

Changes of carbonyl bond stretch frequency of Vaska's complex with added bromine and sulfur respectively in different solvents.

Introduction

Vaska's complex (bis(triphenylphosphine) iridium (I) carbonyl chloride) is a catalyst molecule that is important for improving rates of chemical reactions. The catalytic process involves binding of reactants to the metal of Vaska's complex. At this stage, the surrounding solvent molecules undergo a rapid rearrangement. The solvent dependency of Vaska's complex in a catalytic process can be studied using Fourier Transform Infrared Spectroscopy (FTIR).

Objective

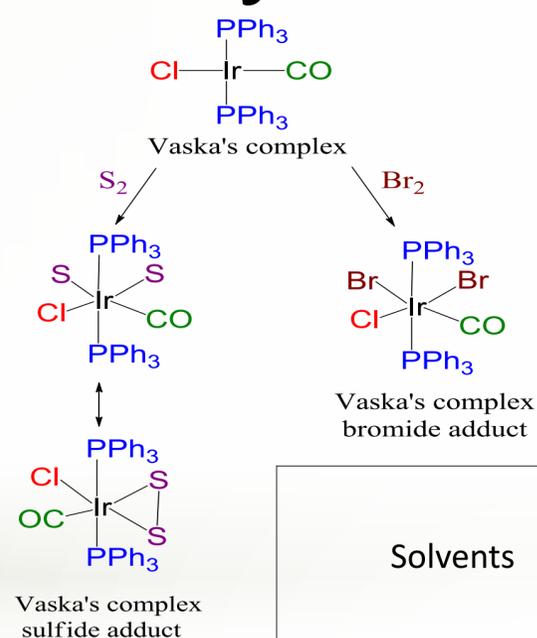
To investigate the changes of carbonyl bond stretch of Vaska's complex with added bromine and sulfur respectively in 16 different solvents.

Hypothesis

If the adduct is sensitive to the solvents, the frequency of the carbonyl bond stretch would vary significantly.

Reference

Jones, B. H.; Huber, C. J.; Massari, A. M. Solvation Dynamics of Vaska's Complex by 2D-IR Spectroscopy *J. Phys. Chem. C* **2011**, 115, 24813-24822



Methods

Vaska's complex bromine adducts were prepared by mixing 5mg Vaska's complex, 0.7 μ L bromine and 1mL solvent. Vaska's complex sulfur adducts were prepared by mixing 5mg Vaska's complex, 1mg sulfur and 1mL solvent. The solution was placed in a sample cell and the IR spectrum of the solution was taken using Nicolet 6700 FT-IR.

Results

| Solvents | Carbonyl stretch frequencies, ν_{CO} in Vaska's complex Adducts (cm^{-1}) | |
|--------------------------|--|------------------|
| | Bromine | Sulfur |
| chloroform | 2076.0 | 2051.7 |
| benzene | 2075.9 | 2053.4 |
| dimethylformamide (DMF) | 2076.5 | 2047.7 |
| acetonitrile | 2075.9 | 2046.7 |
| toluene | 2075.4 | 2054.1 |
| tetrahydrofuran (THF) | 2075.5 | 2049.5 |
| 1,2-dichlorobenzene | 2075.7 | 2046.2 |
| chlorobenzene | 2075.9 | 2051.4 |
| acetone | 2074.2 | 2048.6 |
| pyridine | 2076.6 | 2058.1 |
| benzonitrile | 2074.1 | 2053.8 |
| dimethylsulfoxide (DMSO) | 2067.7 | 2049.9 |
| dichloromethane | 2073.5 | 2054.2 |
| 2-phenylethanol | 2076.4 | 2053.1 |
| benzyl alcohol | 2076.4 | 2053.2 |
| m-cresol | no peak observed | no peak observed |

Nicolet 6700 FT-IR



Conclusions

Addition of bromine increased the carbonyl vibration more than the addition of sulfur to the Vaska's complex indicating addition of bromine had weakened the bond between carbon of carbonyl and iridium compared to the addition of sulfur. From the results, the bromine adducts are less sensitive to the nature of the solvents, while the sulfur adducts experience moderate frequency shifts in different solvents. This difference is attributed to the different ways sulfur and bromine bind to the iridium in Vaska's complex.

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