

Oxide Chlorides and Organometalloid Oxides as Donor Molecules

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A model of an idealized structure has been suggested, which can be used for the discussion of adducts of oxide chlorides and organometalloid oxides. No safe distinction between single and double bond structures can be made with the experimental data available at present. The results show, however, the importance of inductive effects in donor-acceptor reactions, and some predictions can be made about other adducts than those studied.

In an earlier paper ¹ it was pointed out that the semipolar formulation of the donor-acceptor bond is misleading in most addition compounds. In the compounds which in the preceding paper ¹ were formally described as addition compounds with oxygen atoms, the formulation is more appropriate, although not at all necessary. The typical example is amine oxide R_3NO , which is written $R_3N^+O^-$ in the semipolar formulation. In this case, the formal charges on the atoms really indicate a strongly increased heteropolar interaction in the N—O bond (while the R—N bond is weakened). There is no possibility of double bond formation in the amine oxides, and the picture of the bond as a covalent bond with strong additional ionic attraction is obvious. In phosphine oxides on the other hand, the possibility of double bond formation cannot be excluded, and the formulation $R_3P=O$ has been advanced as more accurate than $R_3P^+O^-$.

In this paper, this question will be discussed together with the inductive effects of donor-acceptor reactions involving the above-mentioned donors. The available structural information will be used, and the compound $SbCl_5(OPCl_3)$ will be taken as an example for the discussion.

THE IDEALIZED STRUCTURE

First it is assumed that the single bond structure is correct; the P—O bond is considered as a donor-acceptor bond. The bond picture of the adduct will then be $Cl_3P—O—SbCl_5$ with strong primary inductive effects due to the formation of the donor-acceptor bonds P—O and Sb—O.

Because of the difficulty of making direct comparisons of the measured bond lengths with predicted values, an idealized charge distribution must first be assumed, for which at least some predictions can be made. The deviations of the actual charge distribution from the idealized one are then estimated and the inductive effects on the bond lengths are predicted in a way suggested in the preceding paper ¹. Finally a comparison is made with the experimental results.

The idealized charge distribution selected for this purpose is the following: The *charge distribution in the bond system Cl—P—O* is assumed to be *the same as if the adduct molecule had a perfectly symmetrical distribution around the oxygen atom* (the fictive ion $\text{Cl}_3\text{POPCl}_3^{2+}$). A similar assumption is made for the *O—Sb—Cl* bond system (the fictive ion $\text{Cl}_5\text{SbOSbCl}_5^{2-}$). The bond lengths P—Cl and P—O are then only influenced by the effective electronegativity differences between P and Cl and O, respectively, and the bond lengths Sb—Cl and Sb—O only by the electronegativity differences between Sb and Cl and O.

The difference between the bond lengths to the chlorine and oxygen atoms: $|\text{P—Cl}| - |\text{P—O}|$ and $|\text{Sb—Cl}| - |\text{Sb—O}|$ can rather safely be assumed to have almost equal values because the difference in electronegativity between P and Sb is not very large. If the Shomaker-Stevenson formula $r_{\text{AB}} = r_{\text{A}} + r_{\text{B}} + 0.09 |x_{\text{A}} - x_{\text{B}}|$ were valid, the differences should always have a constant value independent of the atoms bonded to Cl and O, but this is probably too far-going a simplification.

The value of this "reference difference" must be larger than the difference between the atomic radii of chlorine and oxygen, 0.25 Å. The Shomaker-Stevenson formula predicts a value of 0.30 Å, but it generally underestimates the bond contraction as shown by comparison with the difference between the recommended ² C—Cl and C—O bond lengths which is 0.34 Å. The slightly arbitrary assumption is here introduced that the *reference difference* in adduct molecules with symmetrical arrangement around the central atoms (tetrahedron around P and octahedron around Sb in the example) is independent of the nature of the central atoms and has a value of 0.32 ± 0.02 Å.

This is the most arbitrary assumption introduced so far in these discussions and its limitations must be kept in mind.

THE ACTUAL STRUCTURE

The deviations from the idealized charge distribution in the actual molecule can be discussed as a substitution effect. The P—Cl and P—O bonds are influenced by the fictive substitution of SbCl_5 for PCl_3^{2+} . As the electronegativity of P is higher than of Sb, and furthermore a positive charge is placed on the PCl_3 group, it can safely be assumed that the effective electronegativity of the PCl_3^{2+} group is larger than that of SbCl_5 . Electrons are thus released to the bridging oxygen atom at the substitution. This is the primary effect. As the net charge on P in POCl_3 is positive and the heteropolarity is $\text{P} \rightarrow \text{O}$ the electron addition will lead to an increased P—O bond energy (an electron withdrawal would lead to loss of bond energy according to the discussion in Ref. ¹). The secondary effect is a transfer of electrons from oxygen to phospho-

rus and to a smaller extent to chlorine. As the net charge on chlorine is negative and the heteropolarity is $P \rightarrow Cl$, the electron addition will decrease the P—Cl bond energy. The P—Cl bond will thus be longer and the P—O bond shorter than in the idealized structure, and the difference $|P-Cl| - |P-O|$ should have a larger value than 0.32 Å.

The Sb—Cl and Sb—O bonds are in the same way influenced by the fictive substitution of PCl_3^{2+} for $SbCl_5$. This corresponds to a transfer of electrons away from oxygen (compared with in the idealized structure): the Sb—O bond will be weaker and longer. The secondary effect is a withdrawal of electrons from Sb and to some extent from chlorine: the Sb—Cl bond will be stronger and shorter. The difference $|Sb-Cl| - |Sb-O|$ should thus be smaller than 0.32 Å.

Because of the mutual character of the fictive substitutions, the effects on the P—O and Sb—O bonds should be very similar, while the effect on Sb—Cl should be slightly smaller than on P—Cl because the secondary inductive effect is transmitted to five atoms from Sb and to only three from P. (Variations in polarizability might also be of importance.) If the secondary effect is low, the deviations from the reference difference, 0.32 Å, should, however, be very similar in magnitude, the deviation being possibly somewhat larger on the donor side ($POCl_3$). The values found ³ in $SbCl_5$ ($OPCl_3$) are (averaged values):

$$\begin{aligned} |P-Cl| - |P-O| - 0.32 \text{ \AA} &= 0.18 \text{ \AA} \\ |Sb-Cl| - |Sb-O| - 0.32 \text{ \AA} &= -0.17 \text{ \AA} \end{aligned}$$

Considering the uncertainty in the reference difference and the experimental bond lengths, the agreement is striking.

An equal or slightly larger effect would be expected in the compound $TiCl_4(OPCl_3)$ (the electronegativity of Ti is a little lower than that of Sb). This is actually a dimeric molecule ⁴, but the chlorine bridge formation will influence the Ti—Cl bonds (to nonbridging Cl) and the Ti—O bond to the same extent (*cf.* the discussion of halogen bridges in Ref.¹) and the relation should still be valid. The averaged values in $[TiCl_4(OPCl_3)]_2$ are:

$$\begin{aligned} |P-Cl| - |P-O| - 0.32 &= 0.20 \text{ \AA} \\ |Ti-Cl| - |Ti-O| - 0.32 &= -0.20 \text{ \AA} \end{aligned}$$

The assumption of a single bond structure is thus in complete accordance with the experimental evidence available at present. In the next section the consequences of the assumption of a double bond structure will be discussed.

THE DOUBLE BOND PICTURE

The introduction of a double bond [giving the bond system $Cl-P=O-Sb-Cl$] is tantamount to an electron transfer from the oxygen towards the phosphorus atom compared with in the bond system $Cl-P-O-Sb-Cl$ discussed above.

If the double bond exists, the P=O bond must be stronger than the P—O bond: the new homopolar bond energy must be larger than the loss of heteropolar bond energy (or there would not be any double bond). The P—Cl will be weakened, and the difference $|P-Cl| - |P-O|$ will increase further. Likewise the Sb—O bond energy will decrease and the Sb—Cl bond energy increase. The difference $|Sb-Cl| - |Sb-O|$ will be reduced accordingly.

The effect of a double bond will thus run parallel with the inductive effect of the donor-acceptor reaction, and no distinction can be made between the two bond pictures only from these data.

ADDUCTS OF SELENIUM OXYCHLORIDE

The discussion of $SbCl_5(OPCl_3)$ can easily be extended to adducts of $SeOCl_2$. The only structure known at present is that of $SnCl_4(OSeCl_2)_2$. The experimental data for this compound are ⁵ (averaged values):

$$\begin{aligned} |Se-Cl| - |Se-O| - 0.32 &= 0.09 \text{ \AA} \\ |Sn-Cl| - |Sn-O| - 0.32 &= -0.06 \text{ \AA} \end{aligned}$$

This structure is complicated by weak chloride bridge formation between Se and Sn, and the agreement with the predicted effect must be considered as good.

The smaller effect of the donor-acceptor reaction with $SeOCl_2$ is not only reflected in the smaller value of the deviations from the reference differences but also directly in the Sn—O and Sb—O distances. The Sn—O bond length is actually shorter than the Sb—O bond lengths (in the two compounds discussed earlier) although the radius of antimony should be smaller than that of tin. (In all periods the same trend is found near the inert gas end, that the covalent radius decreases with increasing atomic number.)

The reason why the effect is larger for $POCl_3$ than for $SeOCl_2$ will not be discussed in this paper.

EXTENSION TO OTHER ADDUCTS

If the ideas advanced here are correct, some predictions can be made about the effect in other adducts.

Adducts of phosphine oxides might first be compared with adducts of $POCl_3$. The only difference is that the positive net charge on the PCl_3^{2+} group must be larger than on PR_3^{2+} , and the effective electronegativity accordingly higher. The deviations from the reference differences should therefore be larger in the $POCl_3$ than in the POR_3 adducts. The structure of $SbCl_5[OP(CH_3)_3]$ is at present being investigated in order to test this conclusion.

A comparison between adducts of amine and phosphine oxides would be quite different. It is true that the inductive effect must be largest for the amine oxide if only single bond structures are compared, but two complicating factors must be considered. One is the fact that the heteropolarities of the bonds to carbon are different, $N \leftarrow C$ and $P \rightarrow C$. The net charge on carbon

is therefore positive in the amine oxide and negative in the phosphine oxide. The secondary effect of the electron addition (compared with in the idealized structure) will thus be a weakening of the P—C bond while the N—C bond energy will be augmented. (Electron addition gives opposite effects to electron withdrawal.) The difference $|N-C| - |N-O|$ is therefore not increased by the effect on the N—C bond and the deviation from the reference difference can be expected to be reduced to some extent. On the other hand there might be a double bond P=O in the phosphine oxides which cannot have a correspondence in the amine oxide. This would increase the deviation from the reference difference for the phosphine oxide adduct.

Both these factors thus work against the larger inductive effect in the single bond structure of the amine oxide adducts and the deviations from the reference difference might very well be larger for the phosphine oxide adducts than for the amine oxide adducts. Part of these difficulties might also be encountered in a comparison of sulfur and selenium compounds such as sulfides and selenium oxides. Structure determinations are in progress which probably will give information about these problems.

THE FREE DONOR MOLECULES

The idealized structure can also be used for a discussion of the free donor molecules. The inductive effect of subtracting of PCl_3^{2+} from the idealized structure $Cl_3POPCl_3^{2+}$ must be even larger than at the fictive substitution discussed for donor-acceptor interaction. The difference $|P-Cl| - |P-O| - 0.32 \text{ \AA}$ is actually $+ 0.23 \text{ \AA}$ in $POCl_3$, of the order of 0.05 \AA larger than in the adducts studied. A corresponding comparison cannot be made for $SeOCl_2$ because its structure is not known, but a study is in progress.

The discussion of the adducts of amine and phosphine oxides in the preceding section can obviously be directly applied to the free donor molecules. The reference differences $|N-C| - |N-O|$ and $|P-C| - |P-O|$ are 0.12 \AA (obtained as described earlier). The assumption that the differences should be equal is doubtful in this case with different heteropolarities in the bonds to carbon, but no other reasonable proposal can be made at present.

The values are:

$$\begin{aligned} |N-C| - |N-O| - 0.12 &= 0.06 \text{ \AA} \text{ (alternative value } -0.07 \text{ \AA)} \\ |P-C| - |P-O| - 0.12 &= 0.21 \text{ \AA} \text{ (Ref. } ^6) \end{aligned}$$

The larger deviation in the phosphine oxide is not unexpected in view of the preceding discussion. The quite different magnitudes of the two deviations indicates, however, that the phosphine oxide probably contains a double bond P=O: the difference between the single bond structures would be expected to be smaller. This is in agreement with the interpretation of the dipole moment measurements⁷. More structural information is necessary, however, before it can be safely stated that the structural evidence can distinguish between the single and double bond pictures. It would be particularly interesting to

know the S—O bond lengths in adducts of sulfones. A number of such adducts have recently been prepared ⁸ and the crystal structure determinations have shown that only one of the oxygen atoms functions as a donor atom ⁹.

CONCLUSION

The preceding discussions indicate that the donor action of oxide halides and organometalloid oxides can be explained, or at least rationalized in a rather simple fashion, if the inductive effects are fully considered in the way proposed. The limitations of the approach must be kept in mind until the experimental evidence is more complete. The arbitrariness of the present paper is obviously greater than in the general discussion of inductive effects in the preceding paper ¹, but no other approach seems at present to offer similar possibilities to compare bond length differences in a rather exact way. The future experimental results will show how far this is correct and in which respects the treatment must be modified or amended.

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