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Carbonyl Fluoride of Molybdenum (Synthesis and Structural Investigation)

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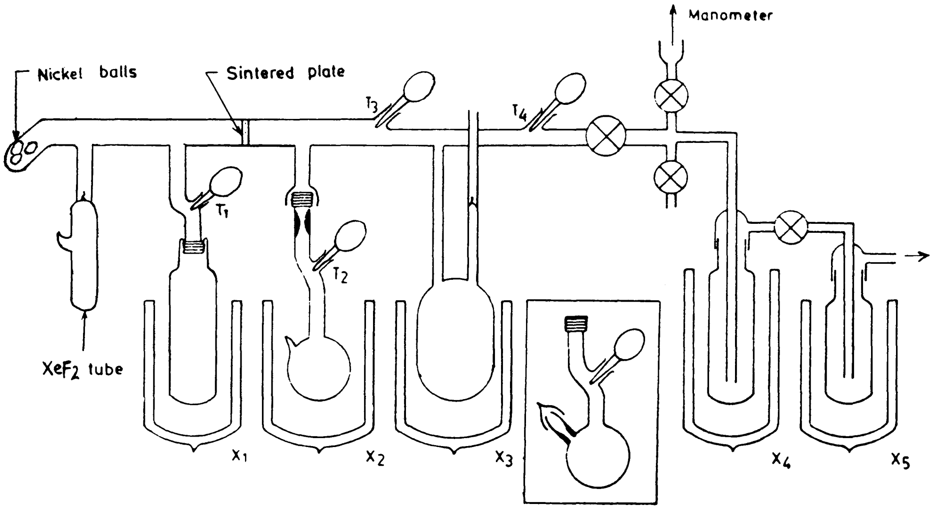
Synopsis. Difluorotricarbonylmolybdenum $MoF_2(CO)_3$ has been synthesized by selective fluorination of molybdenum carbonyl by xenon difluoride in perfluoro solvents as well as in anhydrous hydrogen fluoride. The titled compound was isolated as an orange yellow solid and its composition was established by elemental analysis. It decomposes very slowly at room temperature, but on heating at 100 °C it decomposes completely to yield molybdenum carbonyl, molybdenum fluoride oxide and molybdenum fluoride. The compound was structurally characterized using IR, mass spectral, and X-ray powder diffraction analysis.

Sharp in 1960 reported[1)] the preparation of dicarbonyl octafluoro platinum $PtF_8(CO)_2$ and dicarbonyl trifluoro rhodium $RhF_3(CO)_2$, though the existence of these compounds is still considered to be doubtful. Haig[2)] later proved that dicarbonyl octafluoro platinum was nothing but dibromo dicarbonyl platinum. O'Donnell and Phillips[3)] reported the isolation of $MoF_4(CO)_4$ from the reaction mixture of molybdenum hexacarbonyl and molybdenum hexafluoride in Kel-F system. The product obtained by Donnell and Phillips,[3)] was however, contaminated with molybdenum tetrafluoride oxide and unreacted molybdenum carbonyl as well molybdenum pentafluoride. The same authors[4)] also studied the fluorination of rhenium carbonyl by rhenium fluoride and have isolated a compound which was formulated to be $ReF_3(CO)_3$. Bruce and coworkers[5)] have made a systematic study of the reaction of rhenium carbonyl with rhenium hexafluoride in anhydrous hydrogen fluoride and have isolated two types of products: orange presin and green platelets in very high yield. O'Donnell and Phillips[6)] later modified their version and have reported the formation of $ReF(CO)_5$ from the reaction between rhenium carbonyl and rhenium hexafluoride; further reaction of $ReF(CO)_5$ with XeF_2, they asserted yielded $ReF_3(CO)_3$. One of the authors (SNM) attempted the selective fluorination of rhenium carbonyl by xenon difluoride in perfluoro solvents and had isolated a complex having the composition $3[ReF_2(CO)_3]\cdot ReF_5$. Similar interesting results were obtained when iridium system was studied. In view of this we have tried to prepare difluorotricarbonyl molybdenum; isolation and structural characterization of this compound are reported in this paper.

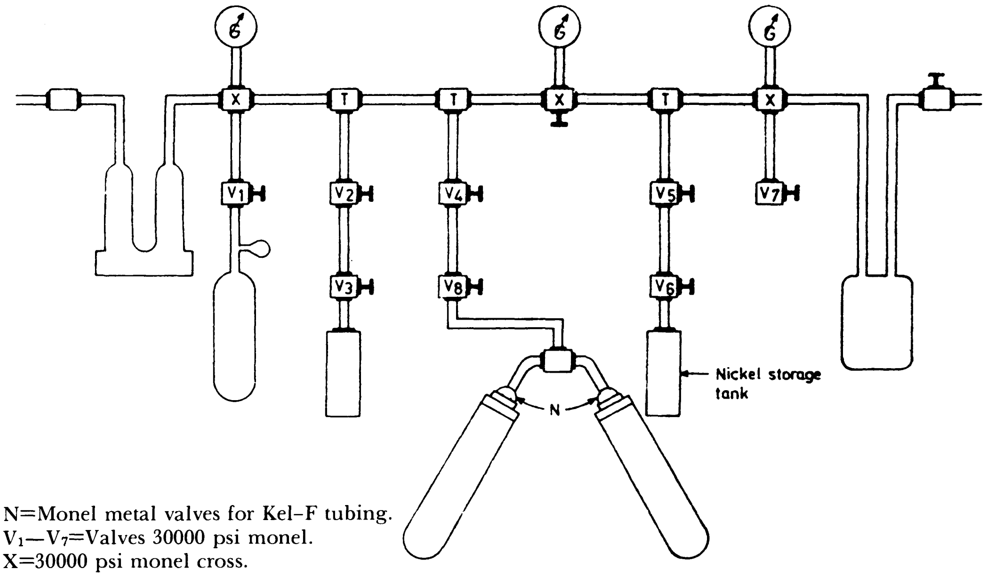
Experimental

Reaction of Molybdenum Carbonyl and Xenon Difluoride in Inert Solvent Genetron/Perfluoro Hydrocarbons Like PP-3 (Perfluoro-1,3-dimethylcyclohexane) and PP-9 (Perfluoro-1-methyldecaline). The apparatus used is shown in Fig. 1. Hexacarbonyl molybdenum (0.360 g) was transferred to the reaction flask and it was connected to the vacuum line and evacuated. The glass vacuum line was evacuated to exclude moisture and air. Perfluoro hydrocarbons or genetron was condensed in the reaction flask by the help of Taps T_1, T_2, T_3. All the taps were closed and the delicate glass seal of xenon difluoride tube was broken by dropping nickel balls through a magnet and xenon difluoride was condensed in the reaction flasks maintained at liquid oxygen temperature. The reaction was exothermic and resulted in the isolation of orange solid. Excess solvent was then distilled out and the



T_1—T_4: Rotoflow taps.
X_1—X_5: Dewar flask kept at liquid oxygen temperature.
Inset showing reaction vessel.

Fig. 1. An assembly used for the synthesis of carbonyl fluorides of molybdenum, tungsten, and rhenium.



N=Monel metal valves for Kel-F tubing.
V_1—V_7=Valves 30000 psi monel.
X=30000 psi monel cross.
G=Welded monel bourdon gauge 0—1500 mmHg.

Fig. 2. Metal vacuum line with Kel-F reaction vessel.

system was pumped for overnight to remove unreacted xenon difluoride and other volatile contaminant. The reaction vessel was then disconnected from the line by sealing off its narrow end and immediately transferred to the inert box (yield 63%). Found: Mo, 43.6; C, 15.8; F, 18.4%. Calcd for $MoC_3O_3F_2$: Mo, 44.5; C, 16.3; F, 17.2%.

Reaction of Molybdenum Carbonyl and Xenon Difluoride in Stoichiometric Ratio 1:2 in Anhydrous Hydrogen Fluoride in Metal Vacuum Line. The reaction was carried out in assembly shown in the Fig 2. Both Kel-F tubes were first seasoned with hydrogen fluoride overnight. One of the tubes was removed from the line and placed in the dry box. A weighed amount of molybdenum carbonyl (0.4 g) was then transferred to the tube and the tube was connected to the vacuum line and evacuated. Anhydrous hydrogen difluoride (0.5 g) was condensed in another Kel-F tube which already had xenon difluoride. Both the tubes were then connected by opening the values in between them so that xenon difluoride hydrogen fluoride mixture slowly gets condensed in the tube containing molybdenum carbonyl. This assembly was left as such overnight. An orange crystalline solid separated out from the resulting orange solution. The solvent was then removed with the isolation of more and more solid. The product was purified by repeated washing with anhydrous hydrogen fluoride in the vacuum line. Found: Mo, 44.0; F, 18.0%. Calcd for $MoC_3O_3F_2$: Mo, 44.5; F, 17.2%.

Purification of Carbonyl Fluoro Molybdenum. Tricarbonyl difluoro molybdenum was taken in quartz tube B in the inert box and the assembly was evacuated by attaching it to the vacuum line. Tungsten hexafluoride was condensed at tube B by cooling it at liquid air temperature. After collecting sufficient amount of WF_6 the tube B was warmed up to the room temperature and left for two hours. The whole assembly was then rotated by 180° so that insoluble carbonyl fluoro molybdenum remained in the tube B while soluble fluorides of molybdenum collected in the tube A. Excess WF_6 was pumped back to the storage tube and the product in the tube B was dried in vacuo and characterized by analysis and IR.

Molybdenum in this complex was estimated by fusing with NaOH and Na_2O_2 mixture followed by precipitating metal gravimetrically as 8-hydroxy quinolinate. Fluorine in this compound was estimated by Seels' method.

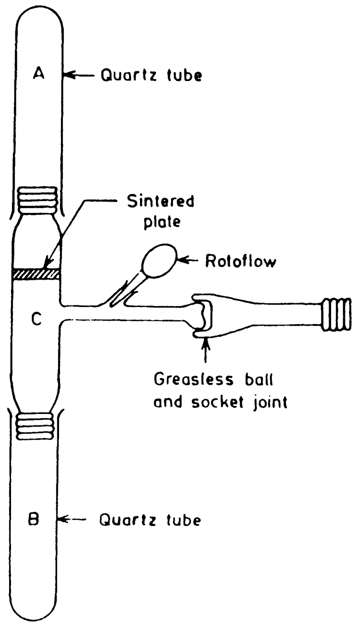


Fig. 3. Assembly used for the purification of cabonyl fluoride.

The molecular weight of carbonylfluoromolybdenum was determined in anhydrous hydrogen fluoride cryoscopically; this revealed a molecular complexity of around 4, thus indicating the molecules to be a tetramer, having the composition $[MoF_2(CO)_3]_4$.

Results and Discussion

O'Donnell and Phillips claimed to have isolated a polymeric dicarbonyltrifluoromolybdenum(III)[6] from the reaction mixture of molybdenum hexafluoride and hexacarbonyl molybdenum(0) in Kel-F apparatus. However, an attempt made by Edward and coworkers[8] to study the same reaction in glass apparatus resulted in the formation of fluorides of molybdenum and with no evidence for the formation of any other compounds. O'Donell's samples were invariably contaminated with molybdenum pentafluoride and molybdenum tetrafluoride oxide.

Holloway and Szary[9] have made a systematic study of molybdenum carbonyl molydbenum pentafluoride system in genetron and in anhydrous hydrogen fluoride in the stoichiometric ratio of 1 : 1. They have observed that the reaction was slow in genetron but faster in anhydrous hydrogen fluoride. The product showed carbonyl stretching at 2145 (s) and 2060 (s) cm^{-1}. This compound was neither molybdenum pentafluoride nor carbonylfluoro complex, which is generally formed in xenon difluoride reaction. The resulting product was identical with the one isolated by O'Donnell; however, Holloway and Szary have proposed the following formulation for the resulting compound:

$[Mo(CO)_6]^+[MoF_6]$ or $[Mo(CO)_6]^+[Mo_2F_{11}]$ or
$[Mo(CO)_5]^+[Mo_3F_{16}]$ or $[Mo(CO)_4F_2][Mo_2F_{11}]$

Elemental analyses of the products obtained in our reactions established the stoichiometry unequivocally as $Mo(CO)_3F_2$. The bands observed in the region 2200—1900 cm^{-1} in the infrared spectrum of carbonylfluoromolybdenum are typical of terminal carbonyl ligands [ν_{CO} at 2125(s), 2085(s), 2035(s), 1980(s), 1950(s)]. Since the carbonyl fluoride contains highly electronegative fluorine as substituent, it is not surprising that the carbonyl frequencies are also observed at higher wavenumber than the parent carbonyl complex. A comparison of the infrared spectra of the carbonylhalogeno complexes of molybdenum [$MoCl_2(CO)_3$ ν_{CO} at 2100(s), 2050(s), 1980(s), 1956(s), and $MoBr_2(CO)_3$ ν_{CO} at 2098(s), 2080(s), 2007(s), 1958(s)] confirm that these shift to lower wavenumber as the substituent changes from fluorine to bromine.

The Mo–F stretching frequencies were observed at 660 (w), 620 (w), 600 (w), and 560 (w) cm^{-1} indicating terminal and bridging fluoride ligands.

In the tricarbonyldifluoromolybdenum, the metal has d^4 configuration, which is quite susceptible to Jahn Teller distortion to one of the lower states, which will destroy the electronic degeneracy. When the distortion energy is comparable to the energy of the relevant vibration mode, no static distortion will be observed; however, certain abnormalities in the electronic spectra are expected as a result of electronic coupling.

The mass spectrum of tricarbonyl difluoromolybdenum indicated the presence of some fragments with dimeric units such as $[MoF_2(CO)_2]^+$, $[MoF_2(CO)_3]^+$, and $[MoF_4(CO)_4]^+$ along with several monomeric units, suggesting the molecular complexity to be more than two.

Our efforts to grow single crystals suitable for a detailed X-ray diffraction study were met with no success. However, a decent powder pattern of the substance could be recorded with Ni filtered Cu $K\alpha$ radiation. The analysis of this photograph showed that though the compound gives a pattern similar to that of tricarbonyl difluororuthenium, for which a detailed X-ray study has been carried out by Peacock et al.,[10] the intensities differ somewhat. The powder pattern could be indexed on an orthorhombic cell of dimensions a=11.221, b=10.742, and c=9.384 Å. The density calculated on the basis of 8 formula units per unit cell is 2.560 $g\,cm^{-1}$. The study on the ruthenium[10] compound also indicated that it exists as a tetrameric unit with fluorides in cis arrangement and in bridging positions.

A mechanistic study on the structural arrangement can be attempted on the following lines. The formation of 'cis' isomer from hexacarbonyl complex and fluorine can be tentatively explained by assuming simultaneous attack of hexacarbonyl complex by two atoms of the fluorine molecule. The alternate possibility of heterocyclic cleavage of fluorine molecule to give the nucleophilic fluorine would result in the preliminary introduction of the 'first fluorine'; entry of the second fluorine in the cis position would certainly be statistically favored and most probably electronically favoured too in view of the strong 'trans' effect of the carbon monoxide ligand.

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