Contribution from the Laboratory of Structural Chemistry,
University of Groningen, Groningen, The Netherlands

Bonding in Polyhalogens

By E. H. WIEBENGA and D. KRACHT

Received October 21, 1968

The bonding in interhalogen compounds, polyhalide ions, and positively charged polyhalogen ions is described by the use of a modified Hückel theory in which the electrostatic interaction of the net charges on the atoms and the self-energy of the atoms (including core electrons) as a function of their charges are taken into account. As basis functions only p functions of the valence shell are used. The theory is very simple and contains only one adjustable parameter. The calculated charges, bond orders, and energies are in good agreement with experimental nqr results, bond lengths, stabilities, and spectra.

1. Introduction

Experiments.—The experimental information available on the structure of polyhalogen complexes is rather extensive. From a review given in 1961[1] it appears that most of these structures are characterized by (a) the presence of "polyvalent" halogen atoms, (b) bond angles close to 90 or 180°, and (c) bond lengths which are some tenths of an ångström longer than the sum of the covalent radii.

Apparent exceptions to feature c in the case of ICl_2^-, ICl_4^-, and $BrICl^-$ were later shown to be due to experimental inaccuracies.[2-4] The structures of CsI_2Br, $N(C_2H_5)_4I_3$ (I), and $N(C_2H_5)_4I_3$ (II) which have been determined recently[5,6] show the same features as the other trihalides; the latter two structures have provided interesting information on the deformation of I_3^- ions in a crystal field. A recent refinement of the crystal structure of iodine[7] has shown that the I–I bond length in the solid state is extended by 0.05 Å as compared with that in I_2 molecules in the gas phase. Also, recently, measurements of nqr and Mössbauer effect have given more information on the charges of the atoms in polyhalogen complexes. References to this work are given in section 3A.

Theory.—The hypervalency of halogen atoms in polyhalogens like ClF_3, BrF_5, IF_7, I_3^-, ICl_4^-, etc., has been described in terms of sp^3d, sp^3d^2, or sp^3d^3 hybridization of the valence orbitals of the hypervalent atom and the formation of localized electron pair bonds involving the hybrid orbitals. The formation of these directed bonds has been argued either from Pauling's principle of maximum overlap or from the "Pauli repulsion" between electrons of the same spin. In the latter argument one calculates the most probable configuration for electrons having all parallel spins in the valence shell of the central atom and assumes that the electron pairs in the molecule prefer this configuration of maximum probability.[8-14] This principle of the effective repulsion of electron pairs in molecules is also applied for five or more electron pairs without specifying whether or not d orbitals of the central atom are involved;[15] it should then be realized that if d orbitals do not participate the electron pair repulsion theory is no longer based on the quantum theoretical configurations of maximum probability referred to above.

The electron pair repulsion theory has been very successful in giving a qualitative explanation of the geometry of many polyhalogens and other compounds. In order to obtain quantitative results on the net charges of the atoms in the molecules, bond lengths, and the relative stability of alternative conformations, we have applied a simple molecular orbital theory to the polyhalogen complexes. The present work is a refinement and extension of previous calculations by Pimentel, Rundle, Havinga, and others.[16-20] The theory applied does not use the fundamentals of the electron pair repulsion theory and is essentially a Hückel type molecular orbital theory. Since, however, in polyhalogens the net charges on the atoms prove to be rather large the naive Hückel theory was modified such as to include the interaction of the net charges on different atoms and the change of energy of each atom, including its core electrons, when it becomes charged. In these respects the modified Hückel theory is preferable to the more extensively used extended Hückel theory.[21,22] In principle, it would be still better to account in more detail for the interaction of the electrons, *i.e.*, to apply a Hartree–Fock type molecular

---

(1) E. H. Wiebenga, E. E. Havinga, and K. H. Boswijk, *Advan. Inorg. Chem. Radiochem.*, **3**, 133 (1961).

(2) G. J. Visser and A. Vos, *Acta Cryst.* **17**, 1336 (1964).

(3) R. J. Elema, J. L. de Boer, and A. Vos, *ibid.*, **16**, 243 (1963).

(4) T. Migchelsen and A. Vos, *ibid.*, **22**, 812 (1967).

(5) G. B. Carpenter, *ibid.*, **20**, 330 (1966).

(6) T. Migchelsen and A. Vos, *ibid.*, **23**, 796 (1967).

(7) F. van Bolhuis, P. B. Koster, and T. Migchelsen, *ibid.*, **23**, 90 (1967).

(8) H. K. Zimmerman and P. van Rysselberghe, *J. Chem. Phys.*, **17**, 598, (1949).

(9) J. E. Lennard-Jones and J. A. Pople, *Proc. Roy. Soc.*, **A202**, 166 (1950).

(10) J. W. Linnett and A. J. Poë, *Trans. Faraday Soc.*, **47**, 1033 (1951).

(11) J. W. Linnett and C. E. Mellish, *ibid.*, **50**, 665 (1954).

(12) P. G. Dickens and J. W. Linnett, *Quart. Rev.* (London), **11**, 291 (1957).

(13) R. J. Gillespie and R. S. Nyholm, *ibid.*, **11**, 339 (1957).

(14) R. J. Gillespie, *Can. J. Chem.*, **38**, 818 (1960).

(15) R. J. Gillespie, *J. Chem. Educ.*, **40**, 295 (1963).

(16) G. C. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951).

(17) R. J. Hach and R. E. Rundle, *J. Am. Chem. Soc.*, **73**, 4321 (1951).

(18) R. E. Rundle, *Acta Cryst.*, **14**, 585 (1961).

(19) E. E. Havinga, Thesis, Groningen, 1957.

(20) E. E. Havinga and E. H. Wiebenga, *Rec. Trav. Chim.*, **78**, 724 (1959).

(21) M. Wolfsberg and L. Helmholtz, *J. Chem. Phys.*, **20**, 837 (1952).

(22) R. Hoffmann, *ibid.*, **39**, 1397 (1963).

orbital theory. It is not certain, however, whether approximate versions of the latter such as the CNDO method,[23,24] where a great number of electron interaction integrals is neglected and the inner shells are treated as part of an unpolarizable core, will yield better results.

The molecular orbitals were taken to be a linear combination of only the p orbitals of the atomic valence shells; d orbitals were neglected because of their high energy. The results obtained for IF_7 by the application of the extended Hückel theory[25] may be considered as an indication that in polyhalogens the neglect of d orbitals is, at least for the ground state, a reasonable approximation.

2. Modified Hückel Theory

In Hückel theory the energy of the valence electrons considered is given by

$$E = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu} = \Sigma_{\mu} P_{\mu\mu} H_{\mu\mu} + 2\Sigma_{\mu<\nu} P_{\mu\nu} H_{\mu\nu} \qquad (1)$$

The subscripts μ, ν, . . . denote the basis AO's Φ_μ, Φ_ν, . . . ; $P_{\mu\nu} \equiv 2\Sigma_i c_{\mu i} c_{\nu i}$ over the occupied molecular orbitals of the closed shell system is the population–bond order matrix; $H_{\mu\nu} \equiv \int \Phi_\mu(1) H_{\text{eff}}(1) \Phi_\nu(1) \mathrm{d}\tau_1$, where H_{eff} is the effective one-electron Hückel Hamiltonian.

In the right-hand side of (1) $\Sigma_\mu P_{\mu\mu} H_{\mu\mu}$ obviously represents the energy of the valence electrons when $P_{\mu\mu}$ electrons would be confined to atomic orbital Φ_μ, $P_{\nu\nu}$ to atomic orbital Φ_ν, etc.; the term $2\Sigma_{\mu<\nu} P_{\mu\nu} H_{\mu\nu}$ represents the change in energy when the electrons become delocalized and will be called covalent bond energy.

Our modification of the Hückel theory consists of replacing the term $\Sigma_\mu P_{\mu\mu} H_{\mu\mu}$ in (1) by the energy of the charged atoms as a whole (*i.e.*, core electrons and other "non-Hückel" electrons included) plus the energy of electrostatic interaction between the net charges of these atoms (considered as point charges). The secular equations are then derived from the modified expression (1) by requiring E to be stationary under the condition that the molecular orbitals remain orthonormal.

In order to find the energy E_A of an atom A with a net charge Q_A let us consider Figure 1. If we take the energy of the uncharged atom arbitrarily to be zero the energy of A^+ is I_A and of A^- is $-A_A$, when I_A and A_A denote the ionization energy and the electron affinity, respectively. For fractional charges Q_A the energy can be found from the simple interpolation

$$E_A = \tfrac{1}{2}(I_A + A_A)Q_A + \tfrac{1}{2}(I_A - A_A){Q_A}^2 \qquad (2)$$

Since in our treatment of the polyhalogens the charge is due to p electrons, I_A and A_A refer to a p orbital of the valence shell of the halogen atom.

Making use of (2) we find as a modified eq 1

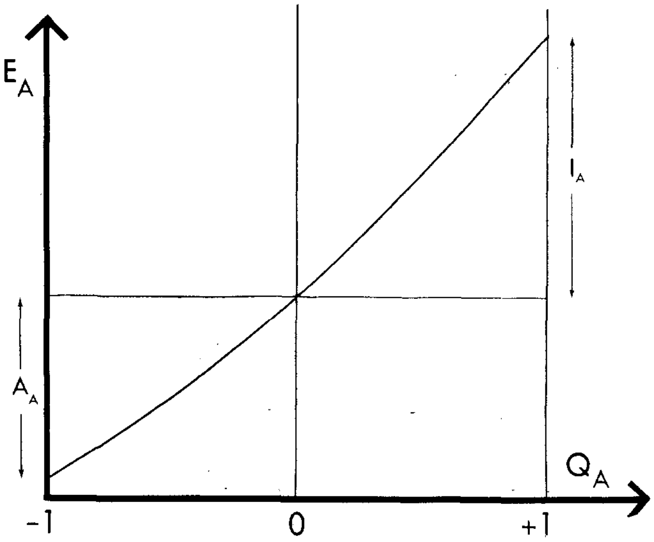


Figure 1.—Energy of an atom as a function of its net charge.

$$E = \Sigma_A\{\tfrac{1}{2}(I_A + A_A)Q_A + \tfrac{1}{2}(I_A - A_A){Q_A}^2\} + \Sigma_{A<B}\frac{Q_A Q_B}{R_{AB}} + 2\Sigma_{\mu<\nu} P_{\mu\nu} H_{\mu\nu} \qquad (3)$$

where the three terms at the right-hand side denote the self-energy of the atoms, their electrostatic interaction energy, and the covalent bond energy, respectively. The charges can be calculated when the coefficients $c_{\mu i}$ are known because

$$Q_A = 5 - \Sigma_{\mu \epsilon A} P_{\mu\mu} \equiv 5 - P_{AA} \qquad (4)$$

Equation 3 does not contain atomic interactions other than the point charge terms $Q_A Q_B / R_{AB}$; repulsions between interpenetrating inner shells are not included. Therefore (3) is only used to find the best coefficients $c_{\mu i}$ and energy E *at given values of* R_{AB}; total molecular energies for different R_{AB} values can only be compared if the inner shell repulsion energies as a function of R_{AB} can be estimated (see section 3B).

The requirement that E be stationary under the conditions $\int \chi_i \chi_j \mathrm{d}\tau = \delta_{ij}$, where χ_i, χ_j, . . . are the molecular orbitals, lead to the secular equations

$$\Sigma_\nu (F_{\mu\nu} - \delta_{\mu\nu}\epsilon_i) c_{\nu i} = 0 \qquad (5)$$

since overlap integrals between different atomic orbitals were neglected. The matrix elements in (5) are given by

$$F_{\mu\mu} = -\tfrac{1}{2}(I_A + A_A) - (I_A - A_A)Q_A - \Sigma_{B \neq A} Q_B / R_{AB}$$
$$F_{\mu\nu} = H_{\mu\nu} \qquad (6)$$

where in the first of these equations $\mu \, \epsilon \, A$; the three p functions of an atom have the same $F_{\mu\mu}$ value.

The diagonal elements $F_{\mu\mu}$ can be calculated for a given atomic configuration (R_{AB} values) because I and A are known for the halogens and Q can be calculated, using (4), from the coefficients obtained in the preceding cycle.

---

[23] J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965).

[24] J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1966).

[25] R. L. Oakland and G. H. Duffey, *ibid.*, **46**, 19 (1967).

The choice of the resonance integrals $H_{\mu\nu}$ was simplified by considering only configurations in which the bond angles are close to 90 or 180°. This is the case in all polyhalogen complexes probably with the exception of IF_7 for which therefore no calculations were done. $H_{\mu\nu}$ was put equal to zero except when μ and ν are on adjacent atoms and directed toward each other (p_σ–p_σ interaction). In this case it was given a value β which is a function of the atomic distance R. This quantity $\beta(R)$ is the only adjustable parameter.

Choice of $\beta(R)$.—For the combination I–I, $\beta(2.67\ \text{Å})$ could be chosen to fit the spectrum of I_2 gas, $\beta(2.93\ \text{Å})$ was obtained analogously by comparing calculated and experimental spectra of I_3^-. Assuming a linear relationship $\beta(R)$ the two values, -3.05 and -2.72 eV, respectively, give

$$\beta = 1.26(R - R_{\text{cov}}) - 3.05 \qquad (7)$$

where R_{cov} is the sum of the covalent radii of the two iodine atoms (2.67 Å).

For combinations of halogen atoms other than I–I, *e.g.*, I–Br, Cl–Cl, etc., the same equation (eq 7) was used with R_{cov} equal to the sum of the covalent radii of I and Br, Cl and Cl, etc. Reasons for this simple assumption were that the relevant transition frequency in the spectrum of Cl_2 and Br_2 is rather close to the value in I_2 and that the difference between the sum of covalent radii and the sum of van der Waals radii is practically the same ($\approx$1.6 Å) for all halogen–halogen combinations thus suggesting that the dependence of β on R might also be similar.

It has been implied[19, 20] that because of the principle of maximum overlap simple Hückel theory based on p orbitals will account automatically for bond angles of 90 and 180°. It was pointed out by Bartell[26] that this is not the case. Moreover it will appear from our results (section 3B) that the Hückel covalent bond energy is often small compared with the self-energy and electrostatic interaction energy of the atoms. We have not attempted yet to predict bond lengths and angles by minimalization of (3) with respect to R_{AB} because of the difficulty of taking inner shell repulsions adequately into account. Indirectly, bond lengths can be derived from the calculated bond orders (section 3A).

Computation.—The modified Hückel procedure was programmed in ALGOL. Self-consistency is attained after about ten iterations. In some cases use was made of the Aitken interpolation procedure. The calculations were performed on the Telefunken TR4 computer of the computing center of the University of Groningen.

3. Results and Discussion

By means of the modified Hückel theory charges, bond orders, and energies were calculated. In the case of the triiodides CsI_2Br, $N(CH_3)_4ICl_2$, and $C_4H_{12}N_2 \cdot 2ICl_2$, the electric potential due to the surrounding crystal field was included in the diagonal matrix element for each atom. The calculations on these compounds were performed by Miss Migchelsen.[27]

A. Charges and Bond Orders.—The calculated charges and bond orders are shown in Table I for all polyhalogen complexes of which the structure is known with the exception of IF_7; the experimental R_{AB} values were used in eq 6.

Charges.—In some cases the calculated net charges can be compared with those obtained from measurements of nqr (or Mössbauer effect).

Assuming that only p orbitals are involved in the bonds, the electrostatic field gradient q in the nucleus of a halogen atom is given by[28]

$$q = q_0\{N_z - \tfrac{1}{2}(N_x + N_y)\} \qquad (8)$$

in which N_z, N_x, and N_y are the populations of the p_z, p_x, and p_y orbitals. The quantity q_0 is the field gradient due to one p orbital. This quantity depends somewhat on the charge Q of the atom because of the contraction or expansion of the p orbitals; usually the following relation

$$q_0 = q_0^0\,(1 + 0.15Q) \qquad (9)$$

is assumed. Nqr measurements yield $|q/q_0^0|$. From eq 8 with, provisionally, $q_0 = q_0^0$ the population N_z can be calculated for atoms in linear complexes ($N_x = N_y = 2$). For the I atom in ICl_4^- and I_2Cl_6 the population N_z is put equal to 2 (z axis perpendicular to the molecular plane) and cylinder symmetry around the z axis is assumed; $N_x = N_y$ can then be calculated from (8). From the N_x, N_y, and N_z values thus obtained the charge Q is known in first approximation; q_0 can then be calculated from (9), and be used to find from (8) final values for N_x, N_y, and N_z; *i.e.*, for Q. These are the experimental values which are compared in Table II with the calculated ones. The agreement is, the simplicity of our one-parameter theory and the uncertainties in the interpretation of the nqr results taken into account, quite satisfactory.

Bond Lengths.—The bonds in polyhalogen complexes have besides a covalent nature indicated by the bond order also an electrostatic character, namely, the attraction or repulsion of the charged atoms in the molecule. The bond orders should be compared with the bond lengths which would be found experimentally if there were no electrostatic interactions. In order to find these bond lengths we have to make a correction that can be calculated easily from the charges and the estimated force constants of the bonds. For the force constant X–Y the arithmetical mean of those for X_2 and Y_2 was assumed. In general the corrections are small ($<$0.01 Å) but in some cases they reach a value of as much as 0.3 Å; the values $>$0.01 Å are listed in Table III.

Since the difference between the bond length for bond order zero (van der Waals distance) and bond order one (sum of the covalent radii) has about the

---

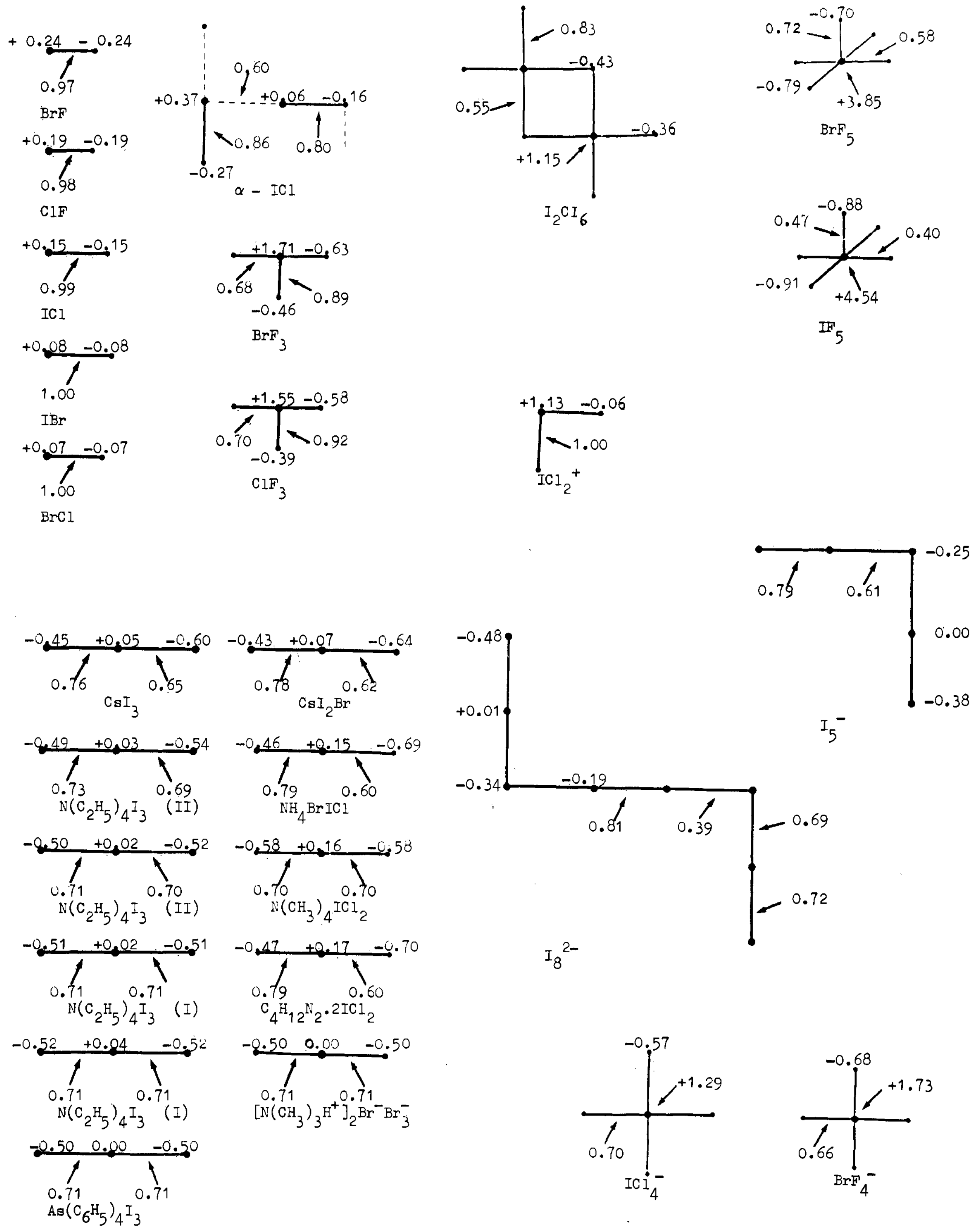
[26] L. S. Bartell, *Inorg. Chem.*, **5**, 1635 (1966).

[27] A. Migchelsen, Thesis, Groningen, 1967.

[28] R. S. Yamasaki and C. D. Cornwell, *J. Chem. Phys.*, **30**, 1265 (1959).

TABLE I

MOLECULAR DIAGRAMS OF POLYHALOGEN COMPLEXES



same value (1.6 Å) for all halogen–halogen combinations, all calculated bond orders can be plotted into *one* graph *vs.* $R-R_{\text{cov}}$, where R is the electrostatically corrected experimental bond length and R_{cov} the sum of the covalent radii. The latter is shown in Table IV for the various halogen–halogen combinations. For

Table II

Comparison of Experimental and Calculated Charges

	Calcd	Exptl	Ref
BrF(g)	+0.24	+0.35	a
ClF(g)	+0.19	+0.28	a
ICl(g)	+0.15	+0.23	b, c
	−0.15	−0.22	
IBr(g)	+0.08	+0.16	a
	−0.08	−0.06	
BrCl(g)	+0.07	+0.12	a
	−0.07	−0.06	
ICl(s)	+0.22	+0.25	b, c
	−0.22	−0.29	
ClF_3(g)	+1.55	+1.24	a
	−0.58	(−0.58)	d
	−0.39	(−0.08)	d
BrF_3(g)	+1.71	+1.39	a
	−0.63	(−0.62)	d
	−0.46	(−0.16)	d
I_2Cl_6(s)	+1.15	+1.21	b
	−0.43	−0.43	c
	−0.36	−0.33	c
CsI_3	−0.43	−0.39	a
	+0.07	+0.07	
	−0.64	−0.66	
$N(C_2H_5)_4I_3$	−0.51	−0.51	e, f
	+0.03	+0.05	
	−0.52	−0.52	
ICl_2^-	+0.16	+0.29	b, c, g
	−0.58	−0.62	
ICl_4^-	+1.29	+1.28	b, c, h
	−0.57	−0.55	
IBr_2^-	+0.06	+0.19	e, i
	−0.53	−0.50	
ICl_2^+	−0.06	−0.25	c

[a] Landolt–Börnstein, Group II, Vol. 4, "Molecular Constants from Microwave Spectroscopy," Springer Verlag, Berlin, 1967. [b] S. Hagiwara, K. Kato, Y. Abe, and M. Minematsu, *J. Phys. Soc. Japan*, **12**, 1166 (1957). [c] J. C. Evans and G. Y. S. Lo, *Inorg. Chem.*, **6**, 836 (1967). [d] No direct measurement. [e] G. A. Bowmaker and S. Hacobian, *Aust. J. Chem.*, **21**, 551 (1968). [f] Average of modifications I and II. [g] Average of K, Rb, and Cs compounds. [h] Average of Na, K, Rb, and Cs compounds. [i] Calculated without crystal field.

F the old covalent radius 0.64 Å was used since the value derived from the interatomic distance in F_2 is probably abnormally high.[29]

Figure 2 shows the bond length *vs.* bond order curve obtained. It may be noted that the bond length variations involved are much larger than those observed in the familiar group of organic π electron systems where a framework of σ bonds keeps the bond length variations as a function of π electron bond order small.

An interesting feature is the different shape of trihalide ions in different compounds.[6,27] For I_3^- this is shown in Table V. In this table, $V_1 - V_2$ and $V_3 - V_2$ represent the electric potential differences (in volts) between the terminal atoms and the central atom, due to the crystal environment. It is seen that the more symmetric the field the more symmetric is the ion; differences in bond lengths are explained quantitatively by the calculated bond orders P. The four different I–Cl bond lengths observed in the ICl_4^- ion in $KICl \cdot H_2O^3$ will also be due to an asymmetry of the crystal field. Those cases were the asymmetry of the

Table III

Electrostatic Corrections to the Experimental Bond Lengths

	Bond length	Correction	Cor bond length
BrF_3	1.81	0.14	1.95
	1.72	0.11	1.83
ClF_3	1.70	0.12	1.82
	1.60	0.09	1.69
I_2Cl_6	2.39	0.06	2.45
	2.70	0.05	2.75
BrF_5	1.78	0.25	2.03
	1.68	0.33	2.01
ICl_4^-	2.50	0.06	2.56

Table IV

Sum of Covalent Radii

I–I	2.67
I–Br	2.48
I–Cl	2.33
Br–Cl	2.14
Br–F	1.78
Cl–F	1.62

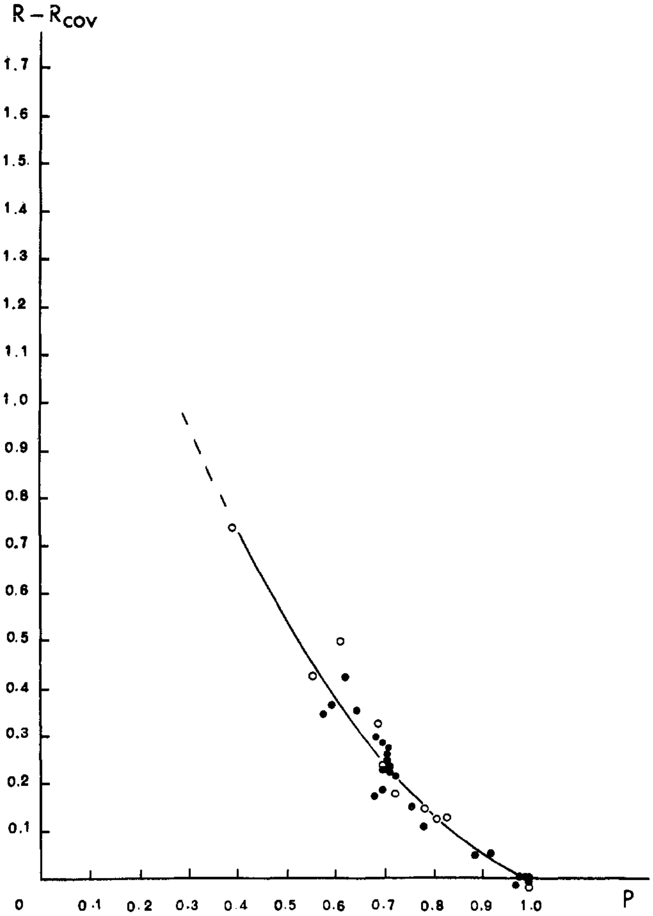


Figure 2.—Electrostatically corrected experimental bond lengths *vs.* calculated bond orders.

---

(29) R. J. Gillespie in "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, ref 15, p 339.

TABLE V

$(I_1–I_2–I_3)^-$ IONS IN DIFFERENT CRYSTAL ENVIRONMENTS

	R_{12}	R_{23}	$V_1 - V_2$	$V_3 - V_2$	P_{12}	P_{23}	Q_1	Q_2	Q_3
CsI_3	2.83	3.04	−0.10	+0.93	0.76	0.65	−0.45	+0.05	−0.60
$N(C_2H_5)_4I_3$ (II)	2.892	2.981	+0.06	+0.38	0.73	0.69	−0.49	+0.03	−0.54
	2.912	2.961	+0.01	+0.19	0.71	0.70	−0.50	+0.02	−0.52
$N(C_2H_5)_4I_3$ (I)	2.943	2.943	−0.27	−0.27	0.71	0.71	−0.51	+0.02	−0.51
	2.928	2.928	−0.02	−0.02	0.71	0.71	−0.52	+0.04	−0.52
$As(C_6H_5)_4I_3$	2.91	2.91	−0.25	−0.25	0.71	0.71	−0.50	+0.00	−0.50

crystal field was not taken into account in the calculation of charges and bond orders are denoted in Figure 2 by open circles.

B. Energy Values.—Energies were calculated not only for known polyhalogen structures but also for some hypothetical alternative conformations and for some hypothetical polyhalogens of nonexistent composition in order to explain the stability of the structures actually observed. In these cases R_{AB} values are not available from experimental data and were derived from the bond length *vs.* bond order graph of Figure 2.

The energy as calculated from the modified Hückel theory is represented by eq 3. Since in this expression inner shell repulsion terms are lacking, an estimate of this repulsion energy should be added if we want to make a more or less realistic comparison of the molecular energy with that of an alternative conformation or with that of a reference state from which the molecule is prepared. For instance, the core repulsions will be different for I_3^- (*two* bonds of 2.93 Å) and $I_2 + I^-$ (*one* bond of 2.67 Å).

The inner shell repulsion energy will be denoted by E_R and was estimated as follows. Consider the reaction $2X \rightarrow X_2$, in which X represents a halogen atom. The calculated change in energy, without E_R, amounts to $2\beta(R = R_{cov}) = -6.10$ eV. The average experimental dissociation energy is only 1.89 eV, from which we find $E_R(R = R_{cov}) = 4.21$ eV. The dependence of E_R on the distance R will in first approximation be represented by

$$E_R = -2.52(R - R_{cov}) + 4.21 \qquad (10)$$

since

$$2\beta = 2.52(R - R_{cov}) - 6.10$$

and the slope of the total energy as a function of the distance is zero (for $R = R_{cov}$).

In Tables VI and VII the energy (in eV) of each complex has been calculated relative to that of the reference state indicated. The inexactness of eq 10 has hardly any bearing on the conclusions to be drawn concerning the relative stability of different complexes provided that the comparison is limited in each case to a group of complexes of the same type, *i.e.*, a group for which the change of the number of bonds is the same when the complex is formed from the reference state. For instance this number of bonds does not change for the interhalogens AB (reference state $^1/_2A_2 + {}^1/_2B_2$), for the interhalogens AB_3 (reference state $^1/_2A_2 + {}^3/_2B_2$) it changes with one, etc. In each group the repulsion energy is only little different for the different complexes and the errors in the repulsion energy do not very much affect the *differences* of the calculated energies of formation. The *absolute values* of these energies of formation are unreliable, however, due to the inexactness of $E_R(R)$ and $\beta(R)$. That for example for I_3^- a small *positive* energy of formation is found is not significant.

Interhalogens.—From Table VI it is seen that the stability of the interhalogens with respect to the elements is mainly due to the electrostatic interaction

TABLE VI

ENERGY OF INTERHALOGEN COMPOUNDS (eV)

μ	Ref state	$2\Sigma P_{\mu\nu}\beta$	ΣE_A	$\Sigma Q_AQ_B/R_{AB}$	E_R	E(tot)	E(exptl)
IF	$^1/_2I_2 + {}^1/_2F_2$	+0.34	−0.17	−0.66	−0.05	−0.54	−1.31
BrF	$^1/_2Br_2 + {}^1/_2F_2$	+0.21	−0.05	−0.47	−0.03	−0.34	−0.80
ClF	$^1/_2Cl_2 + {}^1/_2F_2$	+0.13	−0.00	−0.31	0.00	−0.18	−0.58
ICl	$^1/_2I_2 + {}^1/_2Cl_2$	+0.08	−0.04	−0.14	0.00	−0.10	−0.15
IBr	$^1/_2I_2 + {}^1/_2Br_2$	+0.02	−0.02	−0.04	0.00	−0.03	−0.06
BrCl	$^1/_2Br_2 + {}^1/_2Cl_2$	+0.02	−0.01	−0.03	0.00	−0.02	−0.01
IF_3	$^1/_2 + {}^3/_2F_2$	+0.22	+14.03	−20.30	+3.65	−2.40	
BrF_3	$^1/_2Br_2 + {}^3/_2F_2$	−0.35	+14.80	−19.40	+3.61	−1.34	−2.92
ClF_3	$^1/_2Cl_2 + {}^3/_2F_2$	−0.87	+13.81	−16.79	+3.61	−0.24	−1.68
$\frac{1}{2}I_2Cl_6$	$^1/_2I_2 + {}^3/_2Cl_2$	−2.84	+5.13	−6.40	+5.94	+1.83	−1.24 (s)
IF_5	$^1/_2I_2 + {}^5/_2F_2$	+14.73	+100.64	−143.31	≈+7.1	≈−20.8	−8.82
BrF_5	$^1/_2Br_2 + {}^5/_2F_2$	+4.73	+81.43	−99.76	+6.9	−6.7	−5.39
ICl_3	$^1/_2I_2 + {}^3/_2Cl_2$	−1.48	+5.58	−6.51	+3.25	+0.84	
BrF_2Cl	$^1/_2Br_2 + F_2 + {}^1/_2Cl_2$	−1.43	+8.20	−10.47	+3.48	−0.22	
I_4	$2I_2$	−1.38	+3.15	−2.50	+3.13	+2.40	
$\frac{1}{2}Cl_2F_6$	$^1/_2Cl_2 + {}^3/_2F_2$	−2.74	+7.45	−9.26	+5.50	+0.95	

TABLE VII

ENERGIES CALCULATED FOR TRIHALIDE IONS

	Ref state	$2\Sigma P_{\mu\nu}\beta$	ΣE_A	$\Sigma Q_A Q_B/R_{AB}$	E_R	E(tot)
$\mathrm{(FFF)^-}$	$\mathrm{F_2 + F^-}$	−1.63	−3.67	+1.29	+2.92	−1.09
$\mathrm{(FClF)^-}$	$\mathrm{ClF + F^-}$	−1.71	−2.88	+0.61	+2.89	−1.08
$\mathrm{(FBrF)^-}$	$\mathrm{BrF + F^-}$	−1.74	−2.70	+0.51	+2.92	−1.01
$\mathrm{(FIF)^-}$	$\mathrm{IF + F^-}$	−1.80	−2.51	+0.45	+2.95	−0.92
$\mathrm{(ClIF)^-}$	$\mathrm{ICl + F^-}$	−1.60	−2.31	+0.13	+2.89	−0.89
$\mathrm{(ClBrF)^-}$	$\mathrm{BrCl + F^-}$	−1.60	−2.47	+0.31	+2.89	−0.87
$\mathrm{(ClClF)^-}$	$\mathrm{Cl_2 + F^-}$	−1.61	−2.63	+0.53	+2.89	−0.82
$\mathrm{(BrIF)^-}$	$\mathrm{IBr + F^-}$	−1.57	−2.19	+0.16	+2.87	−0.75
$\mathrm{(BrBrF)^-}$	$\mathrm{Br_2 + F^-}$	−1.60	−2.35	+0.40	+2.89	−0.67
$\mathrm{(BrClF)^-}$	$\mathrm{BrCl + F^-}$	−1.65	−2.51	+0.68	+2.89	−0.58
$\mathrm{(IIF)^-}$	$\mathrm{I_2 + F^-}$	−1.58	−2.05	+0.25	+2.87	−0.52
$\mathrm{(ClFF)^-}$	$\mathrm{ClF + F^-}$	−1.75	−3.28	+1.65	+2.92	−0.47
$\mathrm{(IBrF)^-}$	$\mathrm{IBr + F^-}$	−1.64	−2.19	+0.56	+2.92	−0.36
$\mathrm{(ClFCl)^-}$	$\mathrm{Cl_2 + F^-}$	−1.60	−2.90	+1.38	+2.89	−0.23
$\mathrm{(IClF)^-}$	$\mathrm{ICl + F^-}$	−1.71	−2.35	+0.91	+2.95	−0.20
$\mathrm{(BrFF)^-}$	$\mathrm{BrF + F^-}$	−1.81	−3.13	+1.87	+2.95	−0.12
$\mathrm{(BrFCl)^-}$	$\mathrm{BrCl + F^-}$	−1.60	−2.77	+1.46	+2.87	−0.04
$\mathrm{(BrFBr)^-}$	$\mathrm{Br_2 + F^-}$	−1.55	−2.67	+1.48	+2.87	+0.12
$\mathrm{(IFF)^-}$	$\mathrm{IF + F^-}$	−1.90	−2.89	+2.11	+2.97	+0.28
$\mathrm{(IFCl)^-}$	$\mathrm{ICl + F^-}$	−1.63	−2.61	+1.60	+2.95	+0.31
$\mathrm{(IFBr)^-}$	$\mathrm{IBr + F^-}$	−1.54	−2.51	+1.54	+2.87	+0.35
$\mathrm{(IFI)^-}$	$\mathrm{IF + F^-}$	−1.48	−2.40	+1.51	+2.87	+0.51
*$\mathrm{(ClICl)^-}$	$\mathrm{ICl + Cl^-}$	−1.65	−1.87	+0.32	+2.89	−0.31
$\mathrm{(ClClCl)^-}$	$\mathrm{Cl_2 + Cl^-}$	−1.63	−2.25	+0.73	+2.87	−0.28
$\mathrm{(ClBrCl)^-}$	$\mathrm{ClBr + Cl^-}$	−1.64	−2.07	+0.52	+2.92	−0.28
*$\mathrm{(BrICl)^-}$	$\mathrm{IBr + Cl^-}$	−1.61	−1.75	+0.33	+2.89	−0.15
$\mathrm{(BrBrCl)^-}$	$\mathrm{Br_2 + Cl^-}$	−1.63	−1.95	+0.58	+2.95	−0.04
$\mathrm{(BrClCl)^-}$	$\mathrm{BrCl + Cl^-}$	−1.65	−2.12	+0.85	+2.95	+0.02
$\mathrm{(IICl)^-}$	$\mathrm{I_2 + Cl^-}$	−1.61	−1.60	+0.40	+2.95	+0.14
$\mathrm{(BrClBr)^-}$	$\mathrm{Br_2 + Cl^-}$	−1.63	−2.01	+0.90	+2.92	+0.18
$\mathrm{(IBrCl)^-}$	$\mathrm{IBr + Cl^-}$	−1.65	−1.79	+0.71	+2.92	+0.20
$\mathrm{(IClCl)^-}$	$\mathrm{ICl + Cl^-}$	−1.70	−1.95	+1.04	+2.95	+0.34
$\mathrm{(IClBr)^-}$	$\mathrm{IBr + Cl^-}$	−1.63	−1.84	+1.01	+2.92	+0.45
$\mathrm{(IClI)^-}$	$\mathrm{I_2 + Cl^-}$	−1.59	−1.71	+1.03	+2.87	+0.60
$\mathrm{(BrIBr)^-}$	$\mathrm{IBr + Br^-}$	−1.63	−1.84	+0.44	+2.92	−0.12
$\mathrm{(BrBrBr)^-}$	$\mathrm{Br_2 + Br^-}$	−1.63	−2.06	+0.68	+2.92	−0.09
*$\mathrm{(IIBr)^-}$	$\mathrm{I_2 + Br^-}$	−1.62	−1.69	+0.50	+2.92	+0.10
$\mathrm{(IBrBr)^-}$	$\mathrm{IBr + Br^-}$	−1.65	−1.88	+0.80	+2.92	+0.18
$\mathrm{(IBrI)^-}$	$\mathrm{I_2 + Br^-}$	−1.62	−1.74	+0.83	+2.92	+0.39
$\mathrm{(III)^-}$	$\mathrm{I_2 + I^-}$	−1.63	−1.78	+0.59	+2.92	+0.09

energy and that the covalent bond energy is often less favorable than in the elements. The calculated energies of formation are qualitatively in agreement with the experimental ones, only for I_2Cl_6 a positive energy of formation is found. This compound is the only interhalogen that does not exist in a gaseous state; the low energy in the solid state may be a consequence of intermolecular interactions, which are not taken into account in the calculated energy.

The four hypothetical complexes at the bottom of Table VI have a positive energy of formation except BrF_2Cl which has a lower energy than the elements. Calculation shows, however, that an energy of 0.89 eV is gained in the reaction

$$3BrF_2Cl \rightarrow 2BrF_3 + BrCl + Cl_2$$

which probably explains the nonexistence of this complex.

Trihalides.—The calculated energy values are shown in Table VII. It should be realized that the energies of formation in Table VII relate to the trihalide ion and the reference state *both in the free state.* Actually the systems can only be studied in solution or in crystals. Both the trihalide ion and the ion of the reference state are stabilized by solvatation or lattice energy, the ion

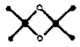
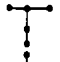
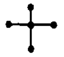
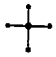
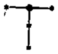
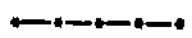
TABLE VIII

SPECTRA OF TRIHALIDE IONS

	$h\nu$ calcd	$h\nu$ exptl
$\mathrm{(I{-}I{-}I)^-}$	3.86	3.86
*$\mathrm{(I{-}I{-}Br)^-}$	4.01	4.01
$\mathrm{(I{-}Br{-}I)^-}$	3.69	
*$\mathrm{(Br{-}I{-}Br)^-}$	4.11	4.13
$\mathrm{(I{-}Br{-}Br)^-}$	3.80	
*$\mathrm{(Br{-}I{-}Cl)^-}$	4.21	4.39
$\mathrm{(I{-}Br{-}Cl)^-}$	3.89	
$\mathrm{(I{-}Cl{-}Br)^-}$	3.64	
*$\mathrm{(Cl{-}I{-}Cl)^-}$	4.30	4.61
$\mathrm{(I{-}Cl{-}Cl)^-}$	3.73	

TABLE IX

ENERGY OF ALTERNATIVE CONFORMATIONS

	Ref state	$2\Sigma P_{\mu\nu}\beta$	ΣE_A	$\Sigma Q_A Q_B/R_{AB}$	E_R	E(tot)
$\overset{\bullet}{I}_2\overset{\circ}{Br}_2\overset{*}{Cl}_4$	$I_2 + Br_2 + 2Cl_2$					
		−2.80	+4.68	−5.68	+5.86	+2.06
		−3.02	+4.51	−5.36	+6.09	+2.22
		−3.01	+2.93	−2.72	+5.84	+3.04
I_3^-	$I_2 + I^-$					
		−1.63	−1.78	+0.59	+2.92	+0.09
		+1.44	−2.09	+1.02	+1.41	+1.78
ICl_2^+	$I^+ + Cl_2$					
		−1.41	−0.76	+1.34	+2.82	+1.99
		−6.23	+0.82	−0.88	+4.18	−2.11
I_5^-	$2I_2 + I^-$					
		−3.15	−2.33	+0.67	+5.69	+0.90
		−3.15	−1.26	−0.33	+5.74	+1.01
		−3.20	+2.05	−3.65	+5.84	+1.06
		−2.58	−2.38	+0.65	+5.39	+1.10
ICl_4^-	$ICl + Cl_2 + Cl^-$					
		−3.21	+4.67	−8.47	+5.76	−1.25
		−3.27	−1.00	−1.51	+5.81	+0.04
		−2.58	−2.71	+0.48	+5.36	+0.56
		−3.28	−2.88	+1.12	+5.81	+0.77

of the reference state probably most, because of its smaller dimension. A reference state involving F^- will be stabilized more than one involving Cl^-, Br^-, or I^-. Since the solvatation or lattice energies can have values of some eV, the energy of formation in solution or crystals may differ appreciately from the values calculated for the free ions. The *relative* values inside a group in which the reference state contains the *same anion* will, however, be reasonably reliable.

In the group with F^- in the reference state most of the calculated energies of formation are negative. According to the comment just made, this does not necessarily mean that the energy of formation in solution is also negative because in solution the reference state will be more stabilized than the trihalide ion. It is remarkable that only one trihalide containing F is described in the literature, namely, CsIBrF.[30] Table VII shows that if this complex really exists as a trihalide, the conformation of the anion would be $(BrIF)^-$. Moreover all trihalides above $(BrIF)^-$ in the table would probably also be stable. Ions like F_3^- have never been found, therefore it is likely that the compound CsBrIF does not exist or is built up from Cs^+F^- and IBr.

As to the other trihalides it may be remarked that the experimentally observed order of the atoms in ICl_2^-, $(BrICl)^-$, and I_2Br (marked by *) has the lowest calculated total energy and that this is due to the favorable electrostatic energy.

Spectra of the Trihalides.—In Table VIII the calculated energy difference (in eV) between the lowest unoccupied MO and the highest occupied MO is compared with the energy corresponding to the experimentally determined absorption band in solution.[31] The agreement is satisfactory; in case of alternative conformations the best agreement is obtained for the conformation (*) which is actually realized in nature.

Energy of Alternative Conformations.—Some examples of energy calculations for alternative conformations of a polyhalogen complex are listed in Table IX. In all cases the experimentally observed conformation is calculated to have the lowest energy; asymmetric $I_2Br_2Cl_4$; linear I_3^-, on the other hand angular ICl_2^+; L-shaped I_5^-, on the other hand square ICl_4^-.

4. Conclusion

It is surprising that a simple molecular orbital theory like the one described is able to account for almost all available experimental data on charges, bond lengths, stabilities, conformations, and spectra in the extensive

---

[30] H. W. Cremer and D. R. Duncan, *J. Chem. Soc.*, 1857 (1931).

[31] A. I. Popov and R. F. Swensen, *J. Am. Chem. Soc.*, **77**, 3724 (1955).

field of polyhalogen complexes. Tentative calculations have shown that this theory may also be successful in other fields, for instance that of the inert gas compounds.

Acknowledgments.—We wish to thank Dr. M. P. Bogaard for the nqr data he made available to us and Miss A. Migchelsen for permission to use the results of her calculations on some trihalide ions. E. H. W. is very much indebted to Professor C. A. Coulson for the hospitality he enjoyed in the Mathematical Institute in Oxford where our calculations were performed in a preliminary form.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CORNELL UNIVERSITY, ITHACA, NEW YORK 14850

Raman Spectroscopic Study of Stepwise Bromide and Chloride Complexes of Indium(III) in Aqueous Solution[1]

BY MERVIN P. HANSON AND ROBERT A. PLANE

Received October 18, 1968

From measured Raman frequencies and intensities in aqueous indium bromide solutions, three complexes were detected. These were indicated to be $InBr^{2+}$, $InBr_2^+$, and $InBr_3$. That no anionic complexes were present was confirmed by the lack of anionic migration, which however was found for the corresponding chloride system. Three complexes were also detected in the chloride system, which were indicated to be $InCl^{2+}$, $InCl_2^+$, and $InCl_4^-$. However, the last of these is not the tetrahedral ion known to exist in ether and nonaqueous solvents. Raman experiments in methanol–water mixtures suggest that, in the presence of water, $InCl_4^-$ coordinates water molecules. This behavior accounts for both the Raman results and the relatively poor extractability of $InCl_4^-$ from water. In addition, absolute Raman intensities are given and discussed for $InCl_4^-$ and $InBr_4^-$ in nonaqueous solvents, and equilibrium quotients are determined for stepwise complex formation in water.

For Raman studies of the halide complexes in solution of various metal ions, indium occupies an interesting position. It lies intermediate between gallium which has been shown by Raman studies to form only the tetrachloro[2] and tetrabromo[3] complexes in aqueous solution and just above thallium which has been shown by Raman studies to form a stepwise series of complexes.[4] In attempting to understand the factors responsible for the different behavior of Ga and Tl, it seems worthwhile to conduct a similar study on the indium halides. An additional motivation for the work is the problem of the apparent uniqueness of indium(III) chlorides in extraction studies. It has been found that the distribution coefficients for indium are abnormally low both in anion exchange[5] and solvent extraction.[6,7] Woodward and Taylor[8] have observed from Raman spectra that $InCl_4^-$ is not present in aqueous solution and have postulated that it is likely that the solutions contain instead anionic chloro complexes containing more than four chlorides per indium. However, Maydan and Marcus[9] noted that anion-exchange results are adequately described without including the penta- or hexachloride complexes. Thus a more detailed Raman study seems in order—one which differs from the earlier study in that Raman intensities as a function of concentration are photoelectrically measured. In addition, from measured Raman intensities it is possible to draw inferences concerning the nature of chemical bonding in complex ions,[10] and in the present study the Raman intensities will be measured in both aqueous and nonaqueous solvents.

Experimental Section

Chemicals used in this study were of analytical reagent grade. The indium stock solutions were prepared by dissolving metallic indium in perchloric acid to which was added a piece of platinum foil to speed the dissolution. The indium concentration was determined gravimetrically by precipitation with 8-hydroxyquinoline.[11] Solutions of $InCl_4^-$ in diethyl ether were prepared by dissolving indium metal in concentrated HCl, saturating the resultant solution with HCl gas, and extracting with diethyl ether.[8]

---

[1] Supported by a research grant from the Office of Saline Waters, U. S. Department of the Interior. From the Ph.D. thesis of M. P. Hanson, Cornell University, 1966.

[2] T. F. Young, L. F. Maranville, and H. M. Smith, "The Structure of Electrolytic Solutions," W. J. Hamer, Ed., John Wiley & Sons, Inc., New York, N. Y., 1959, pp 60, 61.

[3] J. Nixon and R. A. Plane, *J. Am. Chem. Soc.*, **84,** 4445 (1962).

[4] T. G. Spiro, *Inorg. Chem.*, **4,** 731 (1965).

[5] K. A. Kraus, F. Nelson, and G. W. Smith, *J. Phys. Chem.*, **58,** 11 (1954).

[6] R. M. Diamond, *ibid.*, **61,** 1522 (1957).

[7] H. Irving and F. J. C. Rossotti, *J. Chem. Soc.*, 1946 (1955).

[8] L. A. Woodward and M. J. Taylor, *ibid.*, 4473 (1960).

[9] D. Maydan and Y. Marcus, *J. Phys. Chem.*, **67,** 987 (1963).

[10] T. V. Long, II, and R. A. Plane, *J. Chem. Phys.*, **43,** 457 (1965).

[11] I. M. Kolthoff and P. J. Elving, "Treatise on Analytical Chemistry," Part II, Vol. 2, Interscience Publishers, New York, N. Y., 1962, p 89.