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Reactions of Fluorine Perchlorate with Fluorocarbons and the Polarity of the O–F Bond in Covalent Hypofluorites

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Received March 9, 1979

Although $FOClO_3$ has been known for decades,[1,2] its reaction chemistry has remained virtually unexplored and is limited to references to unpublished work, cited in a review.[3] This lack of data is attributed to the previous report[2] that $FOClO_3$ consistently exploded during attempted freezing. During a study[4] of NF_4ClO_4, it was found that very pure $FOClO_3$ could be obtained in high yield by the thermal decomposition of NF_4ClO_4. The $FOClO_3$, prepared in this manner, could be manipulated and repeatedly frozen without explosions, thus allowing us to study some of its properties[5] and reaction chemistry.

Of particular interest to us were the reactions of $FOClO_3$ with fluorocarbons. Previous work[6] in our laboratory had demonstrated that $ClOClO_3$ and $BrOClO_3$ add readily to fluorocarbon double bonds, resulting in covalent fluorocarbon perchlorates. Consequently, one would expect fluorine perchlorate to undergo a similar reaction. However, a literature citation[3] suggested that $FOClO_3$ does not add across the double bond in $Cl_2C{=}CF_2$. Furthermore, reactions of covalent hypofluorites, such as CF_3OF, are commonly interpreted in terms of a highly unusual $CF_3O^{\delta-}$–$F^{\delta+}$ type polarization of the O–F bond ("positive fluorine"). If the O–F bond in CF_3OF is indeed polarized in this direction, the fluorine in $FOClO_3$ should be even more positive because of the higher electronegativity of the perchlorato group. Since the direction of the addition of a hypohalite across an unsymmetrical olefinic double bond strongly depends on the direction and the degree of polarization of the O–Hal bond,[7] a study of the $O_3ClOF/CF_3CF{=}CF_2$ reaction system offered an ideal opportunity to experimentally test the validity of the "positive fluorine" concept.

Experimental Section

Caution! Although no explosions were encountered in the present study, $FOClO_3$ must be considered a highly sensitive material and should be manipulated only in small quantities with appropriate safety precautions.

Apparatus and Materials. Volatile materials were manipulated in a well-passivated (with ClF_3) 304 stainless steel vacuum line equipped with Teflon-FEP U-traps and bellows-seal valves. Pressures were measured with a Heise Bourdon tube-type gage (0–1500 mm, ±0.1%). Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer. The ^{19}F NMR spectra were recorded on a Varian Model EM 390 spectrometer at 84.6 MHz using Teflon-FEP sample tubes (CS Laboratory Supplies) and $CFCl_3$ as an internal standard. Hexafluoropropylene and CF_3I were purchased while $CF_2{=}CF_2$ was prepared by pyrolyzing Teflon. Fluorine perchlorate was obtained from the decomposition of NF_4ClO_4.[4,5]

Reaction with Hexafluoropropylene. A 30-mL stainless steel cylinder was loaded at −196 °C with $FOClO_3$ (1.59 mmol) and C_3F_6 (2.05 mmol). The closed cylinder was warmed to −45 °C and kept at that temperature overnight. Separation of the products was achieved by vacuum fractionation in U-traps cooled at −78, −95, and −196 °C. The coldest trap contained unreacted C_3F_6 together with $FClO_3$, C_2F_5CFO, and a small amount of $(CF_3)_2CO$. In the other traps only the colorless liquid $C_3F_7OClO_3$ was found (1.18 mmol, 74% yield based on $FOClO_3$). The following temperature–vapor pressure data were measured (°C, mm): −46.6, 4; −22.7, 17; −9.3, 36; 0.0, 59; 10.6, 99; 22.0, 161. The vapor pressure–temperature relation is described by the equation $\log P = 7.5257 - (1571.94/T)$ (pressure in mmHg and temperature in K) with a calculated normal boiling point of 65.2 °C and a heat of vaporization of 7.19 kcal/mol. A vapor density of 265 g/mol was measured compared to a calculated value of 268.5 g/mol for $C_3F_7ClO_4$. Strong mass spectral peaks were found for the ions $C_2F_4ClO_4^+$, $C_3F_7^+$, $CF_2ClO_4^+$, $C_3F_5O^+$, $C_3F_5^+$, $C_2F_5^+$, $C_2F_4O^+$, $C_2F_4^+$, $C_2F_3O^+$, ClO_3^+, $C_2F_2O^+$, CF_3^+ (base peak), ClO_2^+, COF_2^+, ClO^+, CF_2^+, and COF^+. The following infrared bands were observed (cm^{-1}, intensity): 1340 (sh), 1325 (sh), 1290 (vs), 1250 (sh), 1235 (vs), 1200 (m), 1171 (w), 1153 (m), 1119 (ms), 1088 (m), 1026 (s), 988 (s), 968 (m–s), 784 (w), 746 (m), 723 (w), 676 (m), 641 (m–s), 614 (s), 530 (w).

Reaction with Tetrafluoroethylene. Fluorine perchlorate (0.61 mmol) and C_2F_4 (0.62 mmol) were combined at −196 °C in a 10-mL stainless steel cylinder. By evaporation of the liquid nitrogen from a liquid nitrogen–dry ice slush used to cool the reaction cylinder, the temperature was allowed to slowly rise to −78 °C and finally over several days by loss of solid CO_2 to about −45 °C. Fractional condensation of the products at −112 and −196 °C permitted the isolation of $C_2F_5OClO_3$ (0.42 mmol, 68% yield) which was identified by its known vibrational, NMR, and mass spectra.[8] Smaller amounts of CF_3CFO, C_2F_6, Cl_2, and O_2 were observed as byproducts.

Reaction with Trifluoromethyl Iodide. Into a cold (−196 °C) 30-mL stainless steel cylinder CF_3I (0.66 mmol) and then $FOClO_3$ (1.40 mmol) were condensed. Warm-up to about −45 °C was accomplished slowly as noted in the preceding example. After several days at −45 °C the reactor was recooled to −196 °C, and the presence of a considerable amount of noncondensable gas (oxygen) was noted. Fractionation of the condensable products showed a mixture of COF_2, CF_4, Cl_2, I_2, IF_5, and a solid iodine oxide to be the principal species present. However, a small amount of CF_3OClO_3 (0.05 mmol, 8% yield) was also found and identified by comparison with reported data.[8]

Results and Discussion

Under carefully controlled reaction conditions, similar to those previously used for the polar additions of $ClOClO_3$ and $BrOClO_3$,[6] fluorine perchlorate was found to add across olefinic double bonds in high yield. With tetrafluoroethylene the following reaction occurred:

$$CF_2{=}CF_2 + FOClO_3 \xrightarrow{-45\ ^\circ C} CF_3CF_2OClO_3$$

With the unsymmetrical olefin perfluoropropylene a mixture of two isomers was found

$$CF_3CF{=}CF_2 + FOClO_3 \xrightarrow{-45\ ^\circ C} \underset{68\%}{CF_3CF_2CF_2OClO_3} + \underset{32\%}{CF_3CF(OClO_3)CF_3}$$

These two perfluoropropyl perchlorates are novel compounds which were identified by vapor density measurements and spectroscopic data. The presence of the covalent $-OClO_3$ group was demonstrated by infrared spectroscopy which showed the intense bands typical of this group[8] at 1290 ($\nu_{as}(ClO_3)$), 1026 ($\nu_s(ClO_3)$), and 614 cm^{-1} (ν(Cl–O)). Additional support for the covalent perchlorate structure was obtained from the mass spectrum which showed strong peaks for the ions, ClO_3^+, ClO_2^+, and ClO^+ but not for ClO_4^+, as is generally the case for fluorocarbon perchlorates. A parent ion was not observed, and the highest m/e was $C_2F_4ClO_4^+$, i.e., the parent minus a CF_3 group.

Gas chromatography of the product revealed a slight asymmetry for the $C_3F_7ClO_4$ peak, thereby indicating the presence of isomers. This was confirmed by ^{19}F NMR spectroscopy, showing that both possible adducts were formed. The observed chemical shifts and coupling constants, together

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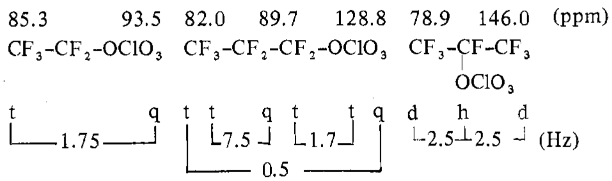
Chart I



with higher resolution data than previously reported[8] for $C_2F_5OClO_3$, are summarized in Chart I (d = doublet, t = triplet, q = quartet, h = heptet). The resonances of fluorines geminal to a perchlorato group were broadened due to chlorine quadrupole relaxation. On the basis of their relative peak areas, the ratio of the two isomers was *n* 68% and iso 32%.

The fact that in the reaction of $FOClO_3$ with $CF_3CF{=}CF_2$ both isomers are formed significantly differs from the previously reported[6] $ClOClO_3$ and $BrOClO_3$ reactions where exclusive Markownikoff type additions occurred. The latter produced 100% of $CF_3CFXCF_2OClO_3$, as expected for a polar addition of the positively polarized terminal halogen to the carbon with the highest electron density.[7]

$$CF_3CF{=}CF_2 + Cl^{\delta+}{-}O^{\delta-}ClO_3 \rightarrow CF_3CFClCF_2OClO_3$$

The formation of both isomers (*n* and iso) in the corresponding $FOClO_3$ reaction suggests that the F–O bond in $FOClO_3$ is not strongly polarized in either direction. This is not surprising in view of the known very small dipole moment (0.023 D) of the closely related $FClO_3$ molecule[9] and the expected similar electronegativities of a $-ClO_3$ and an $-OClO_3$ group. The fact that the percentage of *n* isomer was somewhat higher than that of the iso isomer can be explained by steric effects (bulky CF_3 group) and is insufficient reason to postulate a strongly positive fluorine in $FOClO_3$. The occurrence of a free-radical mechanism is unlikely in view of the high yield of the products (74%), the mild (−45 °C) and well-controlled reaction conditions, and the absence of detectable amounts of C_3F_8 and $C_3F_6(OClO_3)_2$ in the reaction products.

In contrast to the olefin addition reactions, the reaction of $FOClO_3$ with CF_3I was more difficult to control. The primary reaction path appears to have involved oxidation of the iodine followed by degradation to oxygenated and fluorinated species. Nevertheless, a modest yield (8%) of the desired perchlorate, CF_3OClO_3, was realized. By comparison, the $ClOClO_3$–CF_3I reaction is also vigorous but can be controlled to give a nearly quantitative yield of CF_3OClO_3.[8]

In summary, it has been shown that $FOClO_3$ can add to carbon–carbon double bonds to produce alkyl perchlorates in good yield. The formation of two isomers with the unsymmetrical olefin $CF_3CF{=}CF_2$ indicates that the O–F bond in $FOClO_3$ is of low polarity and does not justify the assumption of significant positive character for fluorine. Since a CF_3O- group is considerably less electronegative than a O_3ClO- group, the above results imply that, contrary to general acceptance, covalent hypofluorites, such as CF_3OF, do not contain a positive fluorine. Indeed, it would be most difficult to rationalize how the addition of fluorine to a less electronegative element, such as carbon, would render the latter more electronegative than fluorine itself.

Acknowledgment. We gratefully acknowledge helpful discussion with Dr. L. R. Grant and financial support of this work by the Office of Naval Research, Power Branch.

Registry No. $FOClO_3$, 10049-03-3; $CF_3CF_2CF_2OClO_3$, 70749-47-2; $CF_3CF(OClO_3)CF_3$, 70749-48-3; $C_2F_5OClO_3$, 22675-67-8; CF_3OClO_3, 52003-45-9; C_3F_6, 116-15-4; C_2F_4, 116-14-3; CF_3I, 359-37-5.

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Crystal and Molecular Structure of Bis(μ-acetato)-dichlorobis(dimethylphenylphosphine)dipalladium(II) Chloroformate

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Received February 12, 1979

Powell and Jack[1] examined a series of bridging *cis*-di-μ-carboxylate complexes of palladium(II) and, using IR spectra and variable temperature ^1H NMR techniques, inferred the possible existence of two conformational isomers. We report here details of a structure analysis of one Pd complex of this series, a preliminary account of which has been given in the paper by Powell and Jack.

Experimental Section

Crystals were obtained as red prisms from chloroform.[1] The crystal employed for this investigation had dimensions 0.32 × 0.64 × 0.24 mm and was sealed in a capillary tube with a few other small crystals of the same material at both ends. Preliminary crystal data were determined photographically. Fifteen general reflections in the range $31.0° < 2\theta < 35.3°$ were well centered on a computer-automated Picker diffractometer using filtered Mo Kα radiation to obtain the best least-squares crystal parameters. The density of the crystals was measured by flotation in a mixture of diethyl ether and tribromomethane.

Crystal Data

Bis(μ-acetato)-dichlorobis(dimethylphenylphosphine)dipalladium(II)-chloroform: $C_{20}H_{28}O_4Cl_2P_2Pd_2\cdot{}^1/_2CHCl_3$, $M_r = 797.5$; mp 132–140 °C; monoclinic, space group $P2_1/c$, $a = 8.119$ (3) Å, $b = 15.684$ (4) Å, $c = 22.406$ (6) Å, $\beta = 97.7$ (3)°; $D_m = 1.69$, $D_c = 1.70$ (25 °C) g cm^{-3}; $Z = 4$; λ 0.7107 Å, μ(Mo Kα) = 15.6 cm^{-1}.

A total of 5844 intensities was collected in the θ–2θ scan mode at 2° min^{-1}; $\sigma(I)$ was taken as (scan + $\sum B_c)^{1/2}$ where B_c is the background count. The 3972 reflections with $I > 2\sigma(I)$ were considered to have significant intensity. The structure was solved by the heavy-atom method, scattering factors used being those of Cromer and Mann[2] with anomalous dispersion corrections. For P, Cl, and Pd atoms, $\Delta f'$ and $\Delta f''$ are 0.1 and 0.2, 0.1 and 0.2, and −1.1 and 1.2, respectively.[3] Idealized positions for hydrogen atoms (C–H = 1.00 Å) were included in F_c with isotropic temperature factors, B, taken as 6.0 Å^2. The R value with anisotropic thermal factors for nonhydrogen atoms was 0.083. Atomic coordinates are given in Table I. At this stage of refinement several peaks with electron density as high as 3.5 e A^{-3} were found around the centers of symmetry (0, $^1/_2$, 0) and (0, 0, $^1/_2$). The crystal density indicated that these peaks correspond to solvent chloroform molecules. By use of program HOLE[4] it was found that each site could accommodate only one chloroform molecule, that is, a total of two solvent molecules per unit cell. Since $CHCl_3$ lacks a center of symmetry, it must be disordered at the two sites. The electron density map shows in fact six relatively heavy peaks about the center, and assuming them to be of chlorine atoms, we derived a best-fitting set of chloroform atom coordinates based on a C–Cl distance of 1.762 Å and a Cl–C–Cl angle of 110.9°. These atoms were included (multiplicity 0.5) with fixed positions in the last cycle of least-squares refinement. The temperature factors were large

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