

The Formation of PerCompounds in Relation to Electronegativities

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since variations may be positive or negative, that all the signs in the numerator of the above fraction are taken to be positive in order to obtain the maximum percentage error. The expression for the pressure drop, $p_i - p_e$, will always be positive.

An accuracy of ± 0.1 -mm Hg may be readily attained in the range of pressure measurements that are dealt with. Hence, δp_i and δp_e may each be set equal to 0.1. An accuracy of ± 0.1 milliliter in V_B may also be easily realized, since a calibration of the buret space with mercury is possible before the apparatus is assembled. Therefore, $\delta V_B = 0.1$. The dead space volume is generally determined by a calibration with helium. A reasonable value in the accuracy of such a measurement is 1 percent. The value for δV_D may be determined, consequently, by multiplying the value for V_D by 0.01.

The data contained in Table I were observed in a number of different adsorption tubes. These calculations were made for the first point of each isotherm. The calculation for subsequent points becomes more complicated, and the equation above is not directly applicable. It is obvious that the error in obtaining subsequent points is cumulative. Nevertheless, it is felt that the treatment above is indicative of the relative accuracy of this type of measurement.

It should be noted that the absolute accuracy of the surface determination includes other factors than those treated here. These other quantities are dependent on the validity of the assumptions in the B.E.T. theory and on the density of packing of the adsorbed nitrogen molecules. Since the dead space is obtained by a helium calibration, the above consideration shows that it is necessary to make this calibration with an accuracy adequate to the particular application.

The Formation of Per-Compounds in Relation to Electronegativities

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July 3, 1947

IT is pertinent to add to the letter of M. Haissinsky,¹ under the above title, the following remarks. They are largely taken from recent communications² in which we have surveyed some of the many factors that determine bond strengths.

It is clear that the electronegativity of the groups at either end of a bond is a very important factor in determining the strength of the bond. The bond strength commonly increases with the electronegativity of the bonded groups. Examples are numerous^{3,4} and the point has recently been stressed by Gordy⁵ who has given an empirical relation between bond strength and the product of the electronegativities of the groups concerned. It is equally clear, however, that the increase of bond strength with electronegativity of bonded groups can only be true up to a certain point: if the electronegativities are too great there will be insufficient electron density in the 'shared' region between the nuclei that is all important for bonding purposes. In other words, high bond strength

also requires adequate atomic orbital overlap, and too high an electronegativity of the bonded groups may result in reduced overlap. We therefore expect the rule of increasing bond strength with increasing electronegativity product to break down when we come to consider bonds between highly electronegative groups. Thus it is not surprising that Gordy's relation fails for the OO bond in H_2O_2 and probably for the FF bond.² As regards the OO bond the indications^{2,4} are that the strength *increases* with substitution of *less* electronegative groups for H. Similarly, the FF bond is *weaker* than the FCl bond, FF is weaker than FH, OO weaker than OH, and NN weaker than NH. If we accept the structure (I) advocated by Ingold and Ingold⁵ for N_2O_4 , the dissociation energy of the NN bond is 13 kcal./mole. The bond energy (E) must be distinguished from the dissociation energy^{2,6} but is likely also to be very low since the stretching force constant (k) is only 1.5×10^6 dyne/cm. In hydrazine,² however, $E(NN)$ appears to be ~ 64 kcal./mole, with $k(NN) = 3.6 \times 10^6$ dyne/cm. The great reduction of NN strength in N_2O_4 relative to N_2O can be explained as caused by reduced overlap in the NN bond of N_2O_4 consequent



upon the high dipole $\left(\begin{smallmatrix} \delta + & \delta - \\ NO_2 \end{smallmatrix} \right)$ in each NO_2 group. Glyoxal affords a similar example,² the CC bond strength appearing to be considerably weaker than considerations of the conjugation between its two C=O groups alone would indicate.

The conclusion of M. Haissinsky that elements whose electronegativities are smaller than a certain amount form per-compounds while those whose electronegativities are greater than this amount do not form per-compounds finds a natural explanation in terms of this factor of reduced atomic orbital overlap consequent upon too great an electronegativity. It is an important point of peroxide chemistry that the OO bond, to be strong, needs groups of low electronegativity attached to it.

¹ M. Haissinsky, J. Chem. Phys. 15, 152 (1947).

² Walsh, J. Chem. Soc., in press (2 papers).

³ W. Gordy, J. Chem. Phys. 14, 305 (1946).

⁴ Walsh, Trans. Faraday Soc. 42, 264 (1946).

⁵ Ingold and Ingold, Nature, 159, 743 (1947).

⁶ Walsh, Trans. Faraday Soc. 43, 60 (1947).

Addendum: A Relation between Bond Order and Covalent Bond Distance

[J. Chem. Phys. 15, 284 (1947)]

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THE paper, by G. N. Copley,¹ presenting the same model for obtaining multiple carbon bond distances as that which appeared in the appendix of this paper, has just come to my attention. Copley treats CC, CN, CO bonds and requires an empirical correction factor to his relation between bond order and bond distance.

¹ G. N. Copley, Chem. Ind. 663 (1941).