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Enthalpy of Formation of Dicesium Octabromodirhenium(III), $Cs_2Re_2Br_8$, and a Thermochemical Estimate of the Energy of the Re–Re Quadruple Bond

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Abstract: The enthalpy of formation of $Cs_2Re_2Br_8(c)$ has been determined to be -1171 ± 35 kJ/mol at 298 K by measuring its heat of oxidation by aqueous bromate. The enthalpy of formation of $Re_2Br_8^{2-}(g)$ has been calculated to be -1046 ± 40 kJ/mol by calculating the lattice enthalpy of $Cs_2Re_2Br_8$ in conjunction with other thermodynamic data. From estimates of enthalpies of formation of various Re–Br species, and from estimates of the Re–Br bond energy, the Re–Re quadruple bond strength in $Re_2Br_8^{2-}$ has been estimated to be 408 ± 50 kJ/mol (98 kcal/mol). This value is discussed in comparison with other recent estimates.

The explosive growth in the chemistry of compounds containing metal–metal bonds within the past 15 years has challenged many chemists to characterize these materials. Naturally, the strongest of these bonds have attracted the most interest: the multiple Cr–Cr, W–W, Mo–Mo, and Re–Re bonds are well-characterized, remarkably stable entities. Early and more recent estimates have focused on theoretical molecular-orbital interpretations of the bonding and electronic spectra in these species.^{2–4} Observations drawn from the photochemistry of $Re_2Cl_8^{2-}$ led to alternative estimates for the strength of this metal–metal bond.⁵ In one instance an effort was made to apply classical vibrational spectroscopic techniques to estimate the Re–Re quadruple bond strength.⁶ Most recently there have been attempts to answer this question by the application of traditional thermochemical techniques. Thus, Skinner, Cotton, and co-workers⁷ have reported on their attempts to assess the strength of the Mo–Mo and W–W multiple bonds found in several organometallic compounds, but

their efforts were hampered by uncertainties in ligand enthalpies of formation and metal–ligand bond strengths.

Several years ago in a report detailing the single-crystal structure determination of dicesium octabromodirhenium(III), $Cs_2Re_2Br_8$, Cotton and co-workers⁸ made the perspicacious observation that this particular substance might prove suitable for the necessary thermochemical measurements and lattice-energy calculations required to produce a thermochemical cycle leading to the enthalpy of the Re–Re bond. We report here the results of our determination of this and related quantities for $Cs_2Re_2Br_8$.

Our investigation centered on three problems. The first task was to determine a calorimetric standard enthalpy of formation of $Cs_2Re_2Br_8(c)$, and the second was to calculate the lattice energy (or, more precisely, the lattice enthalpy U_{pot} at 298 K) of this compound. The sum of these two enthalpies would then yield $\Delta H_f^\circ(Re_2Br_8^{2-}, g)$ (eq 1) by the thermochemical cycle⁹ shown in Scheme I. The third problem—and by far the least

Scheme I

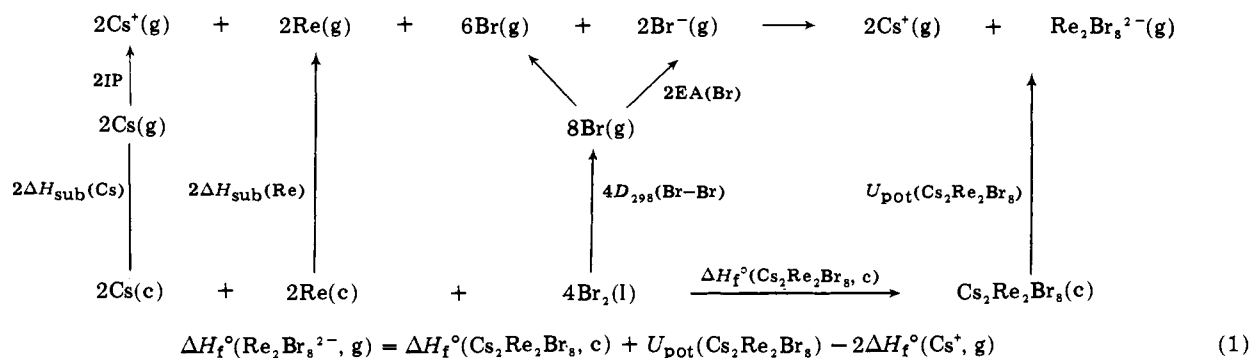
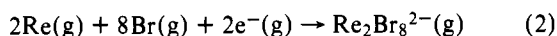


Table I. Heats of Reaction with 0.1 M KBrO₃-0.1 M HClO₄ Solution at 25 °C

compd	mass, mg	heat evolved, ^a J	$\Delta H_{\text{reaction}}$, kJ mol ⁻¹
Cs ₂ Re ₂ Br ₈	58.01	51.48	-1134
Cs ₂ Re ₂ Br ₈	67.31	62.08	-1178
Cs ₂ Re ₂ Br ₈	79.03	72.28	-1168
Cs ₂ Re ₂ Br ₈	58.83	55.16	-1198
KBr	212.04	32.59	-18.29
KBr	259.12	39.61	-18.19
KBr	241.02	37.11	-18.32
KBr	229.27	35.14	-18.24

^a Corrected for evaporation of water into air within ampule.

tractable by conventional approaches—was to determine the separate Re-Re and Re-Br bond energy contributions to the gas-phase reaction



Experimental Section

General. Potassium bromate (99.9%), cesium bromide (99.9%), potassium perrhenate (99.99%), and potassium bromide (99.99%) were purchased from several commercial sources and used without further purification. All solutions were prepared using distilled and deionized water. Unless otherwise stated all other reagents were the highest quality commercially available stock. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Dicesium octabromodirhenium(III), Cs₂Re₂Br₈, was prepared in the following manner. A solution of tetra-*n*-butylammonium octabromodirhenium(III), ¹⁰ [(*n*-C₄H₉)₄N]₂[Re₂Br₈] (1.380 g, 0.922 mmol), in deoxygenated methanol (46 mL) containing 16 mL of 48% aqueous hydrobromic acid was placed in a 250-mL flask containing a Teflon-coated stirring bar. The flask was fitted with a condenser equipped with an addition funnel. The entire system was flushed with and subsequently maintained under an atmosphere of nitrogen. The flask was placed in a bath at 90 °C. The addition funnel was charged with a deoxygenated solution of cesium bromide (0.835 g, 3.92 mmol) in methanol-aqueous 48% hydrobromic acid (2.4, 7.0 mL). With vigorous stirring this solution was added to the flask over a period of 15 min. Heating and stirring were continued for an additional 5 min, after which time the resulting mixture was allowed to cool to ambient temperature, whereupon a deep-violet precipitate gradually formed. These crystals were collected by suction filtration on a fritted glass funnel and rinsed with anhydrous methanol until the rinsings were colorless. The dark, almost black crystals were dried in vacuo. A second crop of crystals was obtained by concentrating and cooling the mother liquor; the total yield was 91%. Anal. Calcd: Cs, 20.81; Br, 50.03. Found: Cs, 20.87; Br, 49.49.

Examination of this material by X-ray powder diffraction techniques indicated *d* spacings and intensities consistent with the structure reported by Cotton et al.⁸

Calorimetry. A suitable oxidizing solvent was sought for determination of $\Delta H_f^\circ(\text{Cs}_2\text{Re}_2\text{Br}_8)$ through an appropriate reaction scheme using the solution calorimeter described by Morss and co-workers.¹¹ Since the isoperibol solution calorimeter is capable of measuring reaction heats in corrosive solvents that extend over periods as long as 30 min, a well-defined reaction was sought that would cleanly oxidize Re(III) to ReO₄⁻. Unfortunately, most suitable oxidants are also likely to oxidize bromide and Cs₂Re₂Cl₈ could not be substituted because it crystallizes as a hydrate, Cs₂Re₂Cl₈·2H₂O, a substance much less tractable to lattice-energy calculations. Thus, an investigation was undertaken to determine an appropriate oxidant.

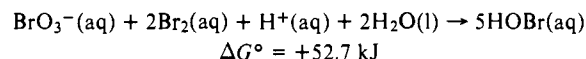
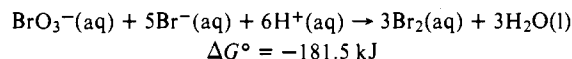
It is reported that slightly alkaline hypochlorite solutions will selectively oxidize bromide to hypobromite.¹² The reaction rate is slow at pH 14 but increases with decreasing pH. However, at pH < 10 further reactions take place; specifically, hypochlorite begins to disproportionate and bromide is oxidized partially to bromate. Still, since preliminary measurements by ultraviolet spectrophotometry (using the 229-nm absorption peak for ReO₄⁻) showed slow but quantitative oxidation of Re(III) to ReO₄⁻ with this reagent, preliminary calorimeter experiments were undertaken with ampules of Cs₂Re₂Br₈(c) and aqueous NaOCl solutions buffered by boric acid-borate between pH 10 and 8.7. At the higher pH reaction was too slow (reaction times

ca. 90 min), while at the lower pH the heat evolved was so great that, if correct, such a value would have required the chemically unreasonable conclusion that Cs₂Re₂Br₈ is unstable with respect to the reaction

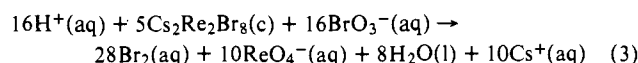


Further confirmation that hypochlorite was not a suitable oxidant was afforded by calorimeter experiments with KBr(c) and hypochlorite buffered at pH 8.8. The quantity of heat evolved in these experiments was much greater than could be accounted for by the sole oxidation of Br⁻ to OBr⁻. We concluded that substantial oxidation of bromide to bromate was also occurring under these conditions.

Preliminary experiments suggested that Cs₂Re₂Br₈ reacts rapidly with excess bromate ion in acidic aqueous solution to form ReO₄⁻ and Br₂. The possibility that bromine would be oxidized to hypobromite by excess bromate was dispelled by considering the free energy¹³ of reaction for the two oxidation pathways outlined below.

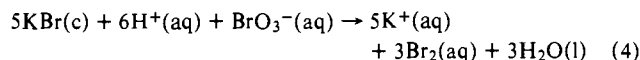


Obviously, only the former reaction occurs, even with bromate in excess. Thus, the overall reaction is



A suitable reaction in hand, a calorimetric determination of its heat, $\Delta H^\circ(3)$, was undertaken.

Four spherical thin-walled borosilicate glass ampules were sealed with weighed quantities of Cs₂Re₂Br₈(c). Each was crushed and the contents allowed to react in the calorimeter¹¹ with 870 cm³ of a solution of 0.1 M KBrO₃-0.1 M HClO₄. The results are shown in Table I. Because of disagreement in the existing values of $\Delta H_f^\circ(\text{BrO}_3^-, \text{aq})$, calibration experiments were carried out under identical conditions with KBr(c) in place of Cs₂Re₂Br₈. The results, representing the reaction

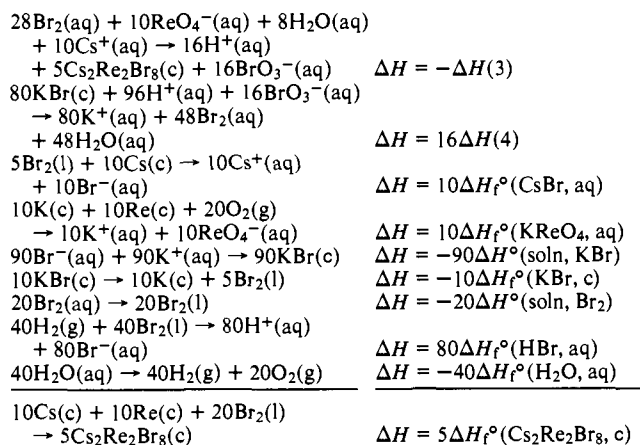


are also included in Table I.

Results and Discussion

$\Delta H_f^\circ(\text{Cs}_2\text{Re}_2\text{Br}_8, \text{c})$. Standard-state enthalpies of formation of all species (except Cs₂Re₂Br₈) in eq 3 are given in ref 13, so that these data could be used with the heat of reaction 3 to calculate $\Delta H_f^\circ(\text{Cs}_2\text{Re}_2\text{Br}_8, \text{c})$. However, reaction 3 was not carried out at infinite dilution; moreover, there is evidence¹⁴ that $\Delta H_f^\circ(\text{BrO}_3^-, \text{aq})$ is less negative than the value in these NBS tables. Therefore, the enthalpy scheme (Scheme II) was adopted to calculate $\Delta H_f^\circ(\text{Cs}_2\text{Re}_2\text{Br}_8, \text{c})$.

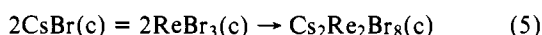
Scheme II *



* In this scheme, "aq" refers to infinite dilution.

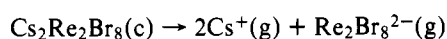
The first two reactions in Scheme II represent reactions studied in this work. The average of results for reactions 3 and 4 are $\Delta H(3) = 5(-1169 \pm 27)$ kJ/mol and $\Delta H(4) = 5(-18.26 \pm 0.11)$ kJ/mol (error limits are twice the standard deviation of the mean). To correct $\Delta H(3)$ to infinite dilution, heats of dilution of HBrO₃ and CsReO₄ were estimated from dilution data¹⁵ for 0.2 M solutions of HNO₃ and KMnO₄, respectively: $\Delta H^\circ(3) = 5(-1169) + 16(0.44) - 10(-0.87) = -5829$ kJ. To correct $\Delta H(4)$ to infinite dilution, heats of dilution of HBrO₃, HClO₄, KBrO₃, and KClO₄ were estimated from dilution data¹⁵ for 0.2 M solutions of HNO₃, HClO₄, KNO₃, and KMnO₄, respectively: $\Delta H^\circ(4) = 5(-18.26) + 0.44 + \frac{1}{2}(0.44) + \frac{1}{2}(0.25) - \frac{1}{2}(-0.50) - \frac{1}{2}(-0.87) = -85.7$ kJ. (Heats of dilution of HBrO₃ are unimportant because they cancel between reactions 3 and 4.) Enthalpies of other reactions were taken from appropriate references.^{13,15-17b} The sum of all enthalpies in the above scheme is $-(-5829) + 16(-85.7) + 10(-379.54) + 10(-1039.7) - 90(19.87) - 10(-393.8) - 20(-0.84) + 80(-121.5) - 40(-285.83) = -5855$ kJ. Thus $\Delta H_f^\circ(\text{Cs}_2\text{Re}_2\text{Br}_8, \text{c}) = \frac{1}{5}(-5855) = -1171 \pm 35$ kJ/mol. Although the error limit shown is in part an estimate of uncertainties in heats of other reactions and dilutions used in this scheme, it represents principally the uncertainty in $\Delta H(3)$.

It is interesting to note that this datum may be combined with literature data^{13,15-17} to yield ΔH° for the reaction



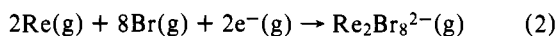
Thus, $\Delta H^\circ(5) = -1171 - 2(-405.5) - 2(-167) = -26$ kJ (mol Cs₂Re₂Br₈)⁻¹. Roughly speaking, this enthalpy represents the difference between 1 mol of Re-Re quadruple bonds and 2 mol of Re-Re double bonds,^{18a} since "ReBr₃" is really $\frac{1}{3}\text{Re}_3\text{Br}_9$, and Re₃Br₉ contains a triangular core of rhenium atoms^{18b} "double bonded"^{18c} to each other.

Lattice Enthalpy of Cs₂Re₂Br₈. The lattice energy of Cs₂Re₂Br₈ was calculated using the method recently proposed by Jenkins and Pratt.¹⁹⁻²² We chose two models for the Re₂Br₈²⁻ ion in order to gauge the accuracy of the calculations made. The first model treated the octabromodirhenate ion as consisting of six spheres centered at the Br atom sites (so ignoring the Re atoms). From this study we obtained a value for U_{pot} , the total lattice enthalpy of Cs₂Re₂Br₈, amounting to 1026 kJ mol⁻¹. The second and probably the more acceptable model considers a ten-sphere model for the Re₂Br₈²⁻ ion and generated a value of 1030 kJ mol⁻¹ for $U_{\text{pot}}(\text{Cs}_2\text{Re}_2\text{Br}_8)$. On the basis of these two treatments, we conclude a value for U_{pot} of 1029 ± 20 kJ mol⁻¹ for the salt. The corresponding charge on the Br atoms of the Re₂Br₈²⁻ ion was calculated as -0.30. Since it is the nature of the lattice energy step¹⁹ to render U_{pot} (the total lattice potential energy) and ΔH (the lattice enthalpy) synonymous quantities in the case of Cs₂Re₂Br₈, the lattice enthalpy for the process



is assigned as $\Delta H = 1029 \pm 20$ kJ mol⁻¹ on the basis of the above calculation. Equation 1 can now be solved for $\Delta H_f^\circ(\text{Re}_2\text{Br}_8^{2-}, \text{g}) = (-1171 \pm 35) + (1029 \pm 20) - 2(76.1 \pm 0.2)^{24} - 2(375.7)^{25} = -1046 \pm 40$ kJ mol⁻¹.

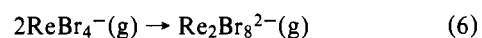
Estimates of the Re-Re Quadruple Bond Enthalpy. To eliminate any effects of condensed species (metal-metal or halogen-halogen bonds), we considered the gas-phase reaction



for bonding comparisons with other gas-phase reactions: $\Delta H(2) = -1046 - 2(774.9)^{24} - 8(111.88)^{13} = -3491$ kJ. (By convention,¹³ the enthalpy of formation of the gaseous electron is taken as zero. Since we will compare cycles with identical

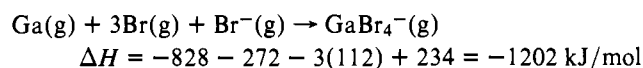
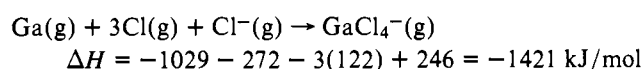
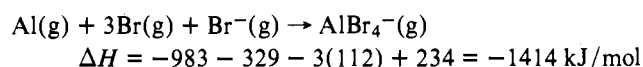
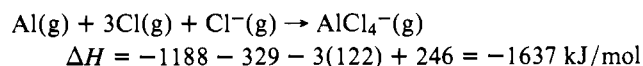
numbers of electrons, this convention has no effect on absolute bond energies.)

1. Comparison of M-Br Bond Enthalpies in MBr₄⁻. The enthalpy change for the process

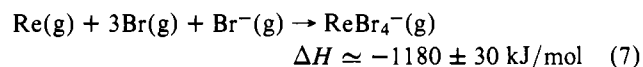


represents the bond enthalpy of the Re-Re quadruple bond; $\Delta H(6)$ can be estimated from $\Delta H_f^\circ(\text{ReBr}_4^-, \text{g})$ and $\Delta H_f^\circ(\text{Re}_2\text{Br}_8^{2-}, \text{g})$. Since the latter quantity is available (vide supra), $\Delta H(6)$ can be calculated if $\Delta H_f^\circ(\text{ReBr}_4^-, \text{g})$ can be estimated.

Enthalpies of formation of tetrahedral gaseous ions AlCl₄⁻, GaCl₄⁻, and GaBr₄⁻ have been calculated.²⁶ For the gas-phase reactions we calculate^{13,24}



We estimate the hypothetical ion ReBr₄⁻(g) to be slightly larger and more weakly bonded than GaBr₄⁻(g) and conclude that



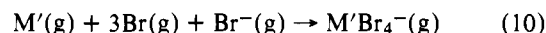
The MX₄⁻ species we have cited are all tetrahedral while the rhenium centers in Re₂Br₈²⁻ are pentacoordinate; however, we do not believe that the Re-Br bonds are repelled more in Re₂Br₈²⁻ than in the hypothetical ReBr₄⁻ ion. Using literature^{13,24} enthalpies of formation, $\Delta H_f^\circ(\text{ReBr}_4^-, \text{g}) = \Delta H(7) + \Delta H_f^\circ(\text{Re}, \text{g}) + 3\Delta H_f^\circ(\text{Br}, \text{g}) + \Delta H_f^\circ(\text{Br}^-, \text{g}) = -1180 + 775 + 3(112) - 234 = -303$ kJ/mol. Thus, $\Delta H(6) = -1046 - 2(-303) = -440$ kJ/mol, i.e., $D_{298}(\text{Re}\equiv\text{Re}) = 400$ kJ.

2. Comparison of M-X Bond Enthalpies in MX₄(g). The molecule OsBr₄ is of interest since it is isoelectronic with the ion ReBr₄⁻. We may estimate the Os-Br bond enthalpy in OsBr₄(g) by considering the gas-phase reactions



Literature data^{13,27} lead to $\Delta H(8)$ and $\Delta H(9)$ of -1967 and -1700 kJ/mol for M = Zr, -1262 and -1065 for Sn, -2031 and -1804 for Th, and -1827 and -1574 for U. The average of these $\Delta H(9)$ is 236 ± 31 kJ less negative than $\Delta H(8)$. Since $\Delta H(8)$ for M = Os is -1350 kJ/mol,¹³ we estimate $\Delta H(9)$ for M = Os to be $-1350 + 236 = -1114$ kJ/mol.

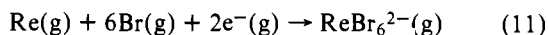
We may use the bond enthalpy in OsBr₄(g) to estimate that in the isoelectronic ion ReBr₄⁻(g) by comparing $\Delta H(9)$ with ΔH for production of isoelectronic ions M'Br₄⁻(g)



For the isoelectronic pair SiBr₄(g) and AlBr₄⁻(g), $\Delta H(9)$ and $\Delta H(10)$ are^{13,24} -1319 and -1414 kJ/mol, respectively. For the pair GeBr₄(g) and GaBr₄⁻(g), $\Delta H(9)$ and $\Delta H(10)$ are -1125 and -1202 kJ/mol, respectively.^{13,24} Since the latter pair more nearly approximate the isoelectronic pair OsBr₄ and ReBr₄⁻, we estimate $\Delta H(10)$ for M' = Re as $-1114 + (-1202) - (-1125) = -1191$ kJ/mol, a value that represents an independent estimate of $\Delta H(7)$. This estimate leads to $\Delta H_f^\circ(\text{ReBr}_4^-, \text{g}) = -1191 + 775 + 3(112) - 234 = -314$

kJ/mol and to $\Delta H(6) = -D_{298}(\text{Re}\equiv\text{Re}) = -1046 - 2(-314) = -418$ kJ/mol.

3. Comparison of Re-Br Bond Enthalpies in $\text{Re}_2\text{Br}_8^{2-}$ and ReBr_6^{2-} . We may consider the bonds in $\text{Re}_2\text{Br}_8^{2-}$ as one $\text{Re}\equiv\text{Re}$ quadruple bond and eight $(\text{Re}-\text{Br})^{1/4-}$ bonds. From eq 2, $\Delta H(2) = -D_{298}(\text{Re}\equiv\text{Re}) - 8D_{298}(\text{Re}-\text{Br})^{1/4-} = -3491$ kJ. To calculate $D_{298}(\text{Re}\equiv\text{Re})$ we need an estimate of $D_{298}(\text{Re}-\text{Br})^{1/4-}$. Although eq 7 could be rewritten to provide this estimate, it would not lead to an independent value of $D_{298}(\text{Re}\equiv\text{Re})$. However, we may take advantage of the enthalpy of formation and lattice enthalpy of K_2ReBr_6 recently reported by Burgess et al.²⁸ For the process



we calculate $\Delta H(11) = \Delta H_f^\circ(\text{ReBr}_6^{2-}, \text{g}) - \Delta H_f^\circ(\text{Re}, \text{g}) - 6\Delta H_f^\circ(\text{Br}, \text{g}) = -692 - 775 - 6(112) = -2139$ kJ. Since ReBr_6^{2-} is octahedral, with six identical $(\text{Re}-\text{Br})^{1/3-}$ bonds, $D_{298}(\text{Re}-\text{Br})^{1/3-} = 2139/6 = 356$ kJ/mol. To compare these Re-Br bonds with those in $\text{Re}_2\text{Br}_8^{2-}$, we must correct for the coordination number and charge on the Re-Br bonds.

Korol'kov et al.²⁹ have pointed out that a unit decrease in coordination number of gaseous heavy transition-metal halides is accompanied by an increase in M-X bond energy from 28 to 42 kJ/mol. Specifically, thermodynamic data¹³ lead to $D_{298}(\text{W}-\text{Cl}) = 347$ kJ/mol in WCl_6 , 377 kJ/mol in WCl_5 , and 410 kJ/mol in WCl_4 . We have argued above that the Re-Br bonds in $\text{Re}_2\text{Br}_8^{2-}$ are repelled no more than those of a four-coordinate ReBr_4^- ion; hence we correct $D_{298}(\text{Re}-\text{Br})^{1/3-}$ from coordination 6 to 4 as $356 + (410 - 347) = 419$ kJ/mol.

We estimate the correction from $(\text{Re}-\text{Br})^{1/3-}$ to $(\text{Re}-\text{Br})^{1/4-}$ as $1/12 \text{EA}(\text{Br}) = 346/12 = 29$ kJ;¹³ hence $D_{298}(\text{Re}-\text{Br})^{1/4-} = 419 - 29 = 390$ kJ/mol. Therefore, for eq 2, $D_{298}(\text{Re}\equiv\text{Re}) = 3491$ kJ/mol $- 8D_{298}(\text{Re}-\text{Br})^{1/4-} = 3491 - 8(390) = 371$ kJ/mol.

4. Comparison with Re Metal by Bond Length Ratio. Housecroft and Wade³⁰ recently proposed a method for estimating metal-metal and metal-ligand bonds in carbonyl clusters by comparing metal-metal bond lengths with the shortest interatomic distance in the metal itself. We apply their equation

$$E(\text{M}-\text{M}) = A[d(\text{M}-\text{M})]^{-4.6} \quad (12)$$

to the Re-Re bond in $\text{Re}_2\text{Br}_8^{2-}$, using its length,⁸ 2.228 Å, in comparison with the interatomic distance in rhenium metal,³¹ 2.75 Å. Rhenium metal is hexagonal closest packed, so that there are 6 mol of Re-Re bonds per mol of Re metal. Thus, in Re metal $E(\text{Re}-\text{Re}) = 774.9/6 = 129.2$ kJ/mol. From eq 12

$$\frac{E(\text{Re}-\text{Re in } \text{Re}_2\text{Br}_8^{2-})}{E(\text{Re}-\text{Re in metal})} = \left[\frac{d(\text{Re}-\text{Re in } \text{Re}_2\text{Br}_8^{2-})}{d(\text{Re}-\text{Re in metal})} \right]^{-4.6}$$

$$E(\text{Re}-\text{Re in } \text{Re}_2\text{Br}_8^{2-}) = (129.2 \text{ kJ/mol}) \left[\frac{2.228}{2.75} \right]^{-4.6} = 340 \text{ kJ}$$

Despite the simplicity of this argument, we believe that quantitative correlations of bond strength and bond lengths such as given in eq 12 are rather too tenuous to enable us to include this value among our estimates of the Re-Re bond strength in $\text{Re}_2\text{Br}_8^{2-}$.

Conclusions

Although estimates of the strength of quadruple bonds have ranged from 334 to more than 1500 kJ/mol,^{5,2a} the most recent estimate for the Re-Re quadruple bond is 480-690 kJ/mol.⁶ Unfortunately, this estimate suffers from the tenuous extension of the Birge-Sponer technique of classical vibrational spec-

troscopy to estimate the bond strengths of diatomic molecules. Indeed, a careful examination of the arguments leading to this estimate reveals several unsubstantiated and severe approximations,³² suggesting that any similarity between the true Re-Re bond energy and the dissociation energy reported by these workers is largely coincidental.

Recent efforts by Skinner⁷ and others to study the thermochemistry of organometallic compounds have included estimates of metal-metal bond strengths. In particular, solution calorimetry studies³³ of molybdenum(II) acetate, $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, yielded a standard enthalpy of formation for this compound from which a value of $D_{298}(\text{Mo}\equiv\text{Mo})$ was "assessed in the region of 500 kJ/mol", a value which Skinner⁷ concludes to be a "provisional . . . upper limit".

We have determined the enthalpy of formation of $\text{Cs}_2\text{Re}_2\text{Br}_8(\text{c})$, calculated the lattice enthalpy of this compound, and derived the enthalpy of formation of $\text{Re}_2\text{Br}_8^{2-}(\text{g})$. From this datum and reasonable bond-enthalpy arguments, we obtain estimates for the Re-Re bond of 440, 418, and 371 kJ/mol. In summary, we believe that the best thermochemical estimate of the rhenium-rhenium quadruple bond in $\text{Re}_2\text{Br}_8^{2-}$ is 408 ± 50 kJ/mol (98 kcal/mol).

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Reduction of Coordinated Carbon Monoxide. Synthesis of Neutral Metal Formyl and Hydroxymethyl Derivatives of the $(C_5H_5)Re(CO)_2(NO)^+$ Cation

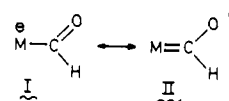
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Abstract: The reaction of $(C_5H_5)Re(CO)_2(NO)^+PF_6^-$ (**1**) with potassium triisopropoxyborohydride in tetrahydrofuran at -78 °C gives the neutral formyl complex $(C_5H_5)Re(CO)(NO)(CHO)$ (**2**) as an orange oil. Dilute solutions of **2** gradually decompose at room temperature to give $(C_5H_5)Re(CO)(NO)(H)$ (**4**). Reduction of **2** with $BH_3 \cdot THF$ yields $(C_5H_5)Re(CO)(NO)(CH_3)$ (**5**), while reduction of **2** with lithium triethylborohydride gives the diformyl complex $(C_5H_5)Re(NO)(CHO)_2^-$ (**7**). Formyl complex **2** is unstable in neat oil form and disproportionates to give the dimeric metallo ester $(C_5H_5)(CO)(NO)ReCO_2CH_2Re(CO)(NO)(C_5H_5)$ (**8**) as a $\sim 1:1$ mixture of two diastereomers. Prolonged solvolysis of **8** in methanol yields the methyl ester $(C_5H_5)Re(CO)(NO)(CO_2CH_3)$ (**6**) and the methoxymethyl complex $(C_5H_5)Re(CO)(NO)(CH_2OCH_3)$ (**9**). Ether **9** can be hydrolyzed with water-tetrahydrofuran under acid catalysis to give the first unsubstituted hydroxymethyl complex, $(C_5H_5)Re(CO)(NO)(CH_2OH)$ (**3**). Previous claims of the isolation of **3** are shown to be inaccurate. Complex **3** may also be more readily obtained by treatment of cation **1** with sodium diethylaluminum dihydride.

Introduction

The shortage of petroleum has caused increased interest in alternative sources of liquid fuels and petrochemical feedstocks. One such alternative that is now being widely investigated is the reduction of coal-derived carbon monoxide-hydrogen mixtures via the Fischer-Tropsch and related reactions.¹ For the past several years, we have been studying some of the unusual intermediates and reactions which have been proposed to occur in CO reduction. Many of our studies have centered around metal formyl species² which may be involved in the initiation step of CO reduction. The first formyl complex, $(CO)_4FeCHO^-$, was synthesized by Collman from $Fe(CO)_4^{2-}$ and acetic-formic anhydride.³ Unfortunately, this route did not prove to be general and we² and others⁴ have developed syntheses of a variety of anionic metal formyl complexes by treatment of neutral metal carbonyl compounds with borohydrides such as potassium triisopropoxyborohydride. The low formyl CO stretching frequencies observed for these anionic species (for example, 1600 cm $^{-1}$ for $(CO)_4FeCHO^-$) indicated a large contribution from carbenoid resonance structures such as II which place extensive negative charge on the formyl oxygen atom. The possibility that anionic metal formyl compounds might be anomalously stabilized by such resonance structures led us to investigate syntheses of neutral



metal formyl complexes by hydride reduction of cationic metal carbonyl compounds.

At the time we began this work, only one neutral metal formyl species had been reported, the unstable and only partially characterized $Os(CO)_2[P(C_6H_5)_3]_2Cl(CHO)$.^{5,14} Neutral metal formyl species had been suggested as intermediates in the substitution reactions of metal carbonyl hydride complexes,^{6a} in the reaction of methoxide with $Ru[P(C_6H_5)_3]_3ClH$ to eventually give $Ru[P(C_6H_5)_3]_3(CO)H$,^{6b} and in the sodium borohydride reductions of the metal carbonyl cations $(C_5H_5)W(CO)_3[P(C_6H_5)_3]^+$ ⁷ and $(C_5H_5)Re(CO)_2NO^+$ ⁸ to methyl and hydroxymethyl metal complexes.

In a preliminary communication, we reported that the reaction of $(C_5H_5)Re(CO)_2NO^+PF_6^-$ (**1**) with $K^+HB[OCH(CH_3)_2]_3^-$ gave the neutral metal formyl complex **2**.⁹ In addition, we found that the claimed synthesis¹⁰ of the only reported hydroxymethyl complex, $(C_5H_5)Re(CO)(NO)(CH_2OH)$ (**3**), was inaccurate and eventually succeeded in preparing authentic **3** by two alternate routes.¹¹ Here we