[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Polarities of Covalent Bonds

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In a previous paper[1] the dipole moments of a large number of bonds have been assembled and examined in the light of Pauling's electronegativity scale based on the excess of observed bond energy values over the calculated values.[2] The present paper aims to present additional single bond values, which help to make effective a graphical comparison of bond moment values with electronegativities, and to examine revised and newly calculated double, triple and semi-polar bond moments.

Single Bond Moments and Electronegativities.—The approximate equation which Mulliken[3] has formulated for the moment of a bond A–B between atoms A and B may be combined with his empirical equation for the net charge on A or B to give the bond moment as

$$\mu_{\text{AB}} = \frac{er}{3}(P_{\text{A}} - P_{\text{B}}) - \frac{er}{48}(P_{\text{A}} - P_{\text{B}})^3 - 4ezab\ S + \mu_s$$

in which e is the electronic charge, r is the distance between the nuclei of A and B, P_{A} and P_{B} are the "absolute electroaffinities" on Pauling's electronegativity scale, z is the distance from the midpoint of the line A–B of the electric center of the moment given by the "homopolar dipole" term $4ezab\ S$, a, b and S are quantities connected with the two independent orbitals ϕ_{A} and ϕ_{B} by the equations $\phi_{\text{AB}} = a\phi_{\text{A}} + b\phi_{\text{B}}$ and $S = \int \phi_{\text{A}}\phi_{\text{B}}dv$, and μ_s is the secondary moment induced in the non-bonding electrons. As the value of e is 4.77×10^{-10} and the values of r lie, for the most part, between 1 and 2.8×10^{-8}, it is evident that the difference $P_{\text{A}} - P_{\text{B}}$ in the first term on the right of the equation will be multiplied by a factor lying between 1.6 and 4.5×10^{-18}. As the second term is small and quite negligible when $(P_{\text{A}} - P_{\text{B}}) < 0.9$, the bond moment cannot be numerically equal to $(P_{\text{A}} - P_{\text{B}}) \times 10^{-18}$ unless $\mu_s - 4ezab\ S = \left(1 - \frac{er}{3}\right)(P_{\text{A}} - P_{\text{B}})$. As there is no apparent reason why such a relation should exist except as a coincidence, it is surprising to find the values of the hydrogen bond moments $\times 10^{18}$ close to those of the "absolute electroaffinities."

The relation of the bond moments to the electroaffinities is shown in Fig. 1, in which the abscissas represent the electroaffinities referred to hydrogen as zero and the ordinates represent the moments $\times 10^{18}$. The point on the horizontal axis corresponding to the electroaffinity value of each element is marked with its symbol. A curve is obtained for each group of bonds in which the positive end of the dipole lies toward the element from which the curve starts on the horizontal axis. Identity of the bond moments with the differences in electronegativity would cause all the curves to be straight lines parallel to the dotted line of slope 1 drawn through the origin, which would contain the points for the hydrogen bonds. The H–P, the H–S and the H–N moments lie above the dotted line by amounts somewhat greater than their probable errors, but, with the exception of the H–C moment, which lies below the line by an amount no greater than its probable error, the hydrogen bond moments ($\times 10^{18}$) not only fall in the same order as the electronegativities but have little different numerical values. The electroaffinity places phosphorus much closer to hydrogen than does the

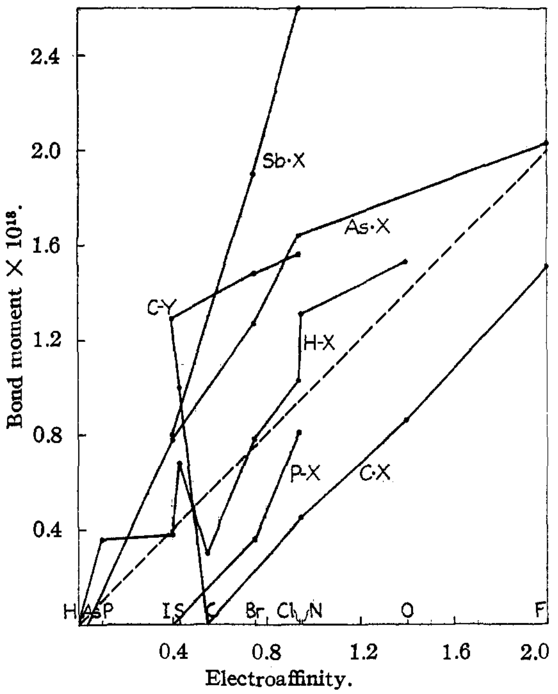

Fig. 1.

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[1] Smyth, *J. Phys. Chem.*, **41**, 209 (1937).

[2] Pauling, THIS JOURNAL, **54**, 3570 (1932).

[3] Mulliken, *J. Chem. Phys.*, **3**, 573 (1935).

bond moment, which makes phosphorus and iodine almost identical. This discrepancy causes the curve for the phosphorus bonds to coincide with the horizontal axis from P to I, after which it is not far from parallel to the H–X curve. As no electroaffinity values have been calculated for arsenic and antimony, the beginning of the arsenic bond curve is located between hydrogen and phosphorus on the horizontal axis where the bond moment would place it and the antimony curve is begun at the Sb–I point. The high moment values which raise the curves above the dotted line are to be attributed to the large polarizabilities of the arsenic and antimony atoms as previously discussed.[1,4]

The carbon bond moments fall into two groups showing such different behavior that they are represented by two curves, C–X and C–Y. The moments of the bonds C–X linking carbon to the small atoms, nitrogen, oxygen and fluorine, give a practically straight line parallel to the dotted line of slope 1 and below it by a distance 0.5 corresponding well with the electronegativity difference of the H–C bond. This evidence for an H–C moment value of 0.5, not far from the previously calculated 0.3, is weakened, if not invalidated, by the totally different behavior of the moments of the bonds C–Y linking carbon to the larger atoms, iodine, sulfur, bromine and chlorine.

The cause for the high values of these moments, which, in the cases of the C–I and C–S bonds, would be expected from the electronegativity curve to be almost negligibly small and actually acting in the opposite direction has been discussed in the case of the carbon–halogen moments by Mulliken,[5] who suggests very tentatively that it may lie primarily in the distribution of the *s* and *p* valences. It is probable also that, as previously concluded,[1] inductive effects may be sufficiently large to account for the seeming abnormality of the values. As calculations of these effects are now being carried out elsewhere, they will not be examined in detail here. It is apparent that, except for those on the C–Y curve, the bond moments plotted in Fig. 1, as well as a few discussed only in the previous paper, however variable because of the influence of their environment, have values roughly consistent with the electronegativities of the elements, the differences observed being readily explainable by differences in size and polarizability of the atoms. This rough consistency of the moment values with the electronegativity differences indicates that the previously calculated value 0.3 for the H–C moment, which differs from the electronegativity difference 0.55 by no more than its possible error, is approximately correct. It also seems probable that the electronegativity difference 2.0 for the H–F bond is close to the value of the H–F moment, which must accordingly be higher than indicated by previous considerations.[1]

New and Revised Results.—The bond moments listed in Table I have been calculated in the same way as those previously obtained.[1] Unless otherwise indicated, the molecular moments have been obtained from the appendix of Fuchs and Wolf's "Dielektrische Polarisation, Hand- und Jahrbuch der chemischen Physik," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1935, and from data in the references given therein. Similarly, the angles between bonds have been taken from the compilation by Brockway [*Rev. Modern Phys.*, **8**, 231 (1936)] or estimated by analogy. In the case of carbon bonds, methyl compounds have been used as far as possible in order to reduce or eliminate the effect of inductance or possible resonance upon the values. All of the carbon moment values are dependent upon the approximate value 0.3 used for the H–C bond. The uncertainty of this value affects the absolute values of the moments by an amount certainly no greater than the magnitude of the inductive effects.

TABLE I

BOND MOMENTS ($\times 10^{18}$)

C–N	0.45	(C=N	0.9)
		C≡N	3.6
		$N\overset{\rightarrow}{\equiv}C$	3.1
C–O	0.86	C=O	2.5
C–S	1.0	C=S	2.8
N–O	(0.3)	N=O	2.0
C–Se	.9	N→O	3.3
C–Te	.7	P→O	3.5
		P→S	2.4
Cl–O	.73	(Cl→O	2.3)
S–Cl	.5	S→O	3.0
Sn–Cl	>3.1	K^+Cl^-	6.3
Sn–Br	>3.0	Na^+I^-	4.9

Discussion

Homopolar Single Bonds.—Figure 1 has shown the consistency of the C–N and C–O bond moments with the differences between the electronegativities of the atoms and the fact that the C–S

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(4) Smyth, *Trans. Faraday Soc.*, **30**, 752 (1934).

(5) Mulliken, *J. Phys. Chem.*, **41**, 318 (1937).

moment is much higher than would be expected from the electronegativities of the atoms. The very approximate value for C–S in Table I was obtained by taking the C–S–C angle to be the same as the C–O–C angle in methyl ether, 112°, an assumption in close agreement with the indications of dipole moment measurements.[6] The value thus obtained from the moment of dimethyl sulfide is 0.05 lower and the value obtained from diphenyl sulfide is 0.06 higher than the value in Table I. The values given for C–Se and C–Te were obtained from the moments of diphenyl selenide and diphenyl telluride by assuming that here also the angle was 112°. Although the uncertainty of the valence angles makes these three moments extremely doubtful, it is interesting to note that there is an increase in moment from C–O to C–S followed by a decrease to C–Se and a further decrease to C–Te, paralleling the trend of the C–F, C–Cl, C–Br and C–I moments. The same trend occurs in the phenyl as well as the methyl halides, in diphenyl oxide, sulfide, selenide and telluride, and in triphenylamine, phosphine, arsine, stibine, and bismuthine. No attempt has been made to calculate values from the moments of this last group of compounds as the zero moments found for triphenylamine and triphenylbismuthine, the former in contrast to the value 0.7 for trimethylamine, indicate a greater effect of valence angle variation or resonance, which makes a bond moment calculation even more inaccurate than in the preceding group. All of the bond moments of this group should be small with the carbon negative in its bonds to antimony and bismuth, but a rough estimate based on the trend of the other two groups of unexpectedly high carbon bond moments as well as on the moments of these triphenyl compounds would give: C–P, 0.7; C–As, 0.5; C–Sb, 0.3; C–Bi, 0, values too rough for inclusion in Table I. As the occurrence of a maximum value in the second moment of each group is not found when hydrogen replaces carbon and is contrary to the requirements of the electronegativities of the elements, the phenomenon is presumably caused by the factors which give rise to the excess in the values of the carbon bond moments over their expected values.

The small moment 0.56 calculated for sulfur dichloride by Smith[7] from measurements of Lowry and Jessop,[8] provides the basis for the calculation of the S–Cl moment, the sulfur valence angle being assumed to be 112°. A large error in this angle would not seriously affect the small value 0.5 obtained, which is identical with the difference between the sulfur and chlorine electroaffinities and only 0.15 higher than the value calculated as the difference between the H–Cl and the H–S moments.

The moments of the $(C_2H_5)_3SnCl$, $(C_2H_5)_3SnBr$ and $(C_2H_5)_2SnCl_2$ molecules are used to obtain lower limits for the Sn–Cl and Sn–Br bond moments. As the stannic chloride molecule is shown by electron diffraction to be tetrahedral and as $Sn(C_2H_5)_4$ has a moment indistinguishable from zero, these three molecules are assumed to be tetrahedral. Without regard for distortion and induction effects, their moments should be [(H–C) − (Sn–C) + (Sn–Cl)], [(H–C) − (Sn–C) + (Sn–Br)] and 1.15[(H–C) − (Sn–C) + (Sn–Cl)]. The ratio 1.12 of the $(C_2H_5)_2SnCl_2$ moment 3.85 to the $(C_2H_5)_3SnCl$ moment 3.44 is far closer to the theoretical ratio 1.15 than is the case with the somewhat analogous carbon compounds $(CH_3)_2CCl_2$ and $(CH_3)_3CCl$, where it is 1.02, and with H_2CCl_2 and H_3C–Cl, where it is 0.85, presumably because of inductive effects. Ignorance of the Sn–C moment, which should have its positive end toward the tin atom and a much smaller value than the Sn–Cl moment, probably less than 1, restricts one to calculation of lower limits for the Sn–Cl and Sn–Br bond moments, which are the values that these bond moments would have if the Sn–C moment were zero. Even the lower limits of the values for these supposedly covalent bonds are more than 60% as large as the moment of the sodium iodide molecule, in which the valence is typically electrovalent. These large moments of the Sn–Cl and Sn–Br bonds are consistent with the fact[9] that the chlorine of stannic chloride has almost the refraction of a chloride ion. It would appear that, although the stannic halides are not salts and have, in general, the properties of covalent compounds, the actual polarities of the individual bonds are little if any smaller than those associated with electrovalence.

Double and Triple Bonds.—Consideration of the moments of double, triple and semipolar bonds is complicated by the existence or, at least, by the possibility of resonance and the consequent contributions of other forms of differing polarities.

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[6] Sutton and Hampson, *Trans. Faraday Soc.*, **31**, 945 (1935).

[7] Smith, *Proc. Roy. Soc.* (London), **138**, 154 (1932).

[8] Lowry and Jessop, *J. Chem. Soc.*, 1421 (1929).

[9] Smyth, *Phil. Mag.*, **50**, 361 (1925).

Sidgwick[10] already has called attention to the fact that the moments of double and triple bonds between atoms of different elements are more than two and three times the values for the single bonds. This is apparent in the somewhat revised values in Table I, where the cyanide moment is eight times that of the single carbon–nitrogen bond and the double bonds between carbon and oxygen and carbon and sulfur have moments slightly less than three times those of the single bonds. Although the C≡N bond is primarily C:::N, contribution from a form $^{+}$C::N^{-} would raise the moment, perhaps, being responsible for the high value observed. It is a semipolar bond acting in the opposite direction in the isocyanide $\mathrm{N}\overset{\rightarrow}{=}\mathrm{C}$ which gives it a large moment opposite in direction to that of the C≡N bond.[11]

The C=O and C=S bonds should be primarily C::O and C::S, but contributions from forms $^{+}$C:O^{-} and $^{+}$C:S^{-} would account for the fairly high values observed for the bond moments. Pauling, Brockway and Beach[12] have concluded that the C–Cl distance found by electron diffraction in phosgene corresponds to 17% double bond character for the carbon–chlorine bonds and that in thiophosgene to 12% double bond character. As the form containing a double bond between one chlorine and the carbon atom has a positive charge on the chlorine, a single semipolar bond between the carbon and the oxygen or sulfur and a negative charge on the oxygen or sulfur, the moments should be considerably increased by the contributions of these forms. It has been shown[13] that the moment of phosgene, 1.18, can be calculated to a good approximation as the difference 1.28 between the moment of acetone and that of methylene chloride. As the moment of phosgene is presumably increased by the contribution of two forms containing a single semipolar bond between the carbon and the oxygen, it is necessary to conclude that a form containing a single semipolar carbon–oxygen bond contributes to the moment of acetone and, hence, to the C=O moment listed in Table I. The opposite conclusion was reached in regard to the carbonyl radical from the zero moment of nickel carbonyl,[14,15] to which a triple bond form $\mathrm{C}\overset{\leftarrow}{=}\mathrm{O}$ was supposed to contribute. Electron diffraction measurements have shown that the carbon–oxygen distance in nickel carbonyl is that of the triple bond while, in phosgene, it is that of the double or semipolar bond. Consequently, we may conclude that the carbonyl group in nickel carbonyl, like carbon monoxide, has a different structure from that of the ordinary carbonyl group as found, for example, in phosgene and the ketones and does not affect our conclusions in regard to the latter. The moment of thiophosgene is not available, but it is probable that the C=S is raised by resonance involving contribution from a polar form. The moment of carbonyl sulfide, 0.65, is higher than the difference between the C=O and the C=S moments, presumably because it is the resultant of contributions from forms containing single and triple bonds as well as from the double-double bond form.[16] Mulliken[17] attributes the unexpectedly low ionization potential of formaldehyde to accumulation of negative charge on the oxygen, which should increase the moment, but considers that the negative charge on thiocarbonyl sulfur must be much less than that on carbonyl oxygen, which should result in a lower moment for the C=S. The higher value of the C=S moment as compared to the C=O is also contrary to what would be expected from the electronegativities of the elements but is not only consistent with but proportional to the single bond values and presumably arises from similar causes.

There are too many uncertainties or complications in the structures of the molecules containing the C=N bond to permit of an accurate calculation of its moment from the data now available. In the treatment of the isocyanide bond previously mentioned,[11] the C=N moment was taken as $^2/_3$ that of the C≡N, but such a value is too high if the C≡N moment contains contributions from ionic structures. A value 0.9, twice that of the single C–N bond, combined with the necessary bond values from Table I and the H–C value, gives calculated values in good agreement with those observed for isocyanates and isothiocyanates if their structures are taken as linear. This value 0.9 also leads to satisfactory solutions of the equations for the moment of the N → O bond in the N-methyl ethers of the two isomeric oximes of *p*-nitrobenzophenone, while higher values fail.

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[10] Sidgwick, "The Covalent Link in Chemistry," Cornell University Press, Ithaca, N. Y., 1933, p. 153.

[11] Sidgwick, *Chem. Rev.*, **9**, 77 (1931).

[12] Pauling, Brockway and Beach, THIS JOURNAL, **57**, 2705 (1937).

[13] Smyth and McAlpine, *ibid.*, **56**, 1697 (1934).

[14] Sutton, New and Bentley, *J. Chem. Soc.*, 1876 (1930).

[15] Sutton, *Trans. Faraday Soc.*, **30**, 789 (1934).

[16] Cross and Brockway, *J. Chem. Phys.*, **3**, 821 (1935).

[17] Mulliken, *ibid.*, **3**, 564 (1935).

The comparatively low value thus indicated very roughly for the C=N bond should be practically free of contributions from polar structures as distinguished from the other double bond values in Table I. Sutton[15] has concluded that two structures containing semipolar bonds between the carbon and nitrogen contribute equally to the isocyanate and isothiocyanate, but, as the polarity of the bond in one structure is opposite to that in the other, they should have little effect upon the C=N moment value unless their contributions are a large fraction of the total.

Sidgwick[10] has used tertiary nitrosobutane and assumed that the moments act in one line to obtain a value 1.9 for the N=O moment. On a similar assumption, the revised bond moment values give 1.8, while the moment of nitrosobenzene gives 2.4 for the N=O moment. An angle of 125° between the nitrogen bonds would increase the value calculated for N=O to 2.0, which is given in Table I, the nitrosobenzene moment being more apt to be increased by resonance than the nitrosobutane. One would expect the N=O moment to be smaller than the C=O because of the smaller difference in the electronegativities of nitrogen and oxygen. Indeed, this difference is so small that the single bond moment 0.3 can be estimated for N–O without serious absolute error, the difference between H–O and H–N being 0.22 and that between C–O and C–N 0.41. It is evidently probable that the much larger value of the double bond receives a contribution from a semipolar form $^{+}N{:}O^{-}$.

Semipolar Bonds.—In the nitro group the two nitrogen–oxygen bonds are identical, each having half double bond character and half single semipolar bond character.[12] The moment listed in Table I for the single semipolar bond is actually the value calculated for this nitrogen–oxygen bond in the accurately investigated nitromethane molecule.[18,19] If the value 3.3 were the mean of the N=O value in Table I and the true N → O value, the latter would be 4.6, considerably larger than the other semipolar bond moments listed. The values calculated for the N → O bond in the N-methyl ethers of the two isomeric oximes of *p*-nitrobenzophenone on the basis of the assumption that the moments all lie in one plane making angles of 120° with the C=N bond are 2.85 and 3.05 giving a rough mean 3.0 not far from the value 3.3. It appears probable, therefore, that the latter is close to the true value for the N → O bond.

The P → O and P → S bonds in phosphorus oxychloride and phosphorus sulfochloride appear to be semipolar bonds without large contributions from other forms, although some resonance is indicated by the P–Cl distances found by means of electron diffraction.[20] The electron diffraction measurements on phosphorus sulfochloride were carried out in this Laboratory by Dr. J. Y. Beach and Mr. D. P. Stevenson in conjunction with dipole moment measurements by Mr. F. B. Jennings on both the oxychloride and the sulfochloride. The P–Cl distances and angles are sufficiently close to those in phosphorus trichloride to warrant adding the moment of the latter to the values observed for the oxychloride and sulfochloride molecules to obtain the P → O and P → S moments, which point in the opposite direction to the resultant of the three P–Cl moments. The lower value of the P → S moment as compared to the P → O is consistent with the lower electronegativity of sulfur as compared to that of oxygen but is in marked contrast to the higher value of C=S as compared to C=O. The lower moment of P → S in spite of the greater interatomic distance is consistent also with the decrease in moment of the phosphorus, arsenic and antimony halides as the size of the halogen increases. The fact that the probable values of the N → O and S → O moments lie between the P → O and the P → S indicates that single bond electronegativity may not necessarily play an important part in determining the moment of a semipolar bond. Indeed, the previously mentioned isocyanide structure, the nickel carbonyl structure, and the single–triple bond forms of carbon dioxide and carbon disulfide have the positive ends of semipolar bonds toward the more electronegative elements.

The value listed in parentheses as a lower limit for the Cl → O in chlorine dioxide has been discussed in a previous paper.[1] If the structure of chlorine dioxide is that which has been attributed to it,[21] this value is the result of contributions from a single semipolar bond form and a five electron bond form and cannot be regarded as a close approximation to a Cl → O value. A serious difficulty is apparent in the case of sulfur dioxide,

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(18) Smyth and McAlpine, THIS JOURNAL, **56**, 1697 (1934).

(19) Brockway, Beach and Pauling, *ibid.*, **57**, 2693 (1935).

(20) Unpublished measurements by Brockway and Beach and by Beach and Stevenson.

(21) Brockway, *Proc. Nat. Acad. Sci.*, **19**, 303, 868 (1933).

for which Cross and Brockway[16] write three forms as likely to contribute to the ground state. As two of these forms contain an $^{+}S{:}O^{-}$ and an S::O bond and the third contains two $^{+}S{:}O^{-}$ bonds, one would expect a moment for the sulfur–oxygen bond at least as large as that found for the nitrogen–oxygen bond in the nitro group, but the value obtained from the moment 1.61 and the valence angle 124° of the sulfur dioxide molecule is 1.7, only half as large as that of the nitrogen–oxygen bond. If, however, the valence angle has the value permitted by the upper limit of the experimental error, 15°, the calculated bond moment is 2.2. Moreover, if significant contributions are made by double–double bond forms and single–triple bond forms, which latter are indicated by the fact that the sulfur–oxygen distance is 0.05 A. shorter than the double bond length should be, a calculated value as low as 2.2 becomes understandable.

The S → O moment has been calculated from the moments of a considerable number of compounds containing it on the assumption that, in a sulfone, R_2SO_2, the angle between the two S → O bonds is 125° and that, in a sulfoxide, the angle between the S → O bond and the line bisecting the R–S–R angle is the same as in the sulfone. An increase of 5° in this angle would raise the S → O moment value 0.3. The contribution of the rest of the molecule to the molecular moment is taken as the moment of R_2S. The value given for the S → O moment by sulfuryl chloride is 2.7 and that by diphenyl sulfone 3.9, while diethyl sulfone and four aromatic and aliphatic sulfoxides give values differing by no more than 0.15 from 3.0. If the angle between the two S → O bonds is taken as having the more probable value 110°, the S → O values in sulfuryl chloride, diethyl sulfone and diphenyl sulfone drop to 2.13, 2.45 and 3.14, respectively, while the values in the four aromatic and aliphatic sulfoxides change less, still remaining within 0.15 of 3.0, which is, therefore, adopted as the best value.

Conclusions

Any values assigned to semipolar bond moments are evidently extremely approximate since, in addition to the difficulties inherent in single bond calculations, the bonds involved commonly receive contributions from forms other than that of the single semipolar bond. These contributions vary somewhat with the nature of the molecule, much as the effects of induction vary in the case of the ordinary single bond moment. Indeed, contribution from another form may alter the apparent moment of an ordinary single bond, as witness the difference in moment between the alkyl and the phenyl halides. It appears, therefore, that, while we cannot say with certainty that a value given for a semipolar bond moment in Table I is the moment of a bond formed wholly by a single electron pair furnished by the first of the two atoms listed, we can say that it is the moment of a bond to which this structure makes a dominant contribution and which, through change in resonance effects, alters its moment by no more than 0.8 when changing from aliphatic to aromatic compounds. In other words, in compounds such as have been considered, we do not find a pure semipolar single bond but a sort of hybrid, the moment of which varies somewhat but lies between 2.4 and about 3.5. The values obtained are not sufficient to indicate any quantitative dependence upon the electronegativities of the elements involved or upon the bond length, which latter effect is undoubtedly subordinate to that of induction. They show very clearly the inadequacy of that type of calculation in which the unknown moment of a supposedly semipolar bond is obtained as the product of an electronic charge by the distance between the bonded nuclei, since such a procedure would give a moment from two to four times that observed. In these single semipolar bonds the direction of the moment is always that which is required by the electronegativities of the atoms, although this direction is reversed in some semipolar bonds occurring in triple bonds. It appears probable that both double and triple bonds commonly receive contributions from semipolar bonds. Even the normally non-polar double and triple carbon–carbon bonds receive contributions from semipolar forms when groups involving good-sized moments are attached to the carbons. The semipolar bond values in Table I are about half as large as those of the electrovalent bonds of the alkali metal halides, which are decreased by inductive distortion, and about the same size as those of the tin–halogen bonds, which one might reasonably regard as, at least, semipolar. It appears that the so-called dative or semipolar bonds really have polarities intermediate between those of the ordinary covalent bonds and those of ordinary ionic or electrovalent bonds.

Summary

The dipole moments of a number of bonds have been calculated from the moments of the molecules containing them and the structures of these molecules as indicated by electron diffraction or other information. A graphical comparison of the moments of single bonds with the electronegativities of the elements involved shows approximate consistency except for the bonds between carbon and larger atoms, which have moments apparently greatly increased by induction.

The moments of double and triple bonds are commonly increased by contributions from forms containing semipolar bonds. Somewhat mixed forms of semipolar bonds affected by resonance have moments between 2.4 and 3.5 × 10^{-18}, the values varying from compound to compound by no more than 0.8 because of resonance. Semipolar bonds have polarities intermediate between those of ordinary covalent bonds and those of electrovalent bonds.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

A Study of Heterogeneous Catalysis in Liquid Ammonia Solutions. I

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Introduction

Solutions of the alkali and alkaline earth metals in liquid ammonia are known to be relatively stable, existing for many hours without appreciable reaction between the metal and the solvent ammonia. Yet a slow reaction does occur, and earlier workers[2–4] with liquid ammonia as a solvent prepared the amides of sodium and potassium in this way. In some cases, days and even months were required for complete reaction. That the rate of the reaction between metals and liquid ammonia could be speeded up by the presence of other substances was first observed by Franklin,[5] who noticed that in tubes containing bits of asbestos fiber, the time for preparation of potassium amide was shortened appreciably. Other catalytic agents were tried and platinum black and oxides of iron were found to be especially effective. Franklin stated that a few milligrams of platinum black so speeded up the reaction that as much as a gram of potassium was converted into potassium amide in the course of fifteen minutes.

From the concept of these metal solutions as developed by Kraus[6] it would seem that the real reaction that occurs when the metal amide is formed is one between ammonia and the free or solvated electrons. The present investigation was undertaken for the purpose of obtaining data that would be of value in interpreting the nature of the reaction, and to show how the reaction rate varies with different metals and with different catalysts.

Experimental Method

The apparatus employed was designed to provide anhydrous and oxygen free reaction conditions at a constant temperature and a uniform rate of stirring, and to permit the collection of the hydrogen formed. Usually the catalyst in the form of a foil was used, and this foil itself served as a stirrer. In some work with powdered catalysts, an efficient glass stirrer was employed. The apparatus is shown in Fig. 1.

A reaction tube (A), Fig. 1, made of 30-mm. tubing and approximately 40 cm. long, fitted through a large rubber stopper into a Dewar tube (C), used to hold commercial liquid ammonia for a cooling bath. This Dewar tube was also provided with a small tube (D) through which dry air could be bubbled, a tube (E) through which air and ammonia vapor escaped, and a thermometer for noting the temperature of the bath. Through the side-arm (B) of the reaction tube passed a tube (F) connected with the supply tank of anhydrous ammonia dried over sodium. The top of the reaction tube was closed with a stopper through which passed the shaft of a stirrer, operated through a mercury seal (G) by means of a one-eighth horse-power motor (H); and tube (I), which, for the preliminary work, was connected to a mercury gage (J), used to regulate the pressure within the system.

In preparing for a run, the reaction tube was cleaned and dried, and then placed in position in the Dewar tube. The catalyst, in the form of a foil previously cleaned and prepared, as described in a later section, was fastened with wires of the same material to the glass rod forming the end of the stirrer shaft, and this placed in position. Other connections, as shown in Fig. 1, then were completed. By a combination of cooling and pressure, condensation of ammonia vapor was carried out until 50 cc., the volume

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[1] This paper is based upon the thesis presented to the Faculty of the Graduate School, University of Cincinnati, by Harry L. Kahler, Jr., in partial fulfilment of the requirements for the degree of Doctor of Philosophy (1934).

[2] Joannis, *Compt. rend.*, **109**, 900 (1889).

[3] Franklin and Kraus, *Am. Chem. J.*, **23**, 277 (1900).

[4] Franklin and Stafford, *ibid.*, **28**, 83 (1902).

[5] Franklin, THIS JOURNAL, **27**, 820 (1905).

[6] Kraus, *ibid.*, **30**, 1323 (1908).