for $P(i\text{-}Bu)_3$ (143°) and $P(OMe)_3$ (107°) appear to systematically underestimate their sizes. The values of (150 ± 2)° and (115 ± 2)°, respectively, place the points for these two ligands on the line in Figure 5. Additional work is in progress to more clearly define the role of ligand steric properties in radical reactions.

Inspection of Table III shows that the electronic parameters for the halogen atom transfer reactions are all quite similar. The corresponding value of *a* for chlorine atom transfer to $Mn(CO)_4L\cdot$ radicals, 0.82, is considerably smaller than for the Re radicals. A smaller value for *a* indicates a lower sensitivity of the reaction to varitions in electron density at the metal. The value of *a* for hydrogen atom transfer to the Re radicals is also smaller than for the halogen atom transfer reactions. This is the expected result; the transition state for hydrogen atom transfer should be less electron-demanding of the metal than for halogen atom transfer.

The steric parameter for halogen atom transfer to $Re(CO)_4L\cdot$ radicals is larger for bromine than for chlorine, as expected. The comparatively large value of *b* for hydrogen atom transfer may reflect the small covalent radius of hydrogen, which requires close approach in the atom transfer step.

The kinetics data for the atom transfer processes studied here do not in themselves reveal the degree of electron-transfer character in the rate-determining process. Both halogen and hydrogen atom transfers are quite fast, even though the transition states in the two cases should differ markedly in polarity. There is evidence in the comparative values for *a* that the transition state for halogen atom transfer is more electron-demanding, but more work is needed to establish whether there is a regular relationship between the rate constant for halogen atom transfer and electron-acceptor ability of the halogen atom donor.

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Registry No. $Re(CO)_5$, 15684-00-1; $Re(CO)_4P(OMe)_3$, 101697-74-9; $Re(CO)_4P(i\text{-}Pr)_3$, 101697-75-0; $Re(CO)_4AsEt_3$, 101697-73-8; $Re(CO)_4PMe_3$, 101697-76-1; $Re(CO)_4P(n\text{-}Bu)_3$, 101697-77-2; $Re(CO)_4P(i\text{-}Bu)_3$, 101697-78-3; $Re(CO)_4PCy_3$, 101697-79-4; CH_2Br_2, 74-95-3; $CHCl_3$, 67-66-3; CCl_4, 56-23-5; $HSn(n\text{-}Bu)_3$, 688-73-3; Br_2, 7726-95-6; Cl_2, 7782-50-5; H_2, 1333-74-0.

Contribution from the Department of Chemistry,
Arizona State University, Tempe, Arizona 85287

The "Inert-Pair Effect" on Electronegativity

R. T. Sanderson[†]

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The quantitative theory of polar covalence has been used to calculate the electronegativity of major group metals in oxidation states lower than their maximum, from experimental bond energies. Presumably by reducing the effective nuclear charge, lone-pair electrons significantly reduce the electronegativity. For example, the value on the relative compactness scale for thallium(I) is only 0.99 compared to 2.25 for thallium (III); for lead(II) it is 1.92 compared to 2.29 for lead(IV). This causes bond polarity to be higher than otherwise expected in compounds exhibiting the lower oxidation states, which in turn accounts for increased stability and other commonly observed differences in physical and chemical properties. Bond energies calculated by using the new electronegativities agree with the experimental values within an average of less than 2% for 55 gaseous compounds of major group elements in lower oxidation states.

The "inert-pair effect" long familiar to inorganic chemists is a term to designate the phenomenon in which certain of the heavier major group metals exhibit a valence less by 2 than expected from their electronic configuration and corresponding periodic grouping. In a general way it has been explained by Pitzer[1] and by Pykko and Descalux[2] as a relativistic effect causing the outer s electrons to be more strongly attracted to the nucleus than normally expected. For many years it has been suspected that the compounds resulting from the inert-pair effect have more polar bonds than might be expected from merely a reduction in valence.[3] However, in a recent revision of electronegativities of the major group elements[4] based on the relative compactness of the electronic clouds of their atoms, values for lower oxidation states were omitted because of lack of quantitative knowledge of the inert-pair effect. The purpose of this paper is to describe an attempt to evaluate these additional electronegativities, using the quantitative theory of polar covalence as a basis for back-calculating the electronegativity values from experimental heats of formation and atomization energies.

Method of Calculation

According to the quantitative theory of polar covalence,[5] a polar covalent bond derives its energy from two contributions, one covalent and the other ionic. The covalent contribution is simply a portion of the maximum possible covalent energy, E_c, which is the geometric mean of the two homonuclear bond energies, E_{AA} and E_{BB}, corrected for any difference between the actual bond length, R_0, and the nonpolar covalent radius sum, R_c ($=r_A + r_B$), by the factor, R_c/R_0:

$$E_c = R_c(E_{AA}E_{BB})^{1/2}/R_0$$

Table I. Effects of Inert-Pair and Single Electrons on Electronegativities of M2, M3, and M4 Elements in Various Oxidation States[a]

element	oxidn state (from a number of examples) I	II	III	IV
Be	1.56 (3)	**1.81**		
Ca	1.13 (2)	**0.95**		
B	1.53 (3)	2.19 (2)	**2.28**	
Al	0.84 (4)	1.63 (2)	**1.71**	
Ga	0.86 (4)		**2.42**	
In	0.71 (3)		**2.14**	
Tl	0.99 (3)		**2.25**	
Si	2.08 (2)		1.99 (2)	**2.14**
Ge		0.56 (4)		**2.62**
Sn		1.49 (3)		**2.30**
Pb		1.92 (4)		**2.29**

[a] Boldface numerals are electronegativities for the usual oxidation states.

The maximum ionic energy, E_i, is assumed to be the Coulombic attraction between unit opposite charges separated by the bond length:

$$E_i = 33200/R_0$$

The factor 33 200 converts the energy to kilocalories per mole and must of course be multiplied by the factor 4.184 to be converted to kilojoules per mole, both assuming distance to be measured in picometers. The two energies are apportioned according to the partial charges. The ionic blending coefficient, t_i, is half the difference between the two partial

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[†] Present address: 4725 Player Drive, Fort Collins, CO 80525.

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Table II. Bond Energies Calculated from Electronegativities of Lower Oxidation States

compd (gaseous)	bond	$-\delta_X$	R_c, pm	R_0, pm	E_c, kcal/mol	E_i, kcal/mol	E_{calcd}, kcal/mol	E_{exptl}, kcal/mol
BF	B—F‴	0.486	150.3	126.2	56.8	127.9	184.7	183
BCl	B—Cl‴	0.399	181.6	171.6	47.0	77.3	124.3	129
BBr	B—Br‴	0.355	196.4	188.7	44.7	62.4	107.1	104.5
BI	B—I‴	0.274	215.5	208	43.5	43.7	87.2	67.8
	B—I′	0.274	215.5	208	39.4	43.7	83.1	67.8
BF_2	B—F‴	0.218	150.3	130	72.1	83.8	155.9	156.3
BCl_2	B—Cl‴	0.156	181.6	173	59.3	45.1	104.4	105.4
BBr_2	B—Br‴	0.125	196.4	187	56.9	33.2	90.1	86.1
BI_2	B—I‴	0.068	215.5	206	54.2	16.6	70.8	52.8
	B—I′	0.068	215.5	206	49.2	16.6	65.8	52.8
BFCl	B—F‴	0.267	150.3	130	72.9	82.0	154.9	
	B—Cl‴	0.107	181.6	173	58.9	46.2	105.1	
	total						260.0	256.7
BFBr	B—F‴	0.292	150.3	130	73.4	80.7	154.1	
	B—Br‴	0.048	196.4	187	56.4	34.4	90.8	
	total						244.9	236.9
BClBr	B—Cl‴	0.182	181.6	173	59.6	44.5	104.1	
	B—Br‴	0.099	196.4	187	56.7	33.7	90.4	
	total						194.5	192
AlF	Al—F‴	0.690	193.9	165	26.8	138.5	165.3	161.1
AlCl	Al—Cl‴	0.604	225.2	213	24.6	94.1	118.7	118
AlBr	Al—Br‴	0.559	240.0	230	24.4	80.7	105.1	106
AlI	Al—I‴	0.478	259.1	253.7	24.5	62.5	87.0	87.2
Al_2O	Al—O′	0.761	196.0	172	19.7	110.2	129.9	124.2
AlF_2	Al—F‴	0.329	193.9	165	43.9	99.4	143.3	141.1
$AlCl_2$	Al—Cl‴	0.265	225.2	212	37.7	62.2	99.9	102
AlClF	Al—F‴	0.373	193.9	163	45.4	98.4	143.8	
	Al—Cl‴	0.220	225.2	214	36.7	63.1	99.8	
	total						243.6	246.7
AlO	Al—O″	0.404	196.0	162	41.5	82.8	124.2	119.3
GaF	Ga—F‴	0.683	193.7	177.4	23.4	127.8	151.2	144.5
GaCl	Ga—Cl‴	0.597	225.0	220.2	22.2	90.0	112.2	113.5
GaBr	Ga—Br‴	0.552	239.8	235	22.2	78.0	100.2	104.0
GaI	Ga—I‴	0.471	258.9	257.5	22.4	68.7	83.1	84
InF	In—F‴	0.737	213.6	198.5	17.3	123.3	140.6	125.7
InCl	In—Cl‴	0.651	244.9	240.1	17.4	90.0	107.3	105.2
InBr	In—Br‴	0.606	259.7	254.1	17.7	79.2	96.9	98.5
InI	In—I‴	0.525	278.8	275.4	18.3	63.3	81.6	81.9
TlF	Tl—F‴	0.640	217.1	208.4	16.2	102.0	118.2	109.9
TlCl	Tl—Cl‴	0.554	248.4	248.5	15.4	74.0	89.4	88.8
TlBr	Tl—Br‴	0.509	263.2	261.8	15.4	64.5	79.9	79.3
TlI	Tl—I‴	0.428	282.3	281.4	15.5	50.5	66.0	64.5
SiF	Si—F‴	0.355	185.0	160.3	58.2	73.6	131.8	131.5
SiCl	Si—Cl‴	0.269	216.3	206	47.8	43.3	91.1	91.3
SiF_3	Si—F‴	0.204	185.0	156	54.9	86.8	141.7	141.4
$SiCl_3$	Si—Cl‴	0.155	216.3	202	46.1	50.8	96.9	97.0
GeO	Ge—O″	0.724	192.5	162.5	18.1	148.0	166.1	156.3
GeS	Ge—S″	0.602	227.2	201.2	23.4	99.3	127.7	131.7
GeSe	Ge—Se″	0.612	239.0	213.5	19.7	95.2	114.9	117 ± 5
GeTe	Ge—Te″	0.537	258.3	234	21.4	76.2	97.6	96
SnF_2	Sn—F‴	0.357	210.1	206	30.1	86.4	116.5	108.9
$SnCl_2$	Sn—Cl‴	0.292	241.4	242	28.4	60.1	88.5	90.1
$SnBr_2$	Sn—Br‴	0.259	256.2	255	28.1	50.5	78.6	78.9
SnI_2	Sn—I‴	0.199	275.3	278	27.5	35.7	63.2	61.8
SnS	Sn—S‴	0.318	246.9	220.9	37.0	47.8	84.8	
	Sn═S‴	0.318	246.9	220.9	55.1	71.1	126.2	
	av						105.5	109.7
PbF_2	Pb—F‴	0.277	216.1	213	31.1	64.7	95.8	93.9
$PbCl_2$	Pb—Cl‴	0.213	247.4	246	28.5	43.1	71.6	73.1
$PbBr_2$	Pb—Br‴	0.181	262.2	260	27.6	34.6	62.2	62.2
PbI_2	Pb—I‴	0.123	281.3	280	26.8	21.8	48.6	49.0
PbO	Pb—O″	0.335	218.2	192.2	30.8	57.9	88.7	89.5
PbS	Pb—S‴	0.213	252.9	228.7	34.7	30.9	65.6	
	Pb═S‴	0.213	252.9	228.7	51.6	46.0	97.6	
	av						81.6	82.7
BeF	Be—F′	0.478	156.8	136	31.3	116.8	148.1	146.1
BeCl	Be—Cl′	0.392	188.1	175	40.7	74.3	115.0	92
BeBr	Be—Br′	0.347	202.9	197	37.4	58.5	95.9	95.4
BeI	Be—I′	0.266	222.0	219	36.6	40.3	76.9	78.3
CaF	Ca—F‴	0.597	242.1	201	28.7	98.6	127.3	126.5
CaCl	Ca—Cl‴	0.510	273.4	244	25.8	69.4	95.2	95.8

charges and the covalent blending coeficient, t_c, is $1 - t_i$. The partial charges are calculated from the principle of electronegativity equalization[6] and the postulate that the molecular electronegativity is the geometric mean of all the individual atomic electronegativities. The total bond energy of the actual polar covalent bond is

$$E = t_c E_c + t_i E_i$$

The basic data needed for calculating the bond energy are the atomic electronegativities, the homonuclear bond energies, the nonpolar covalent radii, and the experimental bond length. It follows that if the experimental bond energy is known, any one of the other quantities can be determined by reversing the usual bond energy calculation. This can best be clarified by an example.

The experimental bond energy of GaCl(g) is 113.5 kcal/mol, and the experimental bond length is 220.2 pm. Practically all gaseous metal halide molecules appear to involve the unweakened bond energy of the halogen, so the homonuclear bond energy of 71.8 kcal for chlorine is used instead of the usual lone-pair-weakened value of 58 kcal. It is assumed that the homonuclear bond energy of gallium remains constant at 40.3 kcal and the nonpolar covalent radius at 125.6 pm. The maximum possible ionic energy is simply

$$33200/220.2 = 150.8\ \text{kcal/mol}$$

The maximum possible covalent energy is

$$225.0(40.3 \times 71.8)^{1/2}/220.2 = 55.0\ \text{kcal/mol}$$

The experimental bond energy is then the weighted sum of these two energies:

$$113.5 = 150.8t_i + 55.0t_i \qquad t_i = 0.611$$

Since GaCl is a diatomic molecule, this coefficient is the same as the partial charge on Ga, which is the negative of the partial charge on Cl. The partial charge is defined as the ratio of the change in electronegativity undergone by the atom in forming the compound to the change it would have undergone had it acquired unit charge. The latter change is 1.57 times the square root of the atomic electronegativity. For chlorine, the electronegativity is 3.475 and the change corresponding to acquisition of one electron is 2.927. The partial charge on Cl, −0.611, is

$$-0.611 = (S_m - 3.475)/2.972 \qquad S_m = 1.688$$

But S_m, the molecular electronegativity of GaCl, is also the geometric mean of the two electronegativities:

$$S_m = (3.475S_{Ga(I)})^{1/2} \qquad S_{Ga(I)} = 0.820$$

Similar calculations for GaF, GaBr, and GaI, all gaseous molecules, gave values of $S_{Ga(I)}$, the electronegativity of Ga(I), of 1.040, 0.743, and 0.829, or an average for the four compounds of 0.86. When this value is used to calculate the bond energies, the following calculated (experimental) values (kcal) result: GaF, 151.2 (144.5); GaCl, 112.2 (113.5); GaBr, 100.2 (104.0); GaI, 83.1 (84). Although these lack the precision of the usual polar bond energy calculation, they seem good enough to be acceptable evidence that the electronegativity of gallium(I) is indeed approximately 0.86, provided all basic assumptions are correct. This is to be compared with the electronegativity of gallium(III), which is 2.42. This indicates a substantial reduction accompanying the presence of the inert pair of electrons.

Results and Discussion

Similar calculations were carried out for other M2, M3, and M4 elements in lower oxidation states, with results summarized in Table I. The basic data were taken largely from standard sources.[7-9] Unfortunately, experimental difficulties in obtaining accurate bond lengths and heats of formation for many of these gaseous molecules have resulted in frequent discrepancies and

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omissions in the literature. When different valus of the same property were reasonably close, they were averaged. Otherwise a selection was based, if possible, on similar data for similar molecules. For these reasons, the values of Table I must be regarded as approximate, but probably accurate enough to reveal the general effects being studied.

In order to demonstrate the validity of this statement, the bond energies or atomization energies of all gaseous molecules of compounds of these elements in these lower oxidation states for which basic data could be found were calculated according to the theory of polar covalence. This is of course a somewhat circular procedure in that experimental bond energies were used to evaluate the electronegativities. However, there are additional compounds in the table, and in any event, the data are shown to be reasonably self-consistent. Where basic data are accurately known, the theory of polar covalence appears capable of producing calculated bond energies within about 1% of the experimental values. From this viewpoint, the agreement in Table II is not ideally satisfactory. However, if four of the compounds wherein the difference exceeds 10% are omitted, the average difference for the remaining 55 compounds is less than 2.0%. It must be recognized, furthermore, that a difference between calculated and experimental bond energy here may indicate experimental difficulty rather than inadequacy in the method of calculation.

Remember that these electronegativity values are based on the assumption that the inert pair affects only the electronegativity, the homonuclear bond energy and radius remaining unchanged from those of the atom in its maximum oxidation state. This assumption may not be exactly true. When the bond energies for the lower oxidation states were calculated by using the electronegativity corresponding to the highest state, in every example the calculated value was substantially smaller than the experimental value. Assuming no very significant change in nonpolar covalent radius, the larger bond energy in the lower oxidation state must signify either a greatly increased homonuclear bond energy of the metal or a decreased electronegativity. There seems to be no way by which the inert pair could possibly cause an increase in homonuclear energy, assuming its principal effect to be reduction of the effective nuclear charge, on which the homonuclear bond energy largely depends. On the other hand, by nuclear screening, the inert pair could easily reduce the electronegativity, thus causing the bond to be more polar and correspondingly stronger.

The question remaining is whether the homonuclear bond energy might also be reduced, making necessary a still larger decrease in electronegativity to compensate by larger ionic energy for a reduced covalent energy. However, since the homonuclear energy is only one of several factors determining the bond energy and since most of the compounds under study are fairly or highly polar, diminishing the importance of the covalent contribution, it seems reasonable to suppose that the principal effect of the inert pair, aside from its effects both in the molecule and in the solid state, is to reduce the electronegativity. In every example in Table I, this is indeed the result, as reinforced by the data of Table II. The lone-pair effect on electronegativity becomes less as the atomic number within a group increases. The differences in electronegativity between oxidation states III and I are as follows: Ga, 1.56; In, 1.43; Tl, 1.26. The differences between oxidation states IV and II are as follows: Ge, 2.02; Sn, 0.81; Pb, 0.37. In the halides, the partial charges in the lower oxidation states are usually more than doubled as a result of the reduction in electronegativity.

As a consequence of this increase in bond polarity, thallium(I) halides resemble the alkali-metal halides, as thallium hydroxide, TlOH, resembles the alkali-metal hydroxides. Similarly, lead(II) compounds are much more polar and more stable than inorganic lead(IV) compounds. In general, the nuclear screening by inert-pair electrons, largely by reducing the electronegativity, accounts for the notable differences between lower and higher oxidation states.

Registry No. Be, 7440-41-7; Ca, 7440-70-2; B, 7440-42-8; Al, 7429-90-5; Ga, 7440-55-3; In, 7440-74-6; Tl, 7440-28-0; Si, 7440-21-3; Ge, 7440-56-4; Sn, 7440-31-5; Pb, 7439-92-1.

Contribution from the Department of Chemistry,
State University of New York at Stony Brook, Stony Brook, New York 11794

Reduction of Nitric Oxide by Hydroxylamine. 1. Kinetics and Mechanism[1]

Francis T. Bonner* and Nun-Yii Wang

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The reaction of nitric oxide with hydroxylamine conforms to the rate law $-\mathrm{d}P_{\mathrm{NO}}/\mathrm{d}t = k_2[\mathrm{NH_2O^-}]P_{\mathrm{NO}}$ in the pH range 7.29–13.14, confirming the rate-determining abstraction of an N-bound H atom by NO. Measured kinetic quantities: $k_2 = 6.68 \times 10^{-3}$ M^{-1} s^{-1} at 25 °C; $\Delta H^* = 29.6$ kJ mol^{-1}; $\Delta S^* = -189$ J K^{-1} mol^{-1}. Thermodynamic values have been obtained for the pK_a of NH_2OH at several temperatures; ΔH of dissociation = 55.29 kJ mol^{-1}. The presence of trace amounts of O_2 in the NO–NH_2OH reaction system catalyzes the reaction and leads to a reduced molar product ratio $n_{\mathrm{N_2}}/n_{\mathrm{N_2O}}$, effects that are ascribed at least in part to reactive N_2O_3. The difference in reactivity between the NO^- intermediate formed in this reaction and that produced in trioxodinitrate decomposition is discussed.

The reaction between nitric oxide and aqueous alkaline hydroxylamine, first noted by Benson et al.,[2] proceeds in 0.5 M NaOH solution according to the stoichiometry of eq 1.[3] Ni-

$$2\mathrm{NO} + 2\mathrm{NH_2OH} = \mathrm{N_2} + \mathrm{N_2O} + 3\mathrm{H_2O} \qquad (1)$$

trogen-15 tracer evidence shows that one atom of NO origin appears in each of the product molecules N_2 and N_2O at pH 13.[3,4] The product ratio $n_{\mathrm{N_2}}/n_{\mathrm{N_2O}}$ declines with decreasing pH, an effect tracer studies have shown to be caused by increasing competition between reduction (eq 4) and dimerization (eq 5) of the intermediate nitrosyl hydride (HNO) in the mechanism of eq 2–5.[4]

$$\mathrm{NO} + \mathrm{NH_2OH} \rightarrow \mathrm{HNO} + \mathrm{NHOH} \qquad (2)$$

$$\mathrm{NO} + \mathrm{NHOH} \rightarrow [\mathrm{ON{-}NHOH}] \rightarrow \mathrm{N_2O} + \mathrm{H_2O} \qquad (3)$$

$$\mathrm{HNO} + \mathrm{NH_2OH} \rightarrow \mathrm{N_2} + 2\mathrm{H_2O} \qquad (4)$$

$$\mathrm{HNO} + \mathrm{HNO} \rightarrow \mathrm{N_2O} + \mathrm{H_2O} \qquad (5)$$

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