

Structure of Triatomic Molecules

RECENT investigations of infra-red and Raman spectra of triatomic molecules have shown that molecules with an odd number of electrons, such as ClO_2 and NO_2 , are similar in structure to the molecules SO_2 and CO_2 , each with one more electron. This observation suggests that the triangular molecules have structures depending on the number of valence electrons binding the three atoms together, and that a scheme might be formulated for obtaining the structures of these molecules from the total number of available valence electrons.

A stable structure is first obtained with four electrons. Examples are H_2O and Cl_2O , molecules which have surprisingly similar structures: both have vertical angles near 90° , both satisfy only the central system of force constants, and both show a large resistance to deformation measured by H-H and Cl-Cl force constants of at least 5×10^5 dynes/cm.; further, the O-H and O-Cl force constants are each 7×10^5 dynes/cm., corresponding to single chemical bonds. In fact, these molecules are excellent examples of the Slater-Pauling molecule formed from a central atom with two p -electrons available for chemical bonds.

Proceeding one step further, a fifth electron is added and a new structure, that characteristic of SO_2 , is obtained. ClO_2 has five available valence electrons, has a vertical angle near 120° , satisfies only the valence system of force constants, and resists deformation to a much less degree than either H_2O or Cl_2O , its tangential restoring force constant being 3.5×10^5 dynes/cm. These structural properties are all repeated in SO_2 , where the sixth electron completely fills the SO_2 type of proper function; this is the one feature distinguishing SO_2 from ClO_2 , for the S-O force constant is approximately 9.6×10^5 dynes/cm. whereas the Cl-O constant is only 7×10^5 dynes/cm., indicating that the sixth electron of SO_2 brings out the full bonding power of this type of proper function.

Next we seek a molecule with seven electrons; the typical example is NO_2 . The addition of a seventh electron again requires formation of a new type of proper function, and this is characterised by a linear structure and small resistance to deformation, measured by a restoring couple constant of 5.5×10^{-12} dynes \times cm. Addition of an eighth electron fills this linear type proper function, and raises the force constant of the chemical bond from 7×10^5 to 14×10^5 dynes/cm. Addition of the eighth electron does not otherwise affect the structure, the similarity of the restoring couple constants being a remarkable feature of the linear molecules NO_2 , N_2O , CO_2 , COS and CS_2 . The C-S force constant is less than 14×10^5 dynes/cm., and may be accounted for by the increased separation of the nuclei.

The above scheme seems also applicable to triatomic radicals, and has been used to explain apparently inconsistent structures observed for the NO_2 group¹. It also predicts an SO_2 structure for NOCl , and preliminary observations of the infra-red absorption spectrum appear to confirm this.

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¹ Bailey and Cassie, NATURE, 131, 239, Feb. 18, 1933.

Hydroxyl Group in Ergosterol and Cholesterol

IN a recent issue of the *Annalen*¹ is a paper by Chuang in which the conversion of ergostane into *allo*-norcholanic acid, $\text{C}_{23}\text{H}_{38}\text{O}_2$, is described. This result is of considerable interest as it definitely establishes the identity of the nuclear skeletons of ergosterol, cholesterol, and the bile acids.

We have also been investigating the same question with the additional object of determining simultaneously whether the hydroxyl group in ergosterol is in the same position as in cholesterol which, as has been shown by Wieland and Dane², is almost certainly attached to carbon atom 3. With this object in view we have oxidised ergostanyl chloride, $\text{C}_{28}\text{H}_{46}\text{Cl}$, with chromic anhydride and have isolated a chloro-acid, m.p. 213° , analysis of which shows that it is a chloro-norcholanic acid (found: C, 72.7; H, 10.0; Cl, 9.7 per cent; required for $\text{C}_{23}\text{H}_{37}\text{O}_2\text{Cl}$: C, 72.5; H, 9.7; Cl, 9.3 per cent). The formulation of this acid has obviously occurred by scission of the ergostanyl side-chain in the following manner:—



We are now engaged in degrading 3-chloro-*allo*-cholanic acid³, $\text{C}_{24}\text{H}_{38}\text{O}_2\text{Cl}$, to the corresponding nor-acid in order to establish its identity or otherwise with our acid.

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¹ *Ann.*, 590, 270; 1933.

² *Z. physiol. Chem.*, 212, 41; 1932.

³ Windaus and Hossfeld, *Z. physiol. Chem.*, 145, 177; 1925.

Constitution of Binary Alloys at Room Temperature

WHEN studying binary organic melts, it is customary to supplement the information obtained from the freezing point curve as to compound formation, solid solutions, etc., by examining the solubility isotherms. In this way, not only can it be decided whether or not the composition of a cold mixture is essentially the same as at its freezing point, but also a very fair approximation to the transition point of a compound can often be obtained by means of a solid model or projection diagram. For the purpose of the solubility measurements, the nature of the solvent is considered immaterial and solvation is not supposed to affect the range of stability of the compound.

This being the case, it occurred to me that a similar procedure might be applied with equally reliable results to binary alloys, using mercury as solvent, and plotting the results on a triangular co-ordinate diagram. Mr. H. D. Carter, working in my laboratory on the system mercury-manganese-tin, at 30° , is obtaining results which show that the procedure is feasible. Dilute tin amalgams are used as cathodes and manganese electro-deposited up to the appearance of solid phase. Perhaps the method may become of general application in metallurgical work.

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