° there was a rapid evolution of carbon dioxide and the mixture darkened considerably. When the frothing had ceased the mixture was poured onto crushed ice. The insoluble material was removed and the filtrate was neutralized with potassium hydroxide. The liberated amine, if liquid, was extracted with several portions of benzene. The combined extracts were dried over sodium hydroxide pellets and then treated with dry hydrogen chloride gas. The precipitated hydrochloride was collected and dried in a desiccator. If the amine was solid

---

(1) Presented in part at the 122nd Meeting of the American Chemical Society, Atlantic City, N. J., September 17, 1952.

(2) H. R. Snyder and R. W. Roeske, THIS JOURNAL, **74**, 5820 (1952).

(3) E. C. Horning, V. L. Stromberg and H. A. Lloyd, *ibid.*, **74**, 5153 (1952).

(4) The authors are indebted to Dr. Howard Adler, Victor Chemical Works, Chicago, Ill., for generous supplies of polyphosphoric acid.

(5) C. R. Hauser and collaborators, THIS JOURNAL, **59**, 121, 2308 (1937); **61**, 618 (1939).