JULY 15, 1931 PHYSICAL REVIEW VOLUME 38

NOTE ON THE STRUCTURE OF THE GROUPS XO_3

By J. C. Slater
Massachusetts Institute of Technology

(Received May 21, 1931)

Abstract

The structure of such radicals as $(NO_3)^-$ on the one hand, $(ClO_3)^-$ on the other, is discussed on the basis of their being partly valence compounds, the oxygen being in the form of O^{-1} with one valence bond. The directional properties of the valence lead to a coplanar structure for the first type of radical, a pyramidal one for the second, as is observed. The energy relations are discussed, it is shown that the valence model will be bound in a stable structure, and that it is stabler and hence nearer the real model than the purely ionic structure.

Directional Properties

The structures of a number of radicals of the form XO_3 have been investigated by x-ray methods, and it has been pointed out by Zachariasen[1] that some of them apparently form plane groups, others pyramidal ones. The criterion governing this is very simple: those groups for which the number of valence electrons is 24 form plane configurations $((NO_3)^{-1}, (CO_3)^{-2}, (BO_3)^{-3})$, while those with 26 valence electrons form pyramids $((ClO_3)^{-1}, (BrO_3)^{-1}, (SO_3)^{-2}, (AsO_3)^{-3})$. If one assumes that those compounds are purely ionic, then as Zachariasen shows we can get an explanation of the difference in behavior. For this purpose we assume that the oxygens form ions O^{-2}. This leaves the positive ions in the first case without valence electrons, since the oxygen ions use up all 24 electrons, while in the second case the positive ions are left with two valence electrons, presumably s electrons. As a result the positive ion in the latter case is much more polarizible, and this polarizibility proves to be enough to make a pyramidal structure more stable than the plane one.

Now it has been pointed out by the present writer,[2] and independently by Pauling,[3] that an explanation of many directional properties in valence bonds can be given on the basis of wave mechanics. Many things suggest that in the groups XO_3 the bonds are partly of a homopolar nature, and it is the purpose of the present note to point out how this explanation fits in with the generalization of Zachariasen. Of course, this is not a new explanation of these compounds; it has been discussed, for example, by Lewis, Huggins,[4] and Pauling.[3] The principal contribution of the present note is to point out that the two explanations, the homopolar and the ionic ones, are not necessarily antago-

---

[1] Zachariasen, Norske Vid. Akad. Skr. Oslo, 1928, No. 4, p. 90; J. Am. Chem. So., now in press; Phys. Rev. **37**, 775 (1931).

[2] J. C. Slater, Phys. Rev. **37**, 481 (1931).

[3] Linus Pauling, J. Am. Chem. Soc. **53**, 1367 (1931).

[4] M. L. Huggins, Phys. Rev. **37**, 1177 (1931).

nistic, but that the real situation is undoubtedly a combination of the two, in proportions, or with probabilities, which can be computed, rather than being the subject of arguments. A suggestive, though very rough, calculation of these relative proportions shows that the homopolar model is the more likely one in the actual case treated.

Let us take $(NO_3)^{-1}$, $(ClO_3)^{-1}$ as examples of the two groups. We can explain $(NO_3)^{-1}$ as being made of the ions $N^{+5}(O^{-2})_3$, or $N^{+2}(O^{-1})_3$, and (ClO_3^{-1}) as being made of $Cl^{+5}(O^{-2})_3$, or $Cl^{+2}(O^{-1})_3$. The first explanation in either case is that in which the attraction is wholly ionic, and it is this which Zachariasen discusses. But the second explanation as well seems plausible, and we wish to show that it leads to the same results. First we take $(NO_3)^{-1}$. The ion N^{+2} contains three valence electrons, and can therefore have three valence bonds; O^{-1} lacks one electron from a complete shell, and so has one bond. Thus there can be a regular valence compound, the N being held by valence bonds to each O, the valences being reinforced by the ionic attractions which still remain. Now we consider the directional properties of the valences. The normal state of N^{+2} would have two s electrons, one p, and would be monovalent. Since we wish a trivalent form, one of the s electrons must be raised to a p state, so that we have one s, two p electrons. Now in the previous paper it was shown that three p electrons and an s can form four functions of tetrahedral symmetry. In the same way two p's and an s could form three functions of triangular symmetry, the valence bonds sticking out in a plane, forming angles of 120° with each other. This form of valence bond could lead to the coplanar form of the nitrate ion, and of the other ions of that structure. Or perhaps, as Pauling suggests, the form could be slightly pyramidal, with the nitrogen or carbon ion oscillating from one side of the plane of the oxygens to the other.

The other group of ions, of which $(ClO_3)^{-1}$ is an example, differs in having two more electrons. The Cl^{+2} has five valence electrons, two s's and three p's, the former not contributing to valence, the latter furnishing three bonds. These bonds, as usual when there are three p valences, tend to be at right angles to each other, so that the radical is pyramidal. The distinction between the two structures thus proves to be just in agreement with observation.

Examination of other radicals containing oxygen shows that the model formed of O^{-1} ions is always possible, and that it leads to valence bonds as well as ionic attractions, and hence to directional properties. For instance, it has just been found by Ziegler[5] that the nitrite ion, $(NO_2)^{-1}$, is angular rather than collinear. If we assume this made of N^{+1} and $(O^{-1})_2$, the nitrogen has four valence electrons, two s's and two p's, giving two p valences to link with the two oxygens, and hence an angular model. In general, in such a radical, we are to assume the oxygens to be in the form of O^{-1} ions, and to assume the other electrons to be located on the positive ions. Then we find that there are just enough valence bonds to go around, and from the nature of the electrons concerned in these valence bonds we can determine the directional properties by the rules of the previous paper.

[5] G. E. Ziegler, Washington Meeting of American Physical Society, April 30, 1931.

ENERGY RELATIONS

It is possible to answer in a fairly definite way the question as to which model of the radical is right, the purely ionic one or the one involving valence bonds. The answer has already been discussed in the previous paper: if both models seem possible, the real situation is a combination of both. Thus if ψ_1 represents the wave function of the purely ionic case, ψ_2 of the case involving valence, the wave-function will be of the form $a\psi_1+b\psi_2$, where the relative sizes of a and b determine which model is nearer the truth. We can get information about these magnitudes by considering the energies of the two models. If, for example, the state ψ_2 lies much below ψ_1, then for the low state of the radical we shall have b large compared with a, and the correct model will be the second, with energy accordingly. On the other hand, if the two energies are nearly the same, a and b will be nearly the same, and the true model will be midway between the two. We can actually make fairly accurate estimates of the energies, and they illustrate our points very nicely.

Suppose we consider the energy of the nitrate ion as a function of the distance R from the nitrogen to any one of the oxygens, supposing that it changes its size while leaving its shape unaltered. We expect the curve of energy against R to resemble those for diatomic molecules. At infinite separation the energy is that of the separate atoms or ions. Take as zero of energy the configuration N^-+3O, which is presumably the lowest level of the separated ion, and the one into which the lowest level of the radical will go at large enough R. Then state $N^{+5}+3O^{-2}$ lies very high above this, by an amount which we can estimate from the shielding constants suggested by the author.[6] It requires about 19.0×13.53 volts to remove the five valence electrons from nitrogen (effective nuclear charge for an L electron in nitrogen $=7-2(0.85)-4(0.35)=3.90$, energy $=5(3.90/2)^2\times 13.53$ volts). Further, the energy of the negative ion is very nearly the same as of the corresponding neutral atom. (For O^{-2}, nuclear charge $=8-2(0.85)-7(0.35)=3.85$, energy $=8(3.85/2)^2=29.6$; for O^{-1}, charge $=4.20$, energy $=7(4.20/2)^2=30.8$; for O, charge $=4.55$, energy $=6(4.55/2)^2=31.0$. According to this, O is more stable than O^{-1} by 0.2, and more stable than O^{-2} by 1.4. Similarly for N^{-1}, charge $=3.55$, energy $=6(3.55/2)^2=18.9$, so that N is more stable by 0.1). Thus the height of our ionic state is about 19.0 units above the zero or more precisely $18.9+3(1.4)=23.1$ units. The other state does not lie nearly as high at infinite R, for we have to remove only two electrons, giving N^{+2} (requiring energy $18.9-3(4.60/2)^2=3.1$ units) and join these to the O atoms (requiring 0.6 more), so that this level is only 3.7 units up from our zero.

As R decreases, both energy levels become lower, on account of the electrostatic attractions between ions, and the polarizations. The energies thus can become lower than those for infinite separation, giving binding. Further, the ionic level decreases so much faster that at the actual dimensions of the radical the two energies are of the same order of magnitude. To compute the energy at distance R, we proceed as follows. There is first the electro-

---

[6] J. C. Slater, Phys. Rev. **36**, 57 (1930).

static attraction of the nitrogen for the three oxygen ions at distance R. Next there is the mutual electrostatic repulsion of the oxygens, at distance $R\sqrt{3}$ Finally there is the polarization energy of the oxygens, $\frac{1}{2}\alpha F^2$ for each, where α is the polarizibility, F the field. The former is 1.55×10^{-24} cc[7] for the O^{-2} ion; we assume the same for O^{-1}, although this is not very accurate. The field at an oxygen ion is composed of two parts, the attraction from the nitrogen, equal to the charge on the nitrogen over R^2; and the repulsions form the two other oxygens, the components of each along the resultant being the charge over $\sqrt{3}R^2$. Combining all terms, we have for the whole energies the following expressions. Here R is in units of a_0, energies in units 13.53 volts, and the factor 2 in the potential energy takes care of these units.

(1) *Ionic case*:

$$23.1 - \frac{2}{R}\left(3\times 2\times 5 - \frac{3\times 2\times 2}{\sqrt{3}}\right) - \frac{2}{R}\cdot\frac{\alpha}{R^3}\cdot\frac{3}{2}\left(5 - \frac{2\times 2}{2\sqrt{3}}\right)^2$$

$$= 23.1 - \frac{4.62}{R} - \frac{44.4}{R}\frac{\alpha}{R^3}\cdot$$

(2) *Valence case*:

$$3.7 - \frac{2}{R}\left(3\times 1\times 2 - \frac{3}{\sqrt{3}}\right) - \frac{2}{R}\frac{\alpha}{R^3}\frac{3}{2}\left(2 - \frac{2}{2\sqrt{3}}\right)^2$$

$$= 3.7 - \frac{8.5}{R} - \frac{2.5}{R}\frac{\alpha}{R^3}\cdot$$

Now in the actual equilibrium position, $R\sqrt{3}$, the distance between oxygens, equals about 2.70A, so that $R = 1.56\text{A} = 2.93\ a_0$, and $\alpha/R^3 = 0.415$. Thus for this part of the energy we have

$$(1) \qquad \textit{Ionic case:}\ 23.1 - \frac{4.62}{2.93} - \frac{44.4}{2.93}\times .415 = 1.1 \text{ unit}$$

$$(2) \qquad \textit{Valence case:}\ 3.7 - \frac{8.5}{2.93} - \frac{2.5}{2.93}\times .415 = 0.0 \text{ units.}$$

In other words, the two levels have both come down nearly to the zero of energy.

In addition to the energies already considered, there are two others to be added in. First is the repulsion arising from the exclusion principle. This begins to be appreciable at about the distance of equilibrium, and causes both curves to turn up again sharply as R decreases still further. The second is the valence attraction in case 2. This will reduce the energy still further in the neighborhood of the minimum, bringing it safely below the zero of energy, and ensuring a stable radical.

---

[7] See Debye, Polar Molecules, for similar calculations, and tables of polarizibilities.

When we consider all the terms in the energy, we see that the valence model seems to correspond to the lower energy, and to stable binding; but the ionic model gives an energy not far above for small R's, although at large R's it goes much higher. We conclude, therefore that the true state of affairs is nearer the valence case although suggesting both; approaching, however, the lowest state, $N^- + 3O$, at very large R. As R is increased, the ionic case becomes less likely. This latter statement is interesting when we look at it in another light: as R is decreased, and the nuclei are pushed together, the oxygens become more highly charged negatively. This is as if the electrons did not follow the nuclei as they approached, but rather formed a cloud of more or less stationary dimensions, and allowed the nuclei to be pushed through them. This is as we should expect, when R becomes quite small; the exclusion principle requires that the electrons stay a reasonable distance apart from each other.

Finally we can get an interesting light on the structure by considering the electric moment of the polarized oxygen ions, which is equal to αF. In the first case, this is $\alpha/R^3 \times eR \times (5-2/\sqrt{3}$, where e is the charge on the electron, and in the second case it is $\alpha/R^3 \times eR \times (2-1/\sqrt{3}$. Substituting, this gives for the equilibrium value of R the two moments 1.60 eR and 0.59 eR respectively. These have an interesting interpretation: in the first case the polarization of each O^{-2} is what we should have if 1.60 electrons moved from the oxygen to the nitrogen, and in the second case if 0.59 moved, leaving in either case about half an electron on each oxygen. Or we can say, in case 1 one electron shifts from oxygen to nitrogen (bringing us to case 2 automatically), and the second extra electron shifts from the oxygen to the position midway between oxygen and nitrogen, as if it were held in a double bond. These results are only suggestive, for of course the oxygen has many electrons, and all can be displaced. Nevertheless they point in the direction of assuming that the structure of the radicals is one in which the separate ions are only moderately charged, and are held together at least partially by valence forces.