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ON THE REALITY OF POSITIVE FLUORINE

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SUMMARY

Recent experimental data are not consistent with the postulate of a positively polarized fluorine for compounds such as hypofluorites.

INTRODUCTION

In their recent paper on fluorination with positive fluorine, Cartwright and Woolf commented [1] on the marked reluctance by fluorine chemists to accept the "reality" of positive fluorine. They cite as evidence for this reality the weakening of aromatic carboxylic acids by o- and p- fluorine substitution and the $CF_3O\overset{\delta-}{-}\overset{\delta+}{F}$ polarity required to explain fluorination reactions. Whereas their first argument is not convincing experimental proof for positively polarized fluorine due to the complexity of the system and the different possible electronic effects, recent experimental studies show that in covalent hypofluorites fluorine is not positively polarized.

RESULTS and DISCUSSION

For example, the addition of $C\ell O_3OF$ to the unsymmetrical olefin $CF_3CF{=}CF_2$ produces 68% of $CF_3CF_2CF_2OC\ell O_3$ and 32% of $CF_3CF(OC\ell O_3)CF_3$. The direction and the nature of these addition products suggest that the O-F bond in $C\ell O_3OF$ is not strongly polarized in either direction, and that the direction of the addition is probably governed by steric effects with the bulkier CF_3 group repelling the larger $OC\ell O_3$ group [2]. Similar results were found for the addition of CF_3OF to olefins. By analogy with $C\ell O_3OF$, low stereospecificity was observed, and the direction of the addition was again governed mainly by steric effects [3].

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Extreme electronegativities, i.e. electronegativities larger than that of fluorine, have previously been postulated not only for the CF_3O- and $C\ell O_3O$- groups, but also for the TeF_5O- and SeF_5O- groups [4-6]. However recent multinuclear nmr and Mossbauer measurements have shown that fluorine is more electronegative than the TeF_5O- group with the latter having a value of 3.87 on the Pauling scale [7]. This is also supported by the results from the addition of TeF_5OF to olefins [8]. which are analogous to those obtained for $C\ell O_3OF$ and CF_3OF.

Since fluorine is the most electronegative element it appears logical that the addition of fluorine to a central atom of lower electronegativity cannot result in a group which has a group electronegativity higher than that of fluorine itself. In the extreme case, the addition of an infinite number of fluorines to a highly electronegative element might produce a group with an electronegativity assymptotically approaching that of fluorine. In the absence of convincing experimental data in favor of a positively polarized fluorine and in view of the existing experimental data to the contrary [2,3,7,8], the postulate of a positively polarized fluorine should be labeled 'misconception' rather than 'reality'.

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