1. [8 points] In your own words, briefly summarize the reason this work is being performed.
2. [4 points] Briefly define monomers and polymers.
3. [4 points] What is the structure of PVC?
4. [8 points] At the end of the second paragraph of the introduction, the authors mention one of their recent studies in which they were able to convert PVC to poly(ethylene-*co*-stryenic) copolymers. Draw the structure of styrene and describe what you think the term to poly(ethylene-*co*-stryenic) copolymers means. While an interesting study, why do the authors suggest that there are limitations to this method?
5. [8 points] The proposed active catalyst in this work is [Rh(Xantphos)Cl] which is shown in Fig. 1b. Using the CBC method, classify the catalyst, provide an electron count, the ligand bond number, the valence on rhodium and the dn count for rhodium.
6. [8 points] If you dig into the supporting information, you discover that the authors do not actually isolate [Rh(Xantphos)Cl], but rather isolate [Rh(Xantphos)(cod)Cl] where cod is η4-cyclooctadiene. This compound is an 18-electron species. Using the CBC method, suggest how this can be an 18-electron species being sure to account for the ligand coordination (hint: it is different than in the previous question) and bond number, the valence on rhodium and the dn count for rhodium. Clearly indicate how the Xanthphos ligand is coordinated.
7. [8 points] The 31P{1H} NMR spectrum of [Rh(Xantphos)(η4-cod)Cl] is shown below. How do you then account for the 31P{1H} spectrum?

[Insert Fig. S2 here]

1. [8 points] The authors were not able to isolate [Rh(Xantphos)Cl] which is shown in Fig. 1b, but if they had, how many signals for the backbone of the Xanthphos ligand (*i.e.* not the Ph groups) would you expect to see in the 1H NMR spectrum of the compound? What would the relatively intensities of those signals be?
2. [12 points] In theory, the authors could have examined the IR of [Rh(Xantphos)Cl] and examined the C-O vibrations. Using group theory, how many IR active C-O vibrations should they have expected to see in this molecule?
3. [8 points] Although the exact method of synthesis is not exactly clear, the structure of [Rh2(Xantphos)2(μ-Cl)2] has been reported (*Catal. Sci. Technol.* **2014**, *4*, 3409). This compound has an electron count of sixteen. Using the CBC method, classify this dimer, provide an electron count, the ligand bond number, the valence on rhodium and the dn count for rhodium. Note that the dimer is symmetric, so you need only determine half of the molecule and that we have seen two different coordination modes of the Xantphos ligand, be clear about how it is coordinated.
4. [8 points] The addition of H2 to [Rh2(Xantphos)2(μ-Cl)2] results in the formation of [Rh(Xantphos)(H)2Cl] (*Organometallics* **2015**, *34*, 711). This compound has an electron count of eighteen. Using the CBC method, classify this compound, provide an electron count, the ligand bond number, the valence on rhodium and the dn count for rhodium. Note that the Xantphos ligand has displayed two different coordination modes so far, clearly indicate how it is coordinated.
5. [8 points] Shown below are the average Rh-O distances and the P-Rh-P angles for the three compounds mentioned previously. What is suggested by these differences and how do you explain why they are observed?

|  |  |  |
| --- | --- | --- |
| **Compound** | **Rh-O in Å** | **P-Rh-P** |
| [Rh(Xantphos)(η4-cod)Cl] | 3.518 | 105.20 |
| [Rh2(Xantphos)2(μ-Cl)2] | 3.450 | 102.38 |
| [Rh(Xantphos)(H)2Cl] | 2.248 | 163.85 |

1. [8 points] The authors suggest two different methods/mechanisms of chloride removal in the second and third paragraphs of the introduction. The second one is hydrodechlorination (HDC), which is the focus of this paper. The specific product for HDC is shown at the top of Fig. 1. There is a little less information provided about the other, dehydrochlorination (DHC), but there are some hints provided. The authors state that “the organic polymer fragment is not prioritized”. From the following sentences, suggest how the product of DHC might be different from that of HDC.
2. [12 points] The proposed mechanism for the catalytic process is proposed in a computational study by the authors (*Phys. Chem. Chem. Phys* **2022**, *24*, 3518). This mechanism is shown in the figure below with 1-chloropropane as the substrate. Suggest what reactions are taking place for each step in the mechanism and provide support for your answers.

[Insert Fig. 1 from *Phys. Chem. Chem. Phys* **2022**, *24*, 3518 here]

1. [8 points] The second step in the previous mechanism could be through of as occurring by two different specific mechanisms. Hopefully in the previous question you used a generic description that would cover either of these two mechanisms. This about the electron count of the product of the first step and some of the previous questions about electron count. Describe how you could rationalize either of the two possible mechanisms for the second step.
2. [8 points] Figure 3 displays the IR results of four different catalytic studies. Which source of hydrogen and solvent appears to be best in this system? Why? Which is the worst? Why?
3. [10 points] Oh no, a calculation! Who would have thought it possible? Consider vinyl chloride (H2C=CHCl) and ethylene (H2C=CH2). Calculate the %C and %H by mass in these two compounds. Compare this data to the Elemental Analysis (EA) data in Figure 4A. What can you conclude from your calculations and this data?
4. [8 points] The authors performed thermalgravimetric analysis (TGA) on the products from various hydrogen sources and compared them to PVC. The TGA plot is shown below. Based on the plot, suggest what is happening in these experiments and how the TGA results are in agreement with those from IR spectroscopy. What might be happening around 300 ˚C?

[Insert Fig. S48 here]

1. [8 points] In Figure 4B, the authors report the differential scanning calorimetry (DSC) data for one of their products. The x-axis is pretty straightforward. What do you think is going on with the y-axis and what might be the significance of the Tm? There is not a lot to work with here in the text, give it your best shot. What do the authors learn about the product of their reaction from the DSC analysis?
2. [8 points] The gel permeation chromatography (GPC) analysis of the product obtained after treatment with the rhodium catalyst and sodium formate was compared to that of PVC with the data presented below. How do the masses of these two materials compare and why is that significant to this study? The PD is a measurement of the distribution of the lengths of the polymer chains. If all of the polymer chains were exactly the same length, the PD would be 1. How do the PD values of these two materials compare and what are the implications of this measurement?

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| --- | --- | --- |
|  | **MW (g/mol)** | **PD** |
| Post catalysis | 10683 | 2.069 |
| PVC | 119152 | 1.732 |

1. [8 points] What is the significance of Figure 5?

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| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **1A****1** |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | **8A****18** |
| 1H1.008 | **2A****2** |  |  |  |  |  |  |  |  |  |  | **3A****13** | **4A****14** | **5A****15** | **6A****16** | **7A****17** | 2He4.003 |
| 3Li6.941 | 4Be9.012 |  |  |  |  |  |  |  |  |  |  | 5B10.811 | 6C12.011 | 7N14.007 | 8O15.999 | 9F18.999 | 10Ne20.180 |
| 11Na22.989 | 12Mg24.305 | **3B****3** | **4B****4** | **5B****5** | **6B****6** | **7B****7** | **←****8** | **8B****9** | **→****10** | **1B****11** | **2B****12** | 13Al26.982 | 14Si28.086 | 15P30.974 | 16S32.066 | 17Cl35.453 | 18Ar39.948 |
| 19K39.098 | 20Ca40.078 | 21Sc44.955 | 22Ti47.867 | 23V50.941 | 24Cr51.996 | 25Mn54.938 | 26Fe55.845 | 27Co58.933 | 28Ni58.693 | 29Cu63.546 | 30Zn65.39 | 31Ga69.723 | 32Ge72.61 | 33As74.922 | 34Se78.96 | 35Br79.904 | 36Kr83.80 |
| 37Rb85.468 | 38Sr87.62 | 39Y88.905 | 40Zr91.224 | 41Nb92.906 | 42Mo95.94 | 43Tc(98.91) | 44Ru101.07 | 45Rh102.905 | 46Pd106.42 | 47Ag107.868 | 48Cd112.411 | 49In114.818 | 50Sn118.710 | 51Sb121.760 | 52Te127.60 | 53I126.904 | 54Xe131.29 |
| 55Cs132.905 | 56Ba137.327 | 57La\*138.906 | 72Hf178.49 | 73Ta180.947 | 74W183.84 | 75Re186.207 | 76Os190.23 | 77Ir192.217 | 78Pt195.078 | 79Au196.967 | 80Hg200.59 | 81Tl204.383 | 82Pb207.2 | 83Bi208.980 | 84Po(209) | 85At(210) | 86Rn(222) |
| 87Fr(223) | 88Ra226.03 | 89Ac†227.03 | 104Rf(267) | 105Db(268) | 106Sg(271) | 107Bh(272) | 108Hs(270) | 109Mt(276) | 110Ds(281) | 111Rg(280) | 112Cn(285) | 113NH(284) | 114Fl(289) | 115Mc(288) | 116Lv(293) | 117Ts(294) | 118Og(294) |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| \* Lanthanides | 58Ce140.116 | 59Pr140.908 | 60Nd144.24 | 61Pm(145) | 62Sm150.36 | 63Eu151.964 | 64Gd157.25 | 65Tb158.925 | 66Dy162.50 | 67Ho164.930 | 68Er167.26 | 69Tm168.934 | 70Yb173.04 | 71Lu174.967 |
| † Actinides | 90Th232.0.8 | 91Pa231.036 | 92U238.029 | 93Np237.05 | 94Pu(244) | 95Am(243) | 96Cm(247) | 97Bk(247) | 98Cf(251) | 99Es(252) | 100Fm(257) | 101Md(258) | 102No(259) | 103Lr(262) |

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| Insert group theory flow chart here |

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| **Cs** | E | σh | Linear f, rotations | Quadratic f |
| Aʹ | 1 | 1 | x, y, Rz | x2, y2, z2, xy |
| Aʹʹ | 1 | -1 | z, Rx, Ry | yz, xz |

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| **C2v** | E | C2 (z) | σv(xz) | σv(yz) | Linear f, rotations | Quadratic f |
| A1 | 1 | 1 | 1 | 1 | z | x2, y2, z2 |
| A2 | 1 | 1 | -1 | -1 | Rz | xy |
| B1 | 1 | -1 | 1 | -1 | x, Ry | xz |
| B2 | 1 | -1 | -1 | 1 | y, Rx | Yz |

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| **C2h** | E | C2 (z) | i | σh | Linear f, rotations | Quadratic f |
| Ag | 1 | 1 | 1 | 1 | Rz | x2, y2, z2, xy |
| Bg | 1 | -1 | 1 | -1 | Rx, Ry | xz, yz |
| Au | 1 | 1 | -1 | -1 | z |  |
| Bu | 1 | -1 | -1 | 1 | x, y |  |

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| **D2h** | E | C2 (z) | C2 (y) | C2 (x) | i | http://symmetry.jacobs-university.de/pics/sigma.gif(xy) | http://symmetry.jacobs-university.de/pics/sigma.gif(xz) | http://symmetry.jacobs-university.de/pics/sigma.gif(yz) | Linear f, rotations | Quadratic f |
| Ag | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | - | x2, y2, z2 |
| B1g | 1 | 1 | -1 | -1 | 1 | 1 | -1 | -1 | Rz | xy |
| B2g | 1 | -1 | 1 | -1 | 1 | -1 | 1 | -1 | Ry | xz |
| B3g | 1 | -1 | -1 | 1 | 1 | -1 | -1 | 1 | Rx | yz |
| Au | 1 | 1 | 1 | 1 | -1 | -1 | -1 | -1 | - | - |
| B1u | 1 | 1 | -1 | -1 | -1 | -1 | 1 | 1 | z | - |
| B2u | 1 | -1 | 1 | -1 | -1 | 1 | -1 | 1 | y | - |
| B3u | 1 | -1 | -1 | 1 | -1 | 1 | 1 | -1 | x | - |

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| **D2d** | E | 2S4 | C2 (z) | 2Cʹ2 | 2σd | Linear f, rotations | Quadratic f |
| A1 | 1 | 1 | 1 | 1 | 1 |  | x2 + y2, z2 |
| A2 | 1 | 1 | 1 | -1 | -1 | Rz |  |
| B1 | 1 | -1 | 1 | 1 | -1 |  | x2– y2 |
| B2 | 1 | -1 | 1 | -1 | 1 | Z | xy |
| E | 2 | 0 | -2 | 0 | 0 | (x, y), (Rx, Ry) | (xz, yz) |

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