With ammonia it forms a monoammine and a pentammine. Methyl gallium dichloride monoammine does not melt up to 80°. Its vapor pressure is below 0.01 mm. at 25°. The pentammine is insoluble in liquid ammonia and has a dissociation pressure of about 25 mm. at room temperature. The ammonia is readily pumped off at 80°.

[1] DUPONT FELLOW in Chemistry.

[2] These PROCEEDINGS, **19**, 292–298 (1933).

[3] Moser and Brukl, *Monatshefte f. Chem.*, **50**, 186 (1928).

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*THE THREE-ELECTRON BOND IN CHLORINE DIOXIDE**

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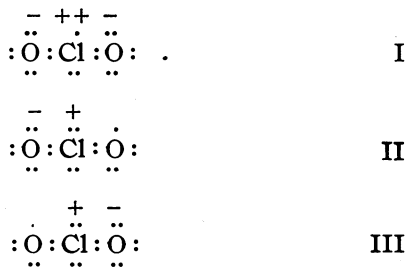
The stability of certain molecules[1] containing an odd number of electrons has been explained on the basis of the formation of three-electron bonds. Evidence has now been obtained which substantiates the validity of a similar explanation for the stability of ClO_2, and in particular for its lack of tendency to polymerize to Cl_2O_4.

The possible electronic structures which may be written for ClO_2 in accordance with the quantum mechanical rules for the formation of electron-pair bonds[2] are represented as follows:



I

II

III

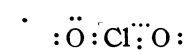
Only the electrons in the incomplete shells are indicated. The unsymmetrical arrangement Cl—O—O is not considered, since it is highly improbable for chemical reasons. The formal charges indicated for the atoms result from splitting shared electron pairs.

The choice of the correct structure among these could be made by a theoretical calculation of the energy of each. If the energy for a single one lay considerably below the energies calculated for the other two, that structure would closely represent the molecule in its normal state. If the separate energy calculations gave nearly the same result, the true value

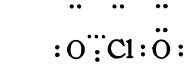
of the energy would be obtained only by considering a combination of all the structures. Normal chlorine and oxygen are rather near to each other on the electronegativity scale,[3] and the electronegativity of positive chlorine is greater than that of neutral chlorine, and may be nearly equal to that of oxygen, so that the transfer of one electron from oxygen to chlorine in ClO_2 may well involve only a small change in the energy of the molecule. Structures I, II and III above would then correspond to energy levels near to one another.

The criterion for the formation of a three-electron bond is that two structures, in one of which there is an unshared pair of electrons on one atom and a single electron on the other, and in the other the single electron and the pair are interchanged, have nearly the same energy. It has been shown[1] that in this case a lower (and hence more nearly correct) value for the energy is obtained by taking a linear combination of the wave functions representing the two structures than corresponds to the use of either function alone. This extra resonance energy which serves to stabilize the molecule may be ascribed to the formation of a bond with the three electrons in the same way that the interchange of two single electrons on two atoms affords a resonance energy which is the principal energy of the electron-pair bond. The formation of the two kinds of bonds may be indicated diagrammatically in the same manner, that is, by placing two dots between the atoms for the electron-pair bond and three dots for the three electron bond.

Since structures I and II or I and III taken together meet the conditions for the formation of a three-electron bond, a better representation of ClO_2 is given by the two formulas:



IV



V

In both IV and V one oxygen atom is bonded to chlorine by an electron-pair bond and a three-electron bond, and the other by an electron-pair bond alone. Since the calculation for the helium molecule-ion He_2^+ to which reference has already been made indicates that the energy and interatomic separation of a three-electron bond is about equal to that of a one-electron bond and about half that of an electron-pair bond, the combination indicated here in ClO_2 should be equivalent to one and one-half single bonds or about midway between a single and a double bond.

It was pointed out in a discussion[4] of resonance between several Lewis electronic structures that the observed bond distances between two atoms corresponds to that of the strongest type of bond involved in the resonating structure and not to a mean (if the elementary structures are of equal

importance). Since the structures IV and V are indistinguishable, they have precisely the same energy and therefore contribute equally to the resonating structure. On this basis the observed chlorine-oxygen separation will be the same for both bonds and should correspond to the com-

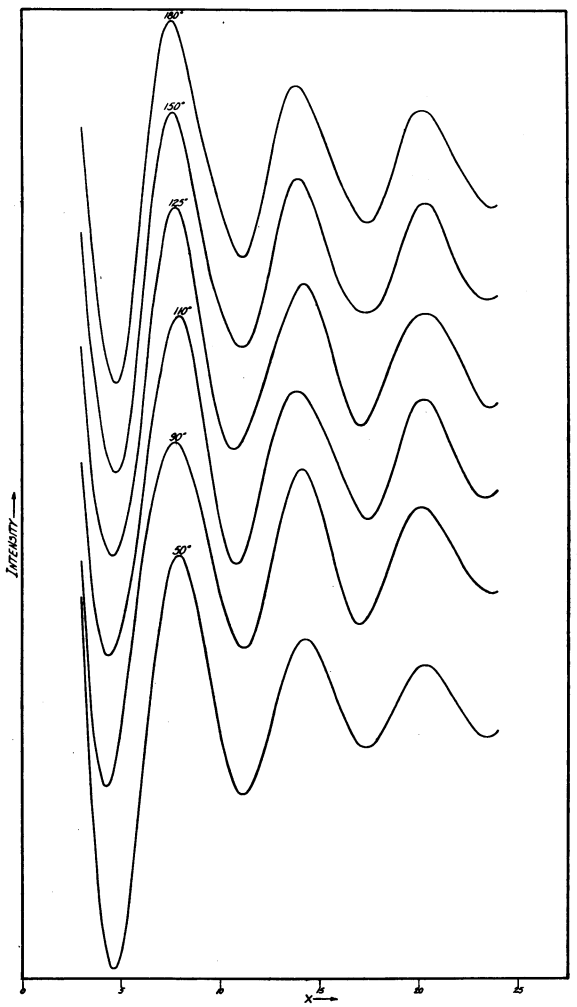


FIGURE 1

bined electron-pair-three-electron bond distance. The predicated value of 1.57 Å for this distance is based upon the properties of the combined bond mentioned above and on the table of covalent radii.[4] The single and double bond distances for Cl—O are 1.65 Å and 1.48 Å, respectively.

I have determined the bond distance in ClO_2 with the aid of electron-

TABLE 1

$\frac{\sin\theta/2}{\lambda}$ OBSERVED	MODEL I 180° x	MODEL I 180° a	MODEL II 150° x	MODEL II 150° a	MODEL III 125° x	MODEL III 125° a	MODEL IV 110° x	MODEL IV 110° a	MODEL V 90° x	MODEL V 90° a	MODEL VI 50° x	MODEL VI 50° a
First min. 0.276	4.72	1.364	4.75	1.372	4.60	1.330	4.35	1.257	4.25	1.228	4.63	1.338
First max. 0.396	7.55	1.518	7.60	1.527	7.80	1.569	7.92	1.592	7.72	1.551	7.90	1.589
Second min. 0.538	11.13	1.648	11.12	1.645	10.65	1.575	10.80	1.597	11.20	1.657	11.15	1.650
Second max. 0.703	13.85	1.568	13.90	1.574	14.30	1.619	13.90	1.574	14.15	1.601	14.30	1.619
Third min. 0.875	17.45	1.587	17.40	1.583	17.10	1.556	17.40	1.583	17.05	1.55	17.30	1.574
Mean value		1.580		1.582		1.580		1.587		1.590		1.608
Average deviation		0.037		0.032		0.020		0.008		0.039		0.026

Final value Cl—O = 1.58 ± 0.03 Å.

diffraction photographs of the gas. The method was the same as that used in the study of the hexafluorides.[5] Theoretical intensity curves for six molecular models corresponding to a range of bond angles from 50° to 180° are reproduced in figure 1. It will be noted that the positions of the maxima and minima change very slightly throughout the range. This is explained by the large scattering power of chlorine relative to that of oxygen; the interference effects observed arise almost exclusively from the chlorine-oxygen separation so that the effect of the change of the oxygen-oxygen separation with variation of the bond angle is scarcely detectable. In table 1 are given the results of the observations as interpreted with the use of each of the theoretical models.

The first column contains the $\frac{\sin\theta/2}{\lambda}$ values for the observed minima and maxima, in which θ is the scattering angle and λ the wave-length associated with the electron beam. Each value is the average of six measurements on three different photographs. The remainder of the table shows the interatomic distance (a = Cl-O separation) as calculated for each minimum and maximum of all the models with the aid of the equation

$$x = 4\pi a \frac{\sin\theta/2}{\lambda}.$$

The mean values for a do not include those calculated for the first minimum since the position of the first minimum on the photograph is always affected by the fogged area around the central image.

The most probable model is considered to be the one giving the most consistent a-values. Since in this case the deviation in the least consistent set is only a little

larger than the experimental error (which is $\pm 1\%$) no very definite conclusion in regard to the bond angle is afforded by these results. An angle near 120° is expected from theoretical considerations. The uncertainty in the value of the angle does not affect the determination of the Cl-O separation, however, if the extremely improbable Model VI is excluded. The most probable value for the Cl—O distance is thus found to be 1.58 $\pm$ 0.03 Å.

The excellent agreement between the observed value and the value predicted for the structure discussed above (1.57 Å) substantiates this electronic structure for ClO_2, and provides positive evidence for the existence of the three-electron bond in this molecule.

I wish to thank Professor Linus Pauling for many invaluable suggestions and criticisms.

* Contribution from the Gates Chemical Laboratory, California Institute of Technology, No. 358.

[1] Linus Pauling, *J. A. C. S.*, **53**, 3223 (1931); *J. Chem. Phys.*, **1**, 56 (1933).

[2] Linus Pauling, *J. A. C. S.*, **53**, 1367 (1931).

[3] Linus Pauling, *Ibid.*, **54**, 3570 (1932).

[4] Linus Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932); *Ibid.*, **18**, 498 (1932).

[5] L. O. Brockway and Linus Pauling, *Ibid.*, **19**, 68 (1933).

THE NEUTRON, ATOM BUILDING AND A NUCLEAR EXCLUSION PRINCIPLE

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I. *Introduction: Discovery of the Neutron.*—The recent experiments of Curie and Joliot,[6] based on those of Bothe and Becker,[5] have been shown by Chadwick[7] to indicate the existence of a new fundamental unit of structure, the neutron, which is undoubtedly of great importance in the building up of atomic nuclei.

Neutrons were found to be emitted by beryllium when it is bombarded by fast α-particles. That the beryllium nucleus consists of a neutron, or a complete condensed hydrogen atom in a nuclear state was an integral part of the hydrogen-helium theory of nuclear constitution developed in 1915 by Harkins and Wilson.[1] The prediction of the existence of a neutron in the beryllium nucleus arose from a curious numerical discrepancy which will be described below. The ordinary beryllium nucleus was considered as a carbon (12) nucleus in which one helium nucleus is replaced by a neutron. It is now found that if the α-particle enters the beryllium nucleus the neutron leaves it.