Thermochemistry of Oxygen Atom Transfer from Cp^*ReO_3

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Summary: The reaction enthalpy for O atom transfer from Cp^*ReO_3 to PPh_3 in toluene solution is measured to be −28.4 ± 0.3 kcal/mol and −28.0 ± 0.6 kcal/mol in THF solution. This allows the strength of the Re═O bond in Cp^*ReO_3 (in solution) to be estimated at 116.8 ± 1.2 kcal/mol.

Introduction

Investigation of the chemistry of rhenium oxo complexes has been an area of intense recent interest. In particular, several closely related species having an ancillary Cp* ligand ($Cp^* = \eta\text{-}C_5Me_5$) are involved in oxygen atom transfer.[1] We have become interested in the ability of rhenium complexes to mediate O atom transfer to and from organic substrates. Given the relative scarcity of thermodynamic data for such reactions,[2] we undertook an examination of the heat of reaction for O atom transfer from Cp^*ReO_3 to PPh_3. Coupled with earlier measurements, this allows a reliable estimation of the Re═O bond strength in Cp^*ReO_3.

Results and Discussion

Measurement of Reaction Enthalpies. It has been known for some time that Cp^*ReO_3 will transfer an oxygen atom to PPh_3, resulting in formation of the bridging oxo dimer $(Cp^*ReO)_2(\mu\text{-}O)_2$.[3] We determined the overall reaction enthalpy for this oxo transfer reaction in toluene and in THF solutions. Considering the enthalpy of solution of Cp^*ReO_3 (+4.5 ± 0.1 kcal/mol in toluene, +5.6 ± 0.1 kcal/mol in THF), the enthalpy of reaction with all species in solution is −28.4 ± 0.3 kcal/mol in toluene and −28.0 ± 0.6 kcal/mol in THF.

We may construct a thermochemical cycle incorporating the ΔH_{rxn} for oxidation of PPh_3 to the phosphine oxide[4−6] to arrive at the enthalpic difference between Cp^*ReO_3 and $(Cp^*ReO)_2(\mu\text{-}O)_2$ in solution. To arrive at this, we first relate the trioxo and dimer compounds (eq 1). This reaction enthalpy is not the Re−O BDE for Cp^*ReO_3. Cp^*ReO_3 has three equivalent multiple (formally double) bonds between Re and O, while in the dimer each rhenium participates in one multiple Re═O and two bridging Re−O single bonds. (There is also probably a Re═Re bond.)[7] To arrive at the BDE, we must include the enthalpy of fragmentation of the dimer, which we have measured previously by NMR as +16.8 ± 0.3 kcal/mol for the dimer.[1a] Adding in this factor (8.4 ± 0.3 kcal/mol per rhenium atom) gives eq 2. This BDE estimate is somewhat lower than our previous lower-bound estimate of 120 kcal/mol [1a] but is more reliable. The previous estimate based on free energy differences included entropy changes, while this one relies on direct enthalpy measurements.

$$\begin{array}{ll}
\mathrm{Cp^*ReO_3\ (toluene) + PPh_3\ (toluene) \rightleftarrows \tfrac{1}{2}(Cp^*ReO)_2(\mu\text{-}O)_2\ (toluene) + O{=}PPh_3\ (toluene)} & \\
 & \Delta H_{rxn} = -28.4\ \mathrm{kcal/mol} \\
\mathrm{O{=}PPh_3\ (toluene) \rightleftarrows O\ (g) + PPh_3\ (toluene)} & \Delta H_{rxn} = +136.8\ \mathrm{kcal/mol} \\
\hline
\mathrm{Cp^*ReO_3\ (toluene) \rightleftarrows \tfrac{1}{2}(Cp^*ReO)_2(\mu\text{-}O)_2\ (toluene) + O\ (g)} & \Delta H_{rxn} = +108.4\ \mathrm{kcal/mol} \\
 & (\pm 1.1\ \mathrm{kcal/mol})
\end{array} \tag{1}$$

$$\begin{array}{ll}
\mathrm{Cp^*ReO_3\ (toluene) \rightleftarrows \tfrac{1}{2}(Cp^*ReO)_2(\mu\text{-}O)_2\ (toluene) + O\ (g)} & \Delta H_{rxn} = +108.4\ \mathrm{kcal/mol} \\
\mathrm{\tfrac{1}{2}(Cp^*ReO)_2(\mu\text{-}O)_2\ (toluene) \rightleftarrows Cp^*ReO_2\ (toluene)} & \Delta H_{rxn} = +8.4\ \mathrm{kcal/mol} \\
\hline
\mathrm{Cp^*ReO_3\ (toluene) \rightleftarrows Cp^*ReO_2\ (toluene) + O\ (g)} & \Delta H_{rxn} = +116.8\ \mathrm{kcal/mol} \\
 & (\pm 1.2\ \mathrm{kcal/mol})
\end{array} \tag{2}$$

The identical analysis with values determined in THF solution provide a Re═O BDE estimate of 117.2 ± 1.3 kcal/mol.[8] The similarity of the thermochemistry in toluene and in THF is somewhat surprising given the difference in polarity (ϵ(toluene) = 2.38, ϵ(THF) = 7.32).[9] One might have expected measurable stabilization of a

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[1] (a) Gable, K. P.; Juliette, J. J. J.; Gartman, M. A. *Organometallics* **1995**, *14*, 3138−3140. (b) Abu-Omar, M. M.; Espenson, J. H. *Inorg. Chem.* **1995**, *34*, 6239−6240. (c) Conry, R. R.; Mayer, J. M. *Inorg. Chem.* **1990**, *29*, 4862−4867.

[2] (a) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401−1449. (b) Holm, R. H.; Donahue, J. P. *Polyhedron* **1993**, *12*, 571−589.

[3] Herrmann, W. A.; Serrano, R.; Küsthardt, U.; Ziegler, M. L.; Guggolz, E.; Zahn, T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 515−517.

[4] Kirklin and Domalski (Kirkland, J. R.; Domalski, E. S. *J. Chem. Thermodyn.* **1988**, *20*, 743−754) report enthalpies of formation of +49.4 ± 0.8 kcal/mol for Ph_3P and −27.8 ± 0.8 kcal/mol for Ph_3PO. These authors report experimentally indistinguishable heats of fusion for the phosphine and its oxide, and other workers[5] report identical enthalpies of solution. With the reported BDE of O_2(g) of 119.2 ± 0.1 kcal/mol,[6] this gives an enthalpy of 136.8 ± 1.2 kcal/mol for the O−P BDE of Ph_3PO in the condensed phase.

[5] Hoff, C. D.; Nolan, S. P. Personal communication.

[6] (a) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. The NBS Tables of Chemical Thermodynamic Properties: Selected Values for Inorganic and C_1 and C_2 Organic Substrances. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. No. 2, pp 2−37. (b) Reference 2b.

[7] Hermann, W. A.; Flöel, M.; Kulpe, J.; Felixberger, J. K.; Herdtweck, E. *J. Organomet. Chem.* **1988**, *355*, 297−313.

[8] Although we have not measured the temperature dependence of the dimer dissociation in THF, we did find that the equilibrium constant at 50 °C in THF was twice that in benzene: Gable, K. P.; Juliette, J. J. J. Unpublished results. This corresponds to a $\Delta\Delta G° = +0.4$ kcal/mol on dimer; if all of this is due to enthalpy the correction is still within our experimental uncertainty.

[9] Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; J. Wiley & Sons: New York, 1972; pp 4−13.

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polarized metal–oxo linkage in a more polar solvent, but in this case there is apparently little effect.

The few measurements of third-row metal oxides have generally given high M–O BDEs in the gas phase. Several examples are as follows: WO_3, 150 kcal/mol;[10] $WOCl_4$, 195 kcal/mol.[11] Even OsO_4, a better oxidant than Cp^*ReO_3, has an average BDE of 127 kcal/mol (gas phase).[9] Mayer estimated the strength in a Re(V) complex to be above 132 kcal/mol.[1c] Holm and Donahue have discussed the available data in their recent review.[2b]

The value calculated from solution calorimetric data for the Re=O bond in Cp^*ReO_3 (117 kcal/mol) is significantly weaker than most of these. Several comments are relevant. First, measures of average bond enthalpies in compounds with more than one oxo ligand should not accurately reflect the BDE for removing the first of these; the latter is what we measured. In the reactions we are concerned with, the BDE of the first oxo ligand is chemically important. Additional data in the literature agree that removal of one oxo requires less than the overall average BDE, particularly in condensed phase, and the following is found for later transition metals: $ReO_3\ (s) \rightleftarrows ReO_2\ (s) + O\ (g)$, 93.6 kcal/mol; $OsO_4\ (g) \rightleftarrows OsO_3\ (g) + O\ (g)$, 72.4 kcal/mol.[2b] In the spectrum of metal oxos for which O atom transfer has been measured,[2] Cp^*ReO_3 actually lies near the middle in terms of its thermodynamic ability to give up an oxo ligand.

Further, it is quite possible that the π donor properties of the pentamethylcyclopentadienyl ring tend to lower the Re=O π bond order in Cp^*ReO_3, preventing any contribution from an Re≡O resonance form. In more Lewis acidic (or coordinatively unsaturated) metal oxo systems, this triple bonding contribution is known to be significant.[12] However, in Cp^*ReO_3, the Re–O bonds have been calculated to have mostly double-bond character.[13] The weak π interaction also shows up in the ability of this molecule to perform net [3 + 2] cycloadditions to particularly reactive alkenes (strained alkenes[14] or ketenes[15]).

Experimental Section

General Considerations. All manipulations involving organorhenium complexes were performed under inert atmospheres of argon in a Vacuum/Atmospheres glovebox containing less than 1 ppm oxygen and water. Cp^*ReO_3 was prepared as described previously.[16] Triphenylphosphine were purchased from Strem Chemicals and recrystallized prior to use. Tetrahydrofuran and toluene were distilled from sodium benzophenone ketyl, stored over Na/K alloy and vacuum transferred prior to calorimetric use. Only materials of high purity as indicated by NMR spectroscopy were used in the calorimetric experiments. Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80) which was periodically calibrated using the TRIS reaction[17] or the enthalpy of solution of KCl in water.[18] The experimentally determined enthalpies for these two standard calibration reactions are the same within experimental error as literature values. This calorimeter has been previously described,[19] and typical procedures are described below. Experimental enthalpy data are reported with 95% confidence limits.

^{1}H NMR Titrations. Prior to every set of calorimetric experiments, an accurately weighed amount (±0.1 mg) of the organorhenium complex was placed in a Wilmad screw-capped NMR tube fitted with a septum, and THF or toluene was subsequently added. The solution was titrated with a solution of the ligand of interest by injecting the latter in aliquots through the septum with a micro syringe, followed by vigorous shaking. The reactions were monitored by ^{1}H NMR spectroscopy, and the reactions were found to be rapid, clean, and quantitative under experimental calorimetric conditions. These conditions are necessary for accurate and meaningful calorimetric results and were satisfied for organorhenium reactions investigated. Only reactants and products were observed in the course of the NMR titration.

Calorimetric Measurement for Reaction between Cp^*ReO_3 (1) and Triphenylphosphine. The mixing vessels of the Setaram C-80 were cleaned, dried in an oven maintained at 120 °C, and then taken into the glovebox. A 20–30 mg sample of **1** was accurately weighed into the lower vessel, and it was closed and sealed with 1.5 mL of mercury. A 4 mL volume of a stock solution of triphenylphosphine (1 g of PPh_3 in 25 mL of toluene) was added, and the remainder of the cell was assembled, removed from the glovebox, and inserted in the calorimeter. The reference vessel was loaded in an identical fashion with the exception that no organorhenium complex was added to the lower vessel. After the calorimeter had reached thermal equilibrium at 30.0 °C (about 2 h), the calorimeter was inverted allowing the reactants to mix. The calorimeter was allowed to return to thermal equilibrium at which point the vessels were removed from the calorimeter, taken into the glovebox, opened, and analyzed using ^{1}H NMR spectroscopy. Conversion to $(Cp^*ReO)_2(\mu\text{-}O)_2$ was found to be quantitative under these reaction conditions. The enthalpy of reaction, −23.9 ± 0.2 kcal/mol, represents the average of five individual calorimetric determinations. The enthalpy of solution of **1** was then subtracted from this value to obtain a value of −28.4 ± 0.3 kcal/mol for all species in solution. The enthalpy of reaction was measured as −22.4 ± 0.5 kcal/mol in tetrahydrofuran, which corresponds to an overall enthalpy with all species in solution of −28.0 ± 0.6 kcal/mol.

Calorimetric Measurement of Enthalpy of Solution of Cp^*ReO_3. In order to consider all species in solution, the enthalpies of solution of **1** had to be directly measured in both solvents utilized. This was performed by using a procedure similar to the one described above with the exception that no ligand was added to the reaction cell. This enthalpy of solution represents the average of five individual determinations and is 4.5 ± 0.1 kcal/mol and 5.6 ± 0.1 kcal/mol in toluene and THF, respectively.

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