mechanism for their interconversion seems to be reprotonation upon wall collisions of NCOH to HNCO and CNOH to HCNO". The NR technique provides walless conditions and so should be well suited for investigating these sensitive molecules. Indeed, the first experimental evidence for the stability of CNOH has been presented. It was also shown that $[HNCO]^{\bullet+}$, $[HCNO]^{\bullet+}$, and $[CNOH]^{\bullet+}$ as well as their neutral counteparts do not isomerize or tautomerize in the microsecond timeframe. All these observations are in keeping with theoretical predictions.[7b]

Finally, experiments on the gas phase protonated analogues are in progress and will be reported in the near future.

Acknowledgment. J.L.H. thanks the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support. J.L.H. and J.K.T. are grateful to the NATO Scientific Affairs Division for a collaborative research award.

Osmium Tetroxide and Its Fragment Ions in the Gas Phase: Reactivity with Hydrocarbons and Small Molecules

Karl K. Irikura and J. L. Beauchamp*

Contribution No. 7797 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125. Received June 13, 1988

Abstract: Gas-phase ion-molecule reactions of OsO_n^+ (n = 0–4) with a number of hydrocarbons and small molecules, including CH_4, C_2H_4, C_2H_6, C_3H_8, C_4H_{10}, H_2, CO, NH_3, and SiH_4, have been investigated by Fourier transform ion cyclotron resonance spectrometry. Anion chemistry was briefly investigated. Thermochemical quantities derived include $D(Os^+–O) = 100 \pm 12$, $D(OsO^+–O) = 105 \pm 12$, $D(OsO_2^+–O) = 105 \pm 12$, $D(OsO_3^+–O) = 71 \pm 12$, $D(OsO_3–O) = 78 \pm 14$, $D(OsO_4^+–H) = 132 \pm 3$ kcal/mol, $D(OsO_3^+–OH) = 101 \pm 16$ kcal/mol, and $PA(OsO_4) = 161 \pm 2$ kcal/mol. Many diverse and novel reactions are observed. Among them are $[2_s + 2_s]$ cycloaddition with H_2, bond metathesis, oxo transfer, and hydrogen atom abstraction. These ions are also extraordinarily active dehydrogenation reagents; the most dramatic example is the sequential, complete dehydrogenation of SiH_4 to mono-, di-, and trisilicides. Another intriguing process is the double bond metathesis with NH_3, in which one or two oxo ligands are exchanged for imido groups. The number of oxo ligands is found to have a striking effect on the chemistry; mechanisms are discussed for the reactions observed. For example, the relative inertness of OsO_3^+ is attributed to a failure of the Os(+7) center to undergo oxidative addition. OsO_2^+ emerges as a potential model catalyst for the conversion of methane and dioxygen to aldehydes.

Gas-phase transition-metal ions have been the focus of much attention in recent years, with the library of reactions and the thermochemical base growing rapidly. The bulk of the early work emphasized the chemistry of naked, unligated metal ions. Although progress is being made in the investigation of ligand effects on reactivity, including some systematic studies by Freiser and co-workers,[1] much remains to be done in order to provide enough specific information for useful generalizations to be drawn.

Previous work on gas-phase transition-metal oxide ions includes studies of FeO^+ and CrO^+, among others. In early work, Kappes and Staley[2] determined that the relatively weak bond in FeO^+ permitted this species to catalyze the oxidation of small organic molecules by N_2O. Jackson et al.[3] subsequently found the oxo ligand to increase the reactivity of Fe^+ as well as appearing to favor C–H over C–C insertion in alkanes. The enhanced reactivity is ascribed to the exothermicity of H_2O elimination. In addition to chemistry typical of unligated metal ions, FeO^+ was found to react with hydrocarbons by radical loss processes. Neither FeO^+ nor Fe^+, however, is reactive with methane. In ion beam studies,[4] CrO^+ was found to react readily with hydrocarbons, while Cr^+ is unreactive. For example, CrO^+ oxidizes ethylene to acetaldehyde[4a] and ethane to ethanol.[4b] In another investigation,[5] MnO^+ has been observed to react with ethylene to yield both C_2H_4O and $MnCH_2^+$, the double bond metathesis products. This metathesis has also been identified as the minor channel in the reaction of ethylene with $ClCrO_2^+$.[6] The major products in this case correspond to oxygen transfer.

Despite the number of cases in which an oxo ligand increases reactivity, it is hazardous to generalize too freely. In the case of VO^+, reactivity is reduced relative to unligated V^+.[7] Since the V^+–O bond is very strong, it is not cleaved during reactions, and the oxygen is thought to have little effect other than to occupy a coordination site on the metal.

Aside from the basic interest in ligand effects, motivation for studying the oxo ligand comes partly from condensed phase studies of metal oxides. In particular, hydrocarbon oxidation is a field of great scope and economic volume. A corresponding amount of effort and ingenuity has been directed to this area of research, and transformations mediated by metals and their oxides are increasingly prominent.[8] From an economic viewpoint, methane is a uniquely attractive target for controlled oxidation; its high abundance and low cost make it an ideal feedstock. For example, direct conversion to methanol would permit natural gas to be transported in a convenient and inexpensive liquid form.[9] Unfortunately, this particular process has not yet materialized on a commercial scale. There is also heavy demand for other potential products of direct methane oxidation, such as formaldehyde.[10]

For the present study, we have chosen to compare reactivity among the series of oxo ions derived from OsO_4. This compound

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Table I. Summary of Thermochemical Limits

bond	limit[a]	reaction	bond	limit[a]	reaction
Os^+–NH	92 ± 2.5	15	$OsC_3H_4^+$–C_3H_4	69	42
OsO^+–NH	92 ± 2.5	16a	Os^+–C_4H_6	56	43b
$OsNH^+$–NH	92 ± 2.5	19	OsO^+–C_4H_6	56	44b
Os^+–CH_2	110 ± 1	21	Os^+–C_4H_4	109 ± 1	43a
OsO^+–CH_2	110 ± 1	22	OsO^+–C_4H_4	109 ± 1	44a
$OsCH_2^+$–CH_2	110 ± 1	25	OsO^+–SiC	179 ± 8	62
$OsOCH_2^+$–CH_2	110 ± 1	26a	Os^+–SiH_2	61 ± 4	50b
$OsOC_2H_4^+$–CH_2	110 ± 1	30	$OsOSi^+$–O	78 ± 14	60
$OsOCH_2^+$–O	78 ± 14	27	OsO_2Si^+–O	78 ± 14	69
$OsOC_2H_4^+$–O	78 ± 14	29	Os^+–Si	99.5 ± 2	50a
Os^+–C_2H_4	48	21, 25	OsO^+–Si	99.5 ± 2	51a
OsO^+–C_2H_4	48	22, 26a	OsO_2^+–Si	99.5 ± 2	52
$OsOCH_2^+$–C_2H_4	48	26a, 30	$OsSi^+$–Si	99.5 ± 2	54
OsO^+–C_3H_6	58	22, 26a, 30	$OsSi_2^+$–Si	99.5 ± 2	55
OsO_2^+–H_2	42	47	$OsOSi^+$–Si	99.5 ± 2	56
Os^+–C_2H_2	74	32b	$OsOSi_2^+$–Si	99.5 ± 2	57
OsO^+–C_2H_2	74	33b	OsO_2Si^+–Si	99.5 ± 2	59
$OsC_2H_2^+$–O	78 ± 14	49	$OsO_2Si_2^+$–Si	99.5 ± 2	60
Os^+–C_3H_4	69	37a	OsO_2–O	105 ± 12	b
OsO^+–C_3H_4	69	38a			

[a] Lower limit in kcal/mol. [b] Inferred from lack of OsO_2^+ product from $Os^+ + OsO_4$; see Discussion.

is of interest for its common use as an oxidizing agent in solution, usually for the cis vicinal dihydroxylation of olefins.[11] It is also well-suited for gas-phase studies; it is volatile, and electron impact gives rise to a complete series of oxo ions, OsO_n^+ (n = 0–4). This represents the first study of the effects of successive oxo ligation on the reactivity of transition-metal ions with hydrocarbons and other small molecules.

Experimental Section

Reactions were investigated with Fourier transform ion cyclotron resonance spectrometry (FT-ICR), of which a number of reviews are available.[12] The 1-in., cubic, trapped-ion cell was built by Bio-Med Tech[13] and driven with an IonSpec data system. Software was extensively modified for use in our laboratory. A Varian 15-in. electromagnet supplied the magnetic field, typically 2.0 Tesla. Pressures were generally in the range 10^{-8}–10^{-6} Torr and were measured with a Schulz-Phelps ion gauge calibrated against a Baratron 390 HA-0001 capacitance manometer. Uncertainties in the absolute pressure are considered to limit rate constants to an accuracy of ca. 20%. Neutral compounds were obtained commercially and purified by freeze–pump–thaw cycling. Ionization was by electron impact, typically at a nominal energy of 50 eV. It is possible that electronically and vibrationally excited ions are produced by this method. Such excited ions may be manifested by upwardly curving kinetic plots.

Unwanted ions were ejected from the cell with the standard fixed-frequency and chirped double resonance pulses, in addition to gated rf excitation applied to the trapping well.[14] In ambiguous cases, reaction sequences were confirmed with standard double resonance techniques, in which suppression of the daughter ion is sought by ejection of the supposed parent. In addition, isotopically labeled ions were generally employed, for increased confidence in peak assignment and precursor identification. The most abundant isotope, ^{192}Os, was used in most cases. Isotopically labeled ions, prepared by selective ejection, were also used to study degenerate reactions. Ion ejections cause translational heating of remaining ions at nearby masses.[15] In order to determine if such translational heating would interfere unduly with kinetics measurements, some control reactions were studied in the pure OsO_4 system. Apparent rates of oxo transfer (vide infra) were measured with both unlabeled OsO_n^+ and isolated $^{192}OsO_n^+$. Translational heating would be expected to be more problematic in the isotopic case, since other isotopomers must be ejected at nearby masses. No significant differences were found, however, suggesting that translational heating is not a problem, at least in these particular reactions.

Proton affinity bracketing experiments were done by following the reactions of OsO_4H^+ with reference bases B and also the reverse reactions of OsO_4 with protonated reference bases BH^+. Methane was used as the chemical ionization reagent for formation of BH^+ and OsO_4H^+ and was present during the subsequent reactions. Low-mass ions due to methane were ejected from the cell with rf excitation of their trapping well motion.

Table II. Measured Rates and Efficiencies

reaction(s)	k^a	k/k_{ADO}^b
$OsO^+ + H_2 \rightarrow Os^+ + H_2O$	7×10^{-12}	0.005
$OsO_2^+ + H_2 \rightarrow OsO^+ + H_2O$	3×10^{-10}	0.2
$OsO_3^+ + H_2 \rightarrow OsO_2^+ + H_2O$	1×10^{-12}	0.0007
$OsO_4^+ + H_2 \rightarrow OsO_4H^+ + H$	3×10^{-10}	0.2
$OsO_4^+ + HD \rightarrow OsO_4(H,D)^+ + (H,D)$	1×10^{-10}	0.08
$OsO_4^+ + D_2 \rightarrow OsO_4D^+ + D$	6×10^{-11}	0.06
$OsO^+ + CO \rightarrow Os^+ + CO_2$	6×10^{-13}	0.0009
$OsO_2^+ + CO \rightarrow OsO^+ + CO_2$	2×10^{-11}	0.03
$OsO_3^+ + CO \rightarrow OsO_2^+ + CO_2$	9×10^{-12}	0.01
$OsO_4^+ + CO \rightarrow OsO_3^+ + CO_2$	1×10^{-10}	0.2
$OsO_4^+ + SO_2 \rightarrow OsO_3^+ + SO_3$	6×10^{-10}	0.6
$Os^+ + CH_2O$ (9)	2×10^{-10}	0.1
$OsO^+ + CH_2O$ (10)	2×10^{-10}	0.1
$OsO_2^+ + CH_2O$ (11)	1×10^{-10}	0.07
$OsO_3^+ + CH_2O$ (12)	2×10^{-10}	0.1
$OsO_4^+ + CH_2O$ (13)	4×10^{-10}	0.2
$Os^+ + NH_3 \rightarrow OsNH^+ + H_2$	2×10^{-10}	0.1
$OsO^+ + NH_3$ (16)	4×10^{-10}	0.3
$OsO_2^+ + NH_3 \rightarrow OsONH^+ + H_2O$	5×10^{-10}	0.3
$OsO_4^+ + NH_3 \rightarrow OsO_4H^+ + NH_2$	6×10^{-10}	0.3
$Os^+ + CH_4 \rightarrow OsCH_2^+ + H_2$	3×10^{-10}	0.3
$OsO^+ + CH_4 \rightarrow OsOCH_2^+ + H_2$	6×10^{-10}	0.6
$OsO_2^+ + CH_4 \rightarrow OsOCH_2^+ + H_2O$	5×10^{-10}	0.5
$OsOCH_2^+ + CH_4 \rightarrow OsOC_2H_4^+ + H_2$	2×10^{-10}	0.2
$OsO_4^+ + CH_4 \rightarrow OsO_4H^+ + CH_3$	6×10^{-10}	0.7
$OsO_4^+ + CH_2D_2 \rightarrow OsO_4(H,D)^+ +$ $CHD(H,D)$	4×10^{-10}	0.4
$OsO_4^+ + CD_4 \rightarrow OsO_4D^+ + CD_3$	2×10^{-10}	0.2

[a] Rate constant in $cm^3\ s^{-1}$. [b] Reaction efficiency; see ref 23.

The extreme reactivity of neutral OsO_4 caused some problems due to apparent degradation of organic residues (such as vacuum grease), as has been reported by other workers.[16] Apparent products include H_2O, CO_2, and CO. Water was the most problematic contaminant, interfering with proton affinity measurements, but was conveniently controlled by packing the OsO_4 finger with Linde 4A molecular sieves. No effective methods for reducing CO or CO_2 contamination were found, and these gases were always present in variable amounts. As a result, the pressure of OsO_4 could not be measured accurately, and absolute rates of ion-molecule reactions involving neutral OsO_4 could not be determined with confidence.

Rate constants were generally determined in a straightforward manner, from the slope of a semilog plot of the decay of reactant over time and from the pressure of the neutral reactant. In the case of degenerate reactions of isotopically labeled ions, the treatment was equivalent to a semilog plot of the approach to equilibrium. The slope of such a plot

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Table III. Self-Reactions in Osmium Tetroxide

reaction	relative rate[a]
$Os^+ + OsO_4 \rightarrow OsO^+ + OsO_3$	1.0
$OsO^+ + OsO_4 \rightarrow OsO_2^+ + OsO_3$	1.3
$OsO_2^+ + OsO_4 \rightarrow OsO_3^+ + OsO_3$	1.1
$^*OsO_3^+ + OsO_4 \rightarrow OsO_3^+ + {}^*OsO_4$	0.6
$^*OsO_4^+ + OsO_4 \rightarrow OsO_4^+ + {}^*OsO_4$	0.8
$^*OsO_3^- + OsO_4 \rightarrow OsO_3^- + {}^*OsO_4$	0.2
$^*OsO_4^- + OsO_4 \rightarrow OsO_4^- + {}^*OsO_4$	0.4
$OsO_3^- + OsO_4 \rightarrow OsO_4^- + OsO_3$	<0.1[b]

[a] A relative rate of 1.0 corresponds approximately to 1×10^{-9} cm^3 s^{-1}. [b] Upward curvature of the kinetic plot prevents accurate rate determination and indicates the presence of translationally or internally excited OsO_3^-.

yields the desired pseudo-first-order rate constant (involving the *total* pressure of neutral reactant).

Results

A number of thermochemical limits and rate constants were determined for the reactions observed. These are summarized in Tables I and II, respectively. Minor products have been ignored when calculating product distributions. Auxiliary thermochemical data are from references 17 and 18 unless otherwise noted.

Reactions with OsO_4. The OsO_4 system exhibits somewhat limited reactions, with formal O-atom transfer dominating. The reactions noted, and their relative rates, are listed in Table III. OsO_4^- and OsO_3^- are the only anions formed in measurable yield by electron impact (from ca. 1.5 to 70 eV). Collision-induced dissociation (CID) of these anions was unsuccessful. Among the cations, the general reaction is given by eq 1, where the asterisk

$$^*OsO_n^+ + OsO_4 \rightarrow {}^*OsO_{n+1}^+ + OsO_3 \tag{1a}$$

$$\rightarrow OsO_{n+1}^+ + {}^*OsO_3 \tag{1b}$$

denotes isotopically labeled Os and n = 0–2. These reactions imply that $D(OsO_3\text{–}O) < D(OsO_n^+\text{–}O)$. It should be noted that product ions containing both labeled and unlabeled osmium are obtained. The branching ratios between paths (1a) and (1b) are 55:45 (n = 0), 40:60 (n = 1), and 25:75 (n = 2). The values for the various branching ratios in this work are only approximate. For n = 3–4, only the degenerate reaction 2 is observed. Figure 1 illustrates the course and method of analysis of these reactions. Double resonance experiments indicated that this reaction does not occur for n = 2.

$$^*OsO_n^+ + OsO_4 \rightarrow OsO_n^+ + {}^*OsO_4 \tag{2}$$

Reactions of the negative ions are relatively slow. Both electron transfer and formal O^+ transfer are observed. In reaction 3, the

$$^*OsO_3^- + OsO_4 \xrightarrow{35\%} OsO_3^- + {}^*OsO_4 \tag{3a}$$

$$\xrightarrow{65\%} OsO_4^- + {}^*OsO_3 \tag{3b}$$

$$^*OsO_4^- + OsO_4 \rightarrow OsO_4^- + {}^*OsO_4 \tag{4}$$

extra electron may reside on either of the separating product fragments. This suggests that the two sets of products (3a and 3b) are of approximately equal energy and that the corresponding electron affinities are about the same, $EA(OsO_3) \approx EA(OsO_4)$.

No clustering was observed for either positive or negative ions. At long delay times (seconds), the terminal ion among the positive ions is OsO_3^+ (see Figure 2). Formation of this species from the lower oxo ions is by O-atom abstraction, as described above, and formation from OsO_4^+ is presumably by reaction with the CO impurity that was always present. The reaction with CO is discussed below.

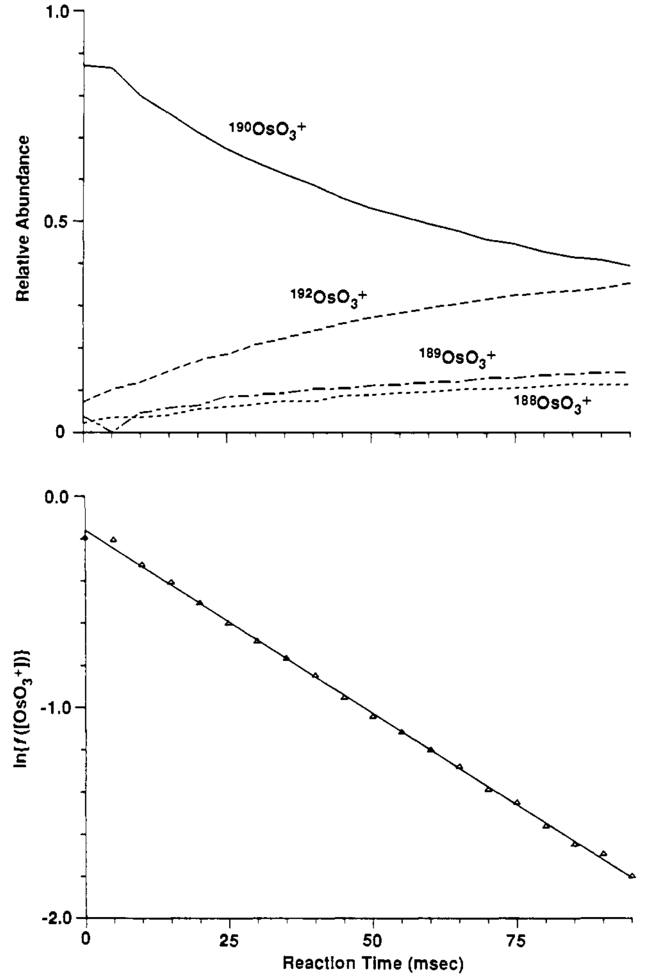

Figure 1. Degenerate reaction between $^{190}OsO_3^+$ (isolated) and OsO_4; formal O^- transfer, eq 2, n = 3. Top: Relative abundances of isotopomers of OsO_3^+. Bottom: Pseudo-first-order plot of concentration vs time; solid line is least-squares fit. The function $f([OsO_3^+]) = [^{190}OsO_3^+] - 0.375([^{192}OsO_3^+] + [^{189}OsO_3^+] + [^{188}OsO_3^+])$ is plotted to correct for the reverse reaction. The lack of curvature suggests that translational heating is not important.

Reactions with Hydrogen. Although Os^+ and the anions (OsO_3^- and OsO_4^-) are unreactive with H_2 on the ICR time scale, the cations OsO_n^+ (n = 1–4) react as shown in eq 5 and 6. The

$$OsO_n^+ + H_2 \rightarrow OsO_{n-1}^+ + H_2O \ (n = 1\text{–}3) \tag{5}$$

$$OsO_4^+ + H_2 \rightarrow OsO_4H^+ + H \tag{6}$$

sequential reactions 5 are displayed in Figure 3; relative rates are also generally indicated by the extent of the reactions. OsO_4H^+ is unreactive with H_2. If we assume that observed reactions are exothermic, then occurrence of these reactions leads us to infer that $D(OsO_{n-1}^+\text{–}O) <$ 117.4 kcal/mol (n = 1–3) and that $D(OsO_4^+\text{–}H) >$ 104.2 kcal/mol. To ascertain that impurities were not responsible for OsO_4H^+ formation, the experiment was repeated with D_2. OsO_4D^+ was formed, confirming the reaction as shown. Further confirmation comes from the observation that $^{192}OsO_4^+$ yields only $^{192}OsO_4H^+$ product, subject to uncertainties due to degenerate electron- and proton-transfer reactions. Reaction of OsO_4^+ with HD gives a roughly 2:1 ratio of OsO_4H^+ to OsO_4D^+. Table II includes the rates and efficiencies of reactions 5 and 6.

Reactions with CO and SO_2. The reactions of OsO_n^+ (n = 1–4) with CO and of OsO_4^+ with SO_2 proceed as shown in eq 7 and 8. Os^+ and OsO_4H^+ are unreactive with CO. Rates and effi-

$$OsO_n^+ + CO \rightarrow OsO_{n-1}^+ + CO_2 \ (n = 1\text{–}4) \tag{7}$$

$$OsO_4^+ + SO_2 \rightarrow OsO_3^+ + SO_3 \tag{8}$$

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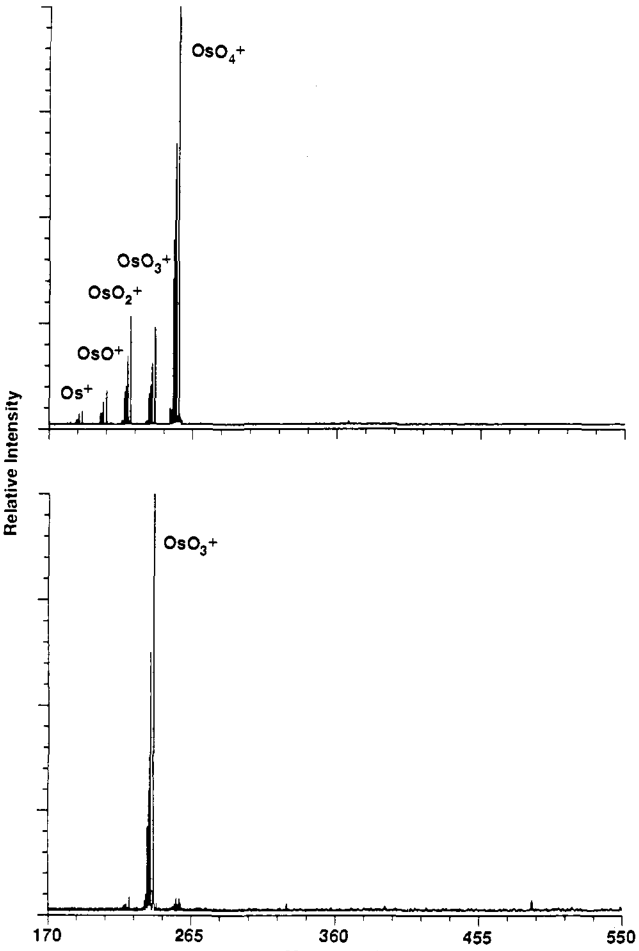

Figure 2. Top: Mass spectrum of OsO_4 under 50-eV electron impact. Bottom: After extensive reaction with neutral OsO_4; no clustering is observed. The terminal ion is OsO_3^+; see text for discussion.

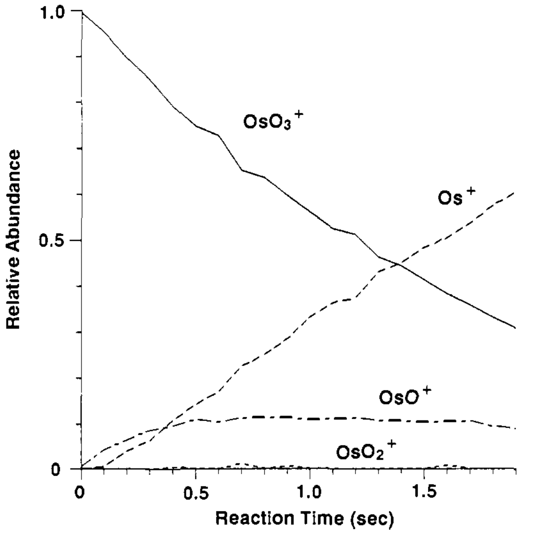

Figure 3. Primary and secondary reactions of OsO_3^+ with H_2, reactions 5; $p(H_2) = 1.6 \times 10^{-5}$ Torr. OsO_2^+ is too reactive to accumulate in any substantial amount.

ciencies for these reactions are included in Table II. The CO_2 eliminations are not thermochemically helpful (they imply bond energies less than 127.3 kcal/mol), but the SO_3 elimination indicates that $D(OsO_3^+\text{-}O) < 83.3 \pm 0.2$ kcal/mol. In other attempts to bracket the strength of this bond, O-atom transfer was sought with NO (to give NO_2) and with N_2O (to give $N_2 + O_2$). There was no reaction in either case, but this cannot be taken to imply reaction endothermicity; the reverse transfer from NO_2 to OsO_3^+ was not observed either. Likewise, although OsO_4H^+ is unreactive with CO, it does not follow that $D(OsO_3H^+\text{-}O)$ is necessarily greater than 127.3 kcal/mol.

Reactions with CH_2O. More possibilities arise for CH_2O than for the molecules considered above, and the chemistry, given by eq 9–14, is correspondingly richer. Reaction rates and efficiencies are included in Table II. Since the endothermicity for decomposition of CH_2O to CO and H_2 is only 0.5 ± 1.5 kcal/mol, these reactions provide no useful lower limits to metal–ligand bond energies.

$$Os^+ + CH_2O \xrightarrow{75\%} OsCO^+ + H_2 \tag{9a}$$

$$\xrightarrow{25\%} OsH_2^+ + CO \tag{9b}$$

$$OsO^+ + CH_2O \xrightarrow{35\%} OsCO_2^+ + H_2 \tag{10a}$$

$$\xrightarrow{35\%} Os^+ + [H_2,CO,O] \tag{10b}$$

$$\xrightarrow{20\%} OsOH_2^+ + CO \tag{10c}$$

$$\xrightarrow{10\%} OsCO^+ + H_2O \tag{10d}$$

$$OsO_2^+ + CH_2O \xrightarrow{50\%} OsO_2H_2^+ + CO \tag{11a}$$

$$\xrightarrow{30\%} OsO^+ + [H_2,CO,O] \tag{11b}$$

$$\xrightarrow{20\%} OsCO_2^+ + H_2O \tag{11c}$$

$$OsO_3^+ + CH_2O \xrightarrow{50\%} OsO_2^+ + [H_2,CO,O] \tag{12a}$$

$$\xrightarrow{25\%} OsO_3H_2^+ + CO \tag{12b}$$

$$\xrightarrow{25\%} OsO_3H^+ + HCO \tag{12c}$$

$$OsO_4^+ + CH_2O \xrightarrow{55\%} OsO_4H^+ + HCO \tag{13a}$$

$$\xrightarrow{30\%} OsO_3^+ + [H_2,CO,O] \tag{13b}$$

$$\xrightarrow{15\%} OsO_2^+ + H_2O + CO_2 \tag{13c}$$

$$OsCO^+ + CH_2O \rightarrow Os(CO)_2^+ + H_2 \tag{14}$$

Reactions with NH_3. As shown in eq 15–18, all the oxo ions except for OsO_3^+ are reactive with ammonia. Extrusion of H_2 or H_2O is the principal process, although OsO_4^+ abstracts a hydrogen atom from NH_3, as from H_2. Secondary reactions are also prominent, eq 19 and 20 and Figure 4. Again, rates and efficiencies are included in Table II. Buckner et al. have recently shown ammonia dehydrogenation to be facile for the group 3–5, early transition-metal ions.[19] The dehydrogenation reactions indicate that $D([Os^+]\text{-}NH) > 92 \pm 2.5$ kcal/mol.

$$Os^+ + NH_3 \rightarrow OsNH^+ + H_2 \tag{15}$$

$$OsO^+ + NH_3 \xrightarrow{65\%} OsONH^+ + H_2 \tag{16a}$$

$$\xrightarrow{35\%} OsNH^+ + H_2O \tag{16b}$$

$$OsO_2^+ + NH_3 \rightarrow OsONH^+ + H_2O \tag{17}$$

$$OsO_4^+ + NH_3 \rightarrow OsO_4H^+ + NH_2 \tag{18}$$

$$OsNH^+ + NH_3 \rightarrow OsN_2H_2^+ + H_2 \tag{19}$$

$$OsONH^+ + NH_3 \rightarrow OsN_2H_2^+ + H_2O \tag{20}$$

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(19) Buckner, S. W.; Gord, J. R.; Freiser, B. S. *J. Am. Chem. Soc.*, submitted for publication.

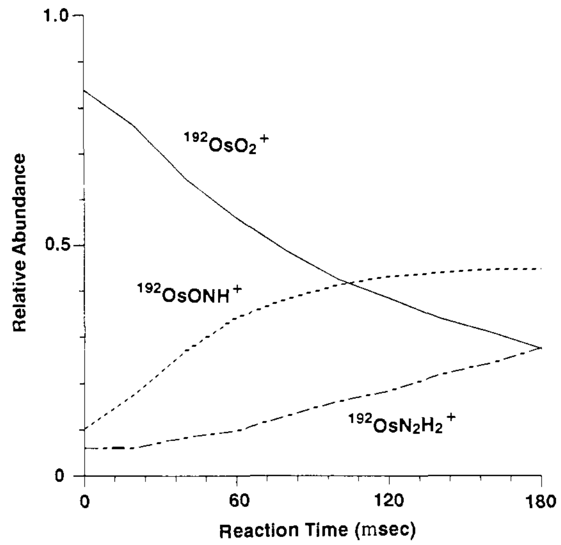

Figure 4. Sequential double bond metathesis of $^{192}OsO_2^+$ with NH_3, reactions 17 and 20. $p(NH_3) = 4 \times 10^{-7}$ Torr.

Reactions with Methane. As with ammonia, all the oxo ions except OsO_3^+ are reactive under our conditions, reactions 21–24. A number of secondary reactions, 25–30, are observed in this system as well. Measured rates and efficiencies are included in Table II. The primary and peculiar secondary reactions of OsO_4^+ were confirmed with CD_4. Reaction of OsO_4^+ with CH_2D_2 gives the statistical 1:1 ratio of OsO_4H^+ to OsO_4D^+. Occurrence of the secondary reaction 30 implies that $\Delta H_f(OsO_3H_2^+) < 111.7 \pm 7.5$ kcal/mol.[20] (Assuming $CH_3O^\bullet$ to be the neutral product yields $\Delta H_f(OsO_3H_2^+) < 105.2 \pm 5.5$ kcal/mol.[21])

$$Os^+ + CH_4 \rightarrow OsCH_2^+ + H_2 \tag{21}$$

$$OsO^+ + CH_4 \rightarrow OsOCH_2^+ + H_2 \tag{22}$$

$$OsO_2^+ + CH_4 \rightarrow OsOCH_2^+ + H_2O \tag{23}$$

$$OsO_4^+ + CH_4 \rightarrow OsO_4H^+ + CH_3 \tag{24}$$

$$OsCH_2^+ + CH_4 \rightarrow OsC_2H_4^+ + H_2 \tag{25}$$

$$OsOCH_2^+ + CH_4 \xrightarrow{80\%} OsOC_2H_4^+ + H_2 \tag{26a}$$

$$\xrightarrow{20\%} OsC_2H_4^+ + H_2O \tag{26b}$$

$$OsOCH_2^+ + OsO_4 \rightarrow OsO_2CH_2^+ + OsO_3 \tag{27}$$

$$OsOC_2H_4^+ + CH_4 \rightarrow OsOC_3H_6^+ + H_2 \tag{28}$$

$$OsOC_2H_4^+ + OsO_4 \rightarrow OsO_2C_2H_4^+ + OsO_3 \tag{29}$$

$$OsO_4H^+ + CH_4 \rightarrow OsO_3H_2^+ + [CH_3O] \tag{30}$$

Other thermochemical limits derived are $D([Os^+]–CH_2) > 109.9 \pm 1$ kcal/mol, $D([Os^+]–C_2H_4) > 48.3 \pm 0.2$ kcal/mol; $D(OsO^+–C_3H_6) > 58.6 \pm 0.4$ kcal/mol, $D(OsO_4^+–H) > 104.8 \pm 0.3$ kcal/mol, and $D([OsOCH_2^+]–O) > D(OsO_3–O)$. The methane dehydrogenation reaction implies facile α-elimination. Although exothermic methane dehydrogenation is unusual, it has previously been observed with Ta^+.[22] Reaction of Os^+ with CH_2D_2 yields $OsCH_2^+$, $OsCHD^+$, and $OsCD_2^+$ in a roughly statistical 1.5:4:1 ratio.

The sole product of the reaction between Os^+ and acetaldehyde is the osmium methylidene complex indicated in eq 31. This is a fast reaction, with a kinetic efficiency of $k_{obsd}/k_{ADO} \approx 0.3$.[23] The reaction was confirmed with acetaldehyde-d_4. Singly labeled CH_3CDO gives a statistical $OsCH_2^+$:$OsCHD^+$ ratio of 1:1.

$$Os^+ + CH_3CHO \rightarrow OsCH_2^+ + [H_2,CO] \tag{31}$$

Ethane. Both single and double dehydrogenation occur with Os^+ and OsO^+; OsO_2^+ and OsO_3^+ effect single dehydrogenation but at lower rates. OsO_4^+ exhibits only H atom abstraction. Results are detailed in eq 32–36. $OsO_4H_2^+$ was also observed from OsO_4^+, but its origin was unclear. These processes imply that $D([Os^+]–C_2H_4) > 32.7 \pm 0.2$ kcal/mol and $D([Os^+]–C_2H_2) > 74.4 \pm 0.3$ kcal/mol.

$$Os^+ + C_2H_6 \xrightarrow{50\%} OsC_2H_4^+ + H_2 \tag{32a}$$

$$\xrightarrow{50\%} OsC_2H_2^+ + 2H_2 \tag{32b}$$

$$OsO^+ + C_2H_6 \xrightarrow{20\%} OsOC_2H_4^+ + H_2 \tag{33a}$$

$$\xrightarrow{45\%} OsOC_2H_2^+ + 2H_2 \tag{33b}$$

$$\xrightarrow{35\%} OsC_2H_2^+ + H_2 + H_2O \tag{33c}$$

$$OsO_2^+ + C_2H_6 \rightarrow OsO_2H_2^+ + C_2H_4 \tag{34}$$

$$OsO_3^+ + C_2H_6 \rightarrow OsO_3H_2^+ + C_2H_4 \tag{35}$$

$$OsO_4^+ + C_2H_6 \rightarrow OsO_4H^+ + C_2H_5 \tag{36}$$

***n*-Propane.** Reactions in this system are shown in eq 37–42. Double dehydrogenation is common. Note that products of C–C bond cleavage are apparent with Os^+ and probably with OsO^+. ($OsC_3H_6^+$ is isobaric with $OsOC_2H_2^+$ and so represents an alternative product assignment.) Dehydrogenation implies that $D([Os^+]–C_3H_4) > 69.2 \pm 0.4$ kcal/mol, in addition to other limits consistent with those established above.

$$Os^+ + C_3H_8 \xrightarrow{65\%} OsC_3H_4^+ + 2H_2 \tag{37a}$$

$$\xrightarrow{25\%} OsC_2H_2^+ + H_2 + CH_4 \tag{37b}$$

$$\xrightarrow{10\%} OsCH_2^+ + C_2H_6 \tag{37c}$$

$$OsO^+ + C_3H_8 \xrightarrow{85\%} OsOC_3H_4^+ + 2H_2 \tag{38a}$$

$$\xrightarrow{15\%} OsOC_2H_2^+ + H_2 + CH_4 \text{ and/or } OsC_3H_6^+ + H_2O \tag{38b}$$

$$OsO_2^+ + C_3H_8 \rightarrow OsOC_3H_4^+ + H_2 + H_2O \tag{39}$$

$$OsO_3^+ + C_3H_8 \rightarrow OsO_3H_2^+ + C_3H_6 \tag{40}$$

$$OsO_4^+ + C_3H_8 \rightarrow OsO_4H^+ + C_3H_7 \tag{41}$$

$$OsC_3H_4^+ + C_3H_8 \rightarrow OsC_6H_8^+ + 2H_2 \tag{42}$$

***n*-Butane.** The experiments with butane were not as clean as those with the simpler molecules. Nonetheless, reactions 43 and 44, double and triple dehydrogenation, were unambiguously identified. Implications are that $D([Os^+]–C_4H_6) > 56.5 \pm 0.4$ kcal/mol (1,3-butadiene) and $D([Os^+]–C_4H_4) > 109 \pm 1$ kcal/mol (butatriene).

$$Os^+ + C_4H_{10} \xrightarrow{50\%} OsC_4H_4^+ + 3H_2 \tag{43a}$$

$$\xrightarrow{50\%} OsC_4H_6^+ + 2H_2 \tag{43b}$$

$$OsO^+ + C_4H_{10} \xrightarrow{75\%} OsOC_4H_4^+ + 3H_2 \tag{44a}$$

$$\xrightarrow{25\%} OsOC_4H_6^+ + 2H_2 \tag{44b}$$

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[20] $\Delta H_f(^\bullet CH_2OH) = -5.8 \pm 3.0$ kcal/mol: Dyke, J. M.; Ellis, R.; Jonathan, N.; Keddar, N.; Morris, A. *Chem. Phys. Lett.* **1984**, *111*, 207.

[21] $\Delta H_f(CH_3O^\bullet) = 0.7 \pm 1.0$ kcal/mol: Engelking, P. C.; Ellison, G. B.; Lineberger, W. C. *J. Chem. Phys.* **1978**, *69*, 1826.

[22] Freiser, B. S. and co-workers, manuscript in preparation.

[23] Collision rates are calculated by using ADO theory: Su, T.; Bowers, M. T. *Int. J. Mass Spec. Ion Phys.* **1973**, *12*, 347.

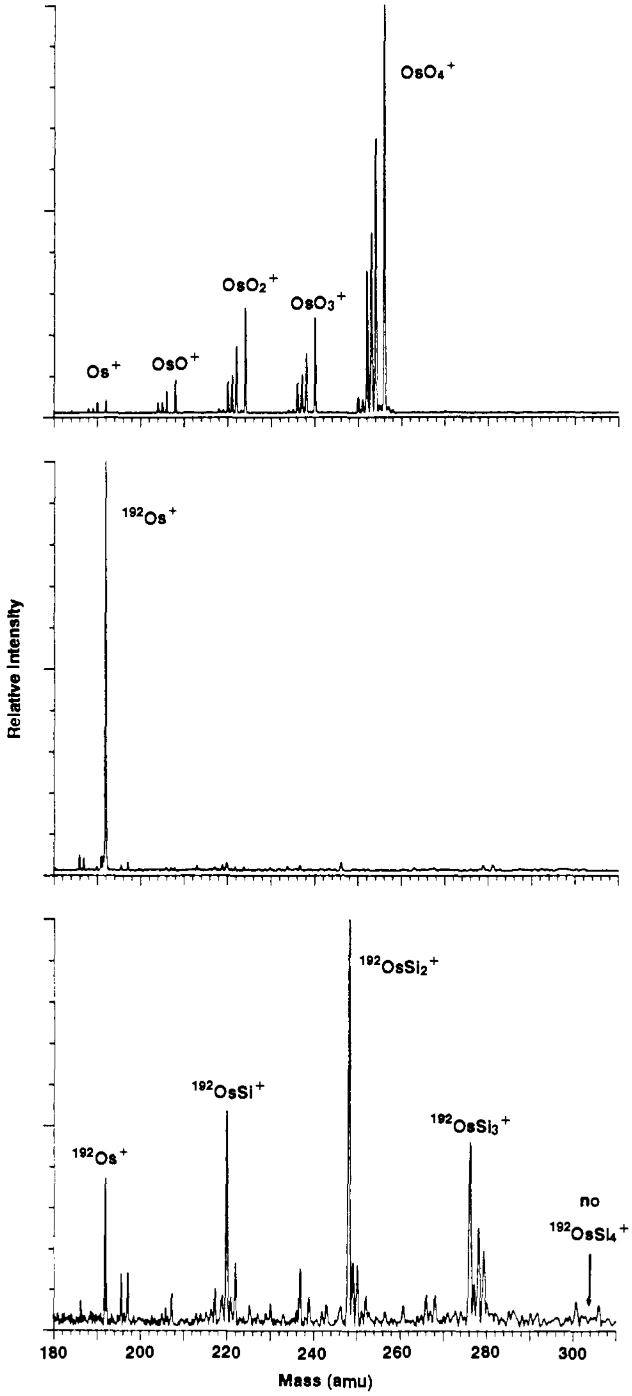

Figure 5. Osmium silicide formation from $^{192}Os^+$ and SiH_4, reactions 50a, 54, and 55. Top: Ions generated by 50-eV electron impact on OsO_4. Center: $^{192}Os^+$ isolated by ejections of all other ions, including those of mass less than 180 amu. Bottom: After 800 ms of reaction with ≈4 × 10^{-7} Torr of SiH_4.

Ethylene. Os^+ effects sequential dehydrogenation, reactions 45 and 48. A weak signal corresponding to $OsC_6H_6^+$ is also

$$Os^+ + C_2H_4 \rightarrow OsC_2H_2^+ + H_2 \tag{45}$$

$$OsO^+ + C_2H_4 \xrightarrow{50\%} OsOC_2H_2^+ + H_2 \tag{46a}$$

$$\xrightarrow{50\%} Os^+ + [C_2H_4,O] \tag{46b}$$

$$OsO_2^+ + C_2H_4 \rightarrow OsO_2H_2^+ + C_2H_2 \tag{47}$$

$$OsC_2H_2^+ + C_2H_4 \rightarrow OsC_4H_4^+ + H_2 \tag{48}$$

$$OsOC_2H_2^+ + OsO_4 \rightarrow OsO_2C_2H_2^+ + OsO_3 \tag{49}$$

observed. These reactions establish that $D(OsO_2^+{-}H_2)$ and $D(OsC_2H_2^+{-}C_2H_2) > 41.7 \pm 0.3$ kcal/mol. Reduction of OsO^+, reaction 46, implies that $D(Os^+{-}O) < 111.8 \pm 0.2$ kcal/mol. OsO_2^+ reacts only slowly, eq 47, and OsO_4^+ and OsO_3^+ appear unreactive with C_2H_4.

Reactions with SiH_4. Complete dehydrogenation of SiH_4 is the dominant reaction, eq 50–60, and was observed to occur sequentially up to three times (see Figure 5).

$$Os^+ + SiH_4 \xrightarrow{85\%} OsSi^+ + 2H_2 \tag{50a}$$

$$\xrightarrow{15\%} OsSiH_2^+ + H_2 \tag{50b}$$

$$OsO^+ + SiH_4 \xrightarrow{90\%} OsOSi^+ + 2H_2 \tag{51a}$$

$$\xrightarrow{10\%} OsSiH_2^+ + H_2O \tag{51b}$$

$$OsO_2^+ + SiH_4 \xrightarrow{65\%} OsO_2Si^+ + 2H_2 \tag{52a}$$

$$\xrightarrow{35\%} OsO^+ + [SiH_4O] \tag{52b}$$

$$OsO_4^+ + SiH_4 \rightarrow OsO_4H^+ + SiH_3 \tag{53}$$

$$OsSi^+ + SiH_4 \rightarrow OsSi_2^+ + 2H_2 \tag{54}$$

$$OsSi_2^+ + SiH_4 \rightarrow OsSi_3^+ + 2H_2 \tag{55}$$

$$OsOSi^+ + SiH_4 \rightarrow OsOSi_2^+ + 2H_2 \tag{56}$$

$$OsOSi_2^+ + SiH_4 \rightarrow OsOSi_3^+ + 2H_2 \tag{57}$$

$$OsOSi^+ + OsO_4 \rightarrow OsO_2Si^+ + OsO_3 \tag{58}$$

$$OsO_2Si^+ + SiH_4 \rightarrow OsO_2Si_2^+ + 2H_2 \tag{59}$$

$$OsO_2Si_2^+ + SiH_4 \rightarrow OsO_2Si_3^+ + 2H_2 \tag{60}$$

OsO_3^+ is unreactive, and OsO_4^+ reacts by H atom abstraction. No Si_4 products are formed. Silicide formation indicates that the strength of each additional bond to Si exceeds 99.5 ± 2 kcal/mol. Reactions 50b and 58 indicate that $D(Os^+{-}SiH_2) > 61 \pm 3$ kcal/mol[24] and $D(OsOSi^+{-}O) > D(OsO_3{-}O)$, respectively. Reaction 52b implies $D(OsO^+{-}O) < 130 \pm 5$ kcal/mol. Note that the products of reaction 52b may be $SiO + 2H_2$, simply a loss of SiO subsequent to reaction 52a. This process would indicate $D(OsO^+{-}O) < 91.8 \pm 3$ kcal/mol.[25]

Reactions with Methylsilane. Many reactions were seen with CH_3SiH_3, eq 61–65, some of them quite novel. Results with

$$Os^+ + CH_3SiH_3 \xrightarrow{75\%} OsSi^+ + CH_4 + H_2 \tag{61a}$$

$$\xrightarrow{25\%} OsCHSiH^+ + 2H_2 \tag{61b}$$

$$OsO^+ + CH_3SiH_3 \xrightarrow{70\%} OsOCHSiH^+ + 2H_2 \tag{62a}$$

$$\xrightarrow{30\%} OsOCSi^+ + 3H_2 \tag{62b}$$

$$OsO_2^+ + CH_3SiH_3 \xrightarrow{30\%} OsO^+ + [SiH_6O] \tag{63a}$$

$$\xrightarrow{30\%} OsO_2Si^+ + CH_4 + H_2 \tag{63b}$$

$$\xrightarrow{30\%} OsO_2SiH^+ + [CH_5] \tag{63c}$$

$$\xrightarrow{10\%} OsOCHSiH^+ + H_2 + H_2O \tag{63d}$$

$$OsO_4^+ + CH_3SiH_3 \rightarrow OsO_4H^+ + [SiCH_5] \tag{64}$$

$$OsSi^+ + CH_3SiH_3 \rightarrow OsSi_2^+ + CH_4 + H_2 \tag{65}$$

$$OsO_2Si^+ + OsO_4 \rightarrow OsO_3Si^+ + OsO_3 \tag{66}$$

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[24] Shin, S. K.; Beauchamp, J. L. *J. Phys. Chem.* **1986**, *90*, 1507.

[25] (a) H_3SiOH implies an upper limit of 130 ± 5 kcal/mol, based upon the following: Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M.-B.; Apeloig, Y.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 260. (b) $H_2SiO + H_2$ implies an upper limit of 86 ± 7 kcal/mol, based upon the following: Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M.-B.; Apeloig, Y.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 270. (c) $SiH_2 + H_2O$ implies an upper limit of 57 ± 4 kcal/mol; see ref 26a.

Table IV. Proton-Transfer Reactions

base	PA[a]	BH^+ xfer?	OsO_4H^+ xfer?	k[b]	k/k_{ADO}[c]
CS_2	166.1[d]	no	yes	9 ± 3	1.0 ± 0.3
CH_3Br	165.7[e]	no	yes	10 ± 3	0.9 ± 0.3
C_2H_4	162.6[d]	no	yes	4 ± 3	0.4 ± 0.3
CF_3COCl	161.2[d]	yes[f]	yes	1.2 ± 0.2	0.12 ± 0.05
SO_2	155.3[d]	yes	no		
$(CF_3)_2CO$	153.8[d]	yes	no		

[a] Proton affinity of base in kcal/mol. [b] Rate constant for proton transfer from OsO_4H^+ to the base, in units of 10^{-10} cm^3 s^{-1}. [c] Reaction efficiency; see ref 23. [d] Value from ref 27. [e] Value from ref 28. [f] Proton transfer from CF_3COClH^+ appears slower than transfer from OsO_4H^+.

labeled CH_3SiD_3 are consistent with those listed below. OsO_3^+ is again unreactive, and OsO_4^+ abstracts a hydrogen atom as indicated in eq 64. Reaction 62b implies that $D(OsO^+–SiC) > 179 \pm 8$ kcal/mol.[26]

Proton Affinity Measurement. The proton affinity of OsO_4 was bracketed with a ladder of reference bases of known proton affinity. Reference proton affinity values were taken from the recent work of McMahon and Kebarle when available.[27] Other values were obtained from the compilation by Lias et al.[28] Proton transfer was sought in both directions, reaction 67, in order to increase confidence in the relative affinities. As mentioned in

$$OsO_4H^+ + B: \rightleftharpoons OsO_4 + BH^+ \qquad (67)$$

the Experimental Section, the pressure of OsO_4 could not be determined reliably, precluding quantitative interpretation of equilibria. Results of the various proton-transfer experiments are summarized in Table IV. The kinetic efficiencies of the proton transfers from OsO_4H^+ are displayed graphically in Figure 6 as well as in Table IV. Bracketing alone leads to PA(OsO_4) = 159 ± 4 kcal/mol. Although competing reactions prevent attainment of equilibrium, proton transfer is seen in both directions for CF_3COCl, so that PA(OsO_4) must be quite close to PA(CF_3COCl). Our recommended value is therefore 161 ± 2 kcal/mol. Observed reactions other than simple proton transfer are described below.

OsO_4H^+ reacts with isobutane to yield a butyl cation, assumed to be the tertiary isomer. This process implies PA(OsO_4) < 166 ± 2 kcal/mol.[29]

$$OsO_4H^+ + i\text{-}C_4H_{10} \rightarrow t\text{-}C_4H_9^+ + OsO_4 + H_2 \qquad (68)$$

Both fluorine-containing bases, $(CF_3)_2CO$ and CF_3COCl, react with OsO_4H^+ to give the products of the novel metathesis reaction 69. Since C–F bonds are typically about 15 kcal/mol stronger

$$O_3OsOH^+ + RCF_3 \rightarrow O_3OsF^+ + RCF_2OH \qquad (69)$$

than C–OH bonds,[30] the OsO_3^+–F bond energy must be greater than roughly 116 ± 16 kcal/mol if reaction 69 is to be exothermic.

Discussion

Bond Energies in the OsO_4 System. Only one study of the bond energies $D(OsO_n^+–O)$ has been reported to date, that by Dillard and Kiser based on electron impact appearance potential measurements.[31] The authors were aware of the limitations of their technique, noting that their derived value for $\Delta H_f(Os^+)$ was too high by 32 kcal/mol. Nonetheless, their results, listed in Table VI, do indicate an interesting alternation in bond strengths $D(OsO_3^+–O) \approx D(OsO^+–O) < D(OsO_2^+–O) \approx D(Os^+–O)$. An earlier Knudsen cell/mass spectrometric study of the gas-phase

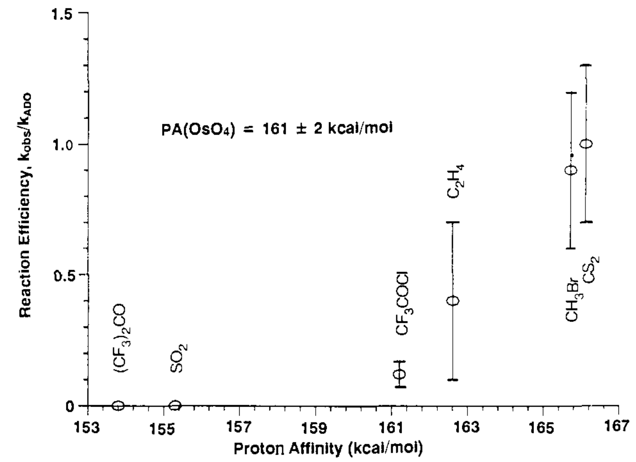

Figure 6. Kinetic efficiency of proton transfer from OsO_4H^+ to reference bases, reaction 67, plotted against the proton affinity of the reference bases.

Table V. Primary Thermochemical Values[a]

quantity	value
$\Delta H_f(OsO_{4,(g)})$	−80.9 ± 2.4 kcal/mol
$\Delta H_f(Os_{(g)})$	188 ± 2 kcal/mol
$\Delta H_f(O_{(g)})$	59.56 kcal/mol
IP(OsO_4)	12.35 ± 0.04 eV
IP(OsO_3)	12.1 ± 0.1 eV
IP(Os)	8.3 ± 0.1 eV

quantity	limit[b]	reaction
$D(Os^+–O)$	<111.8 ± 0.2	46b
$D(OsO^+–O)$	<117.4	5
$D(OsO_2^+–O)$	<117.4	5
$D(OsO_3^+–O)$	<83.3 ± 0.2	8

[a] See Appendix for discussion. [b] In kcal/mol.

equilibrium between OsO_4 and OsO_3 had yielded a value for IP(OsO_3).[32] By combining this with their appearance potentials, Dillard and Kiser calculated $D(OsO_3–O)$ = 108 kcal/mol.[31] This value and another, based on the equilibrium data from the Knudsen cell experiment[32] (72.9 kcal/mol[33]), are also included in Table VI.

Of the many thermochemical limits derived in the Results section, a few are very helpful in delimiting the bond energies just mentioned. These limits are collected in Table V, along with the auxiliary thermochemical quantities employed. A detailed discussion of these other quantities is provided in the Appendix.

Algebraic manipulation of the data in Table V yields an atomization energy for OsO_4^+ of 413.7 ± 7.6 kcal/mol, and furthermore $D(Os^+–O)$ = 99.9 ± 12.1 kcal/mol, $D(OsO^+–O)$ = 105.3 ± 12.1 kcal/mol, $D(OsO_2^+–O)$ = 105.3 ± 12.1 kcal/mol, $D(OsO_3^+–O)$ = 71.4 ± 12.1 kcal/mol, and in the neutral molecule $D(OsO_3–O)$ = 78.3 ± 14.4 kcal/mol.[34] These values are included in Table VI for comparison with the earlier work. Note that the kinetics of the reactions of OsO_n^+ with CO and H_2 is generally supportive of an alternation in bond energies. If the barriers are small and the mechanisms similar, then the relative reaction rates probably correlate with the strengths of the bonds being broken.[35] One then expects that $D(OsO_3^+–O) < D(OsO^+–O) \ll D(Os^+–O) \approx D(OsO_2^+–O)$.

Additional bond energies may be derived. In particular, the proton affinity of 161 ± 2 kcal/mol implies an O–H bond energy $D(OsO_4^+–H)$ = 132 ± 3 kcal/mol. This is similar to $D(CO_2^+–H)$

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(26) Auxiliary thermochemical information from the following: (a) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246. (b) Shin, S. K.; Irikura, K. K.; Beauchamp, J. L.; Goddard, W. A., III *J. Am. Chem. Soc.* **1988**, *110*, 24.

(27) McMahon, T. B.; Kebarle, P. *J. Am. Chem. Soc.* **1985**, *107*, 2612.

(28) Lias, S. G.; Liebman, J.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

(29) Auxiliary thermochemical information from the following: (a) Tsang, W. *J. Am. Chem. Soc.* **1985**, *107*, 2872. (b) Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 4067.

(30) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976; p 309.

(31) Dillard, J. G.; Kiser, R. W. *J. Phys. Chem.* **1965**, *69*, 3893.

(32) Grimley, R. T.; Burns, R. P.; Inghram, M. J. *J. Chem. Phys.* **1960**, *33*, 308.

(33) Schäfer, H.; Tebben, A.; Gerhardt, W. *Z. Anorg. Allg. Chem.* **1963**, *321*, 41.

(34) If the neutral products of reaction (52b) are SiO + $2H_2$, then the following bond energies are implied: $D(Os^+–O)$ = 112, $D(OsO^+–O)$ = 94, $D(OsO_2^+–O)$ = 117, $D(OsO_3^+–O)$ = 83, $D(OsO_3^+–OH)$ = 113, and $D(OsO_3–O)$ = 91 kcal/mol.

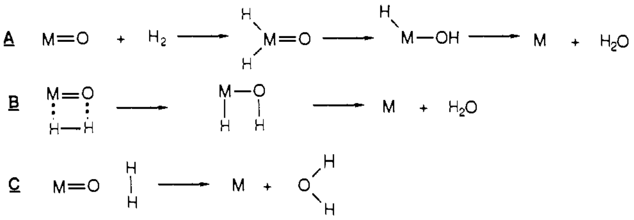
(35) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

Table VI. Derived Bond Energies and Heats of Formation[a]

M–X	previous D(M–X)	this work	ΔH_f(MX)[d]
Os^+			379.4 ± 4.3
Os^+–O	130[b]	99.9 ± 12.1	334.7 ± 12.1
OsO^+–O	96[b]	105.3 ± 12.1	276.9 ± 12.1
$OsO_2{}^+$–O	121[b]	105.3 ± 12.1	219.0 ± 12.1
$OsO_3{}^+$–O	94[b]	71.4 ± 12.1	203.9 ± 3.3
OsO_3–O	108,[b] 72.9[c]	78.3 ± 14.4	−80.9 ± 2.4
OsO_4–H^+		161 ± 2	123.8 ± 4.4
$OsO_4{}^+$–H		132 ± 3	123.8 ± 4.4
$OsO_3{}^+$–OH		101 ± 16	123.8 ± 4.4

[a] In kcal/mol. [b] Reference 31. [c] Reference 33. [d] Stationary electron convention.

Scheme I



= 135[36] but substantially greater than $D(FeO^+–H) = 106 \pm 4$, $D(CoO^+–H) = 107 \pm 4$, and $D(CrO^+–H) = 89 \pm 5$ kcal/mol.[4] $OsO_4{}^+$, like $CO_2{}^+$, is an oxygen-centered cation radical,[16,37] whereas the first-row diatomic MO^+ probably are not. Another derived bond strength is $D(OsO_3{}^+–OH) = 101 \pm 16$ kcal/mol. $D(Fe^+–OH) = 73 \pm 3$, $D(Co^+–OH) = 71 \pm 3$, and $D(Cr^+–OH) = 73 \pm 5$ kcal/mol are all much less, reflecting the relatively weak bonds in the corresponding monoxides.[4]

Reactions with OsO_4. All the reactions of $OsO_n{}^+$, including isotopic scrambling, may be explained by postulating the formation of an intermediate, $[Os_2O_{4+n}{}^+]$, that subsequently dissociates. Dissociation might be expected to yield more ions than those shown in eq 1 and 2. Since $IP(OsO_n) < IP(OsO_{n+1})$,[38] however, only the smaller fragment will carry the charge. This restricts possibilities for multiple O-atom transfer to the reaction of Os^+ to yield $OsO_2{}^+$. Double resonance experiments established that this reaction does not occur, suggesting that it is thermodynamically unfavorable and that $D(OsO_2–O) > D(OsO^+–O)$.

As mentioned above, the absolute rates of reactions with neutral OsO_4 remain uncertain. A crude estimate has been obtained by making a few assumptions, the strongest of which is that the major impurity is carbon monoxide. From the measured rate of reaction of $OsO_4{}^+$ with added CO, a pressure of CO impurity is inferred. This leads indirectly to an estimated rate of 1×10^{-9} cm^3 s^{-1} for the reaction of Os^+ with OsO_4. For comparison, the collision rate between Os^+ and OsO_4 is calculated to be 5.7×10^{-10} cm^3 s^{-1}.[39]

Reactions with H_2. Three possible mechanisms for reaction 5 are illustrated in Scheme I. Mechanism A involves initial oxidative addition of H_2 to the metal center, followed by hydrogen migration to the oxygen, and finally reductive elimination of H_2O. In B we suppose an initial $[2_s + 2_s]$ addition of H_2 across the Os=O bond, with subsequent elimination of water. Finally, mechanism C depicts direct attack of H_2 on the oxygen, resulting in a coordinated H_2O molecule which then departs.

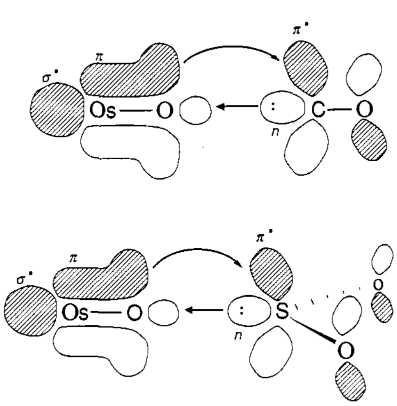


Figure 7. Orbital diagrams for proposed transition states for reactions 7 and 8, reduction with CO and SO_2. This model is directly analogous to the classical Dewar–Chatt–Duncanson model for transition-metal/π-acid bonding.

In general, we will assume that all the oxo ions that react to give analogous products do so by analogous pathways. Although this assumption leads to mechanisms that are somewhat speculative, we feel that it is reasonable, lacking evidence to the contrary. Proceeding in this spirit, mechanism C in the reaction at hand may be eliminated because of its erroneous prediction that $OsO_4{}^+$ will be reactive. For $OsO_3{}^+$, route A involves Os in the unreasonable +9 oxidation state. The mechanism of choice is thus B, involving a four-centered electrocyclic rearrangement. Such rearrangements are symmetry-allowed for systems with substantial d-orbital character in the metal–ligand bond.[40] The net positive charge on the complexes may be important in rendering the osmium–oxo bond sufficiently covalent for it to have the requisite d-orbital participation.

The failure of $OsO_4{}^+$ to react by H_2O elimination is consistent with this mechanism, which requires a vacant coordination site on the metal. The hydrogen atom abstraction, reaction 6, may be understood by noting that $OsO_4{}^+$ is an oxygen-centered radical.[37] An organic analogue is hydrogen atom abstraction by $CO_2{}^+$.[41] The isotope effect observed with HD, OsO_4H^+:OsO_4D^+ $\approx$ 2:1, suggests that the reaction proceeds by a direct mechanism,[42] rather than by a long-lived intermediate, in accord with expectations for a radical abstraction reaction. H atom abstraction has been observed in reactions of CrO^+ and of electronically excited VO^+.[4,2b]

The high kinetic efficiencies of the reactions with H_2 indicate low barriers. For comparison, it may be noted that a related reaction, $[2_s + 2_s]$ addition of H_2 to $Cl_2Ti{=}CH_2$, has been calculated to have a small activation barrier of 6.7 kcal/mol.[43]

Reactions with CO and SO_2. Mechanisms analogous to those of Scheme I may be drawn for reactions 7 and 8 of CO and SO_2. Unlike H_2, these molecules are reactive with $OsO_4{}^+$; no vacant coordination site is required. This suggests a direct attack on oxygen, analogous to mechanism C in Scheme I. Frontier orbital diagrams for the CO and SO_2 reactions are given in Figure 7 and depict $n(\text{C or S}) \rightarrow \sigma^*(MO^+)$ and $\pi(MO^+) \rightarrow \pi^*(\text{CO or } SO_2)$ dative interactions.

Reactions with CH_2O. These reactions are much like those with H_2, with the added possibility of retaining CO in the product ion. With Os^+, H_2 retention is also observed, to form the dihydride $OsH_2{}^+$. A similar reaction has been reported between Gd^+ and CH_2O.[44]

There is a conspicuous lack of products corresponding to loss of CO_2. Since CO oxidation is 10 kcal/mol more exothermic than

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(36) Auxiliary thermochemical information from the following: Franklin, J. L.; Dillard, J. G.; Rosenstock, H. M.; Herron, J. T.; Draxl, K.; Field, F. H. *Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions*; National Standard Reference Data Series, National Bureau of Standards (U.S.) 26; U.S. Government Printing Office: Washington, DC, 1969.

(37) This is the expectation based upon simple oxidation state arguments. See, also: (a) Diemann, E.; Müller, A. *Chem. Phys. Lett.* **1973**, *19*, 538. (b) Burroughs, P.; Evans, S.; Hamnett, A.; Orchard, A. F.; Richardson, N. V. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1895. (c) Our Hartree-Fock calculations place the T_2 level 1.1 eV below the T_1. For a different opinion, see: (d) Foster, S.; Felps, S.; Cusachs, L. C.; McGlynn, S. P. *J. Am. Chem. Soc.* **1973**, *95*, 5521.

(38) From estimated values in ref 31. This ordering is reasonable, based upon IP(Os) = 8.3 eV (see Appendix) and IP(O) = 13.6 eV.[36]

(39) Using $\alpha(OsO_4) = 6.4 \times 10^{-24}$ cm^{-3}, based upon data in the following: Linke, R. *Z. Phys. Chem. B* **1941**, *48*, 193.

(40) Steigerwald, M. L.; Goddard, W. A., III *J. Am. Chem. Soc.* **1984**, *106*, 308.

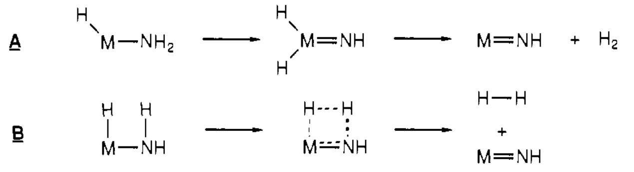
(41) Copp, N. W.; Hamdan, M.; Jones, J. D. C.; Birkinshaw, K.; Twiddy, N. D. *Chem. Phys. Lett.* **1982**, *88*, 508.

(42) Armentrout, P. B. In *Structure/Reactivity and Thermochemistry of Ions*; Ausloos, P., Lias, S. G., Eds.; Reidel: Dordrecht, 1987; pp 97–164.

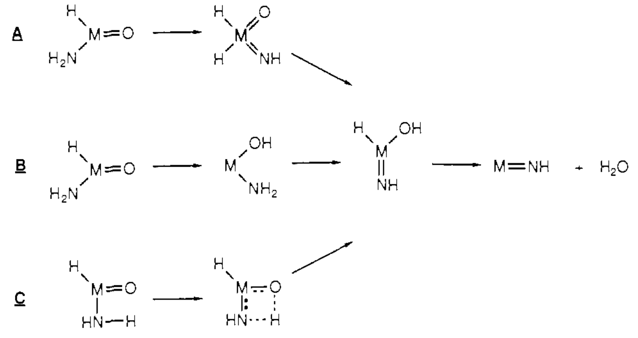
(43) Rappé, A. K. *Organometallics* **1987**, *6*, 354.

(44) Schilling, J. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1988**, *110*, 15.

Scheme II



Scheme III



H_2 oxidation, the prevalence of H_2O loss is initially surprising. Mechanistic considerations, however, can easily rationalize this observation. From Figure 7, we see that CO reacts by attacking the oxygen atom directly, along the Os–O bond axis. In the reactions of CH_2O, however, any CO fragment formed is probably bound to the metal center and therefore unable to attain the required geometry for reaction with the oxo ligand. In contrast, H_2 can react starting from a hydroxy hydride (the intermediate in Scheme I, both A and B) and presumably also from a dihydride (α-migration can be reversible; see the discussion of CH_3CHO below), both of which are reasonable intermediates in CH_2O activation. On the basis of this argument, we believe that the [H_2,CO,O] losses are actually losses of H_2O + CO.

Reactions with NH_3. These reactions appear to occur with initial insertion of the osmium center into the N–H bond. This is inferred from the inertness of OsO_3^+; the required intermediate, $OsO_3(H)(NH_2)^+$, places osmium in the unlikely +9 formal oxidation state. For the dehydrogenation reactions, two possibilities are detailed in Scheme II. In mechanism A, a dihydride intermediate is formed by α-hydrogen migration from N to Os, followed by reductive elimination of H_2. Path B involves a $[2_s + 2_s]$ concerted elimination of H_2. Note that route A is unavailable to OsO_2^+ because the dihydride would involve Os(+9). The failure of OsO_2^+ to yield OsO_2NH^+ therefore argues against pathway B, and we favor mechanism A.

If an oxo ligand is present, H_2O may be eliminated instead, a formal double-bond metathesis reaction. This reaction has also been observed with FeO^+.[19] Three possible mechanisms for this reaction are illustrated in Scheme III. In A, a dihydride intermediate is formed, followed by α-migration of hydrogen to oxygen and reductive elimination of H_2O. In B, the initial adduct rearranges to a hydroxy complex, finally leading to H_2O elimination. In mechanism C, a hydroxy hydride is formed from the adduct directly, through a four-centered transition state. Reactions 17 and 20 of OsO_2^+ and $OsONH^+$ cannot reasonably proceed by mechanism A because of oxidation state restrictions. Since the very directional orbitals of non-hydrogenic atoms are expected to slow $[2_s + 2_s]$ cycloadditions, we favor mechanism B, involving reductive elimination of H_2O from a hydroxy hydride intermediate.

This double-bond metathesis reaction has also been observed in condensed phases. In solution, neutral OsO_4 reacts with bulky amines only once to yield imido complexes. The product complexes are effective in stoichiometric or catalytic cis vicinal oxyamination of olefins.[45] Diimidomolybdenum centers have been implicated

$$OsO_4 + Bu^tNH_2 \rightarrow O_3Os{=}NBu^t + H_2O$$

as the active sites in heterogeneous bismuth molybdate ammoxidation catalysts. These centers are thought to arise from the metathetical transformation of dioxo centers by ammonia,[46] presumably by processes analogous to the sequential reactions 17 and 20.

Reactions with Methane. These reactions exhibit a variety of mechanisms, in which the carbon-containing ligands can have a strong effect on the chemistry. One of the most curious is the secondary reaction 30, to yield $^\bullet CH_2OH$ (or $CH_3O^\bullet$). The corresponding limit on $\Delta H_f(OsO_3H_2^+)$ implies $D(OsO_3^+{-}H_2) > 113.8 \pm 7.6$ kcal/mol. This is far too strong for a dihydrogen complex; assuming the hydrogens to be bonded separately lead to an average bond energy of at least 109.0 ± 8.8 kcal/mol. This high value suggests O–H bonds, rather than Os–H bonds, since typical metal–hydride bond strengths are only 30–60 kcal/mol.[47] Likewise, the inference $D(OsO_2^+{-}H_2O) > 113.9 \pm 17.6$ kcal/mol appears unreasonable for an aquo complex. We therefore conclude that $OsO_3H_2^+$ has the dihydroxy structure $OsO(OH)_2^+$, with an average $[OsO^+]{-}OH$ bond strength of at least 124.2 ± 9.1 kcal/mol. This may be compared with $D(OsO_3^+{-}OH) = 101 \pm 16$ kcal/mol, derived above.

As with NH_3, OsO_3^+ is unreactive with CH_4, again suggesting that initial oxidative addition is required. CH_4 apparently reacts with Os^+ by a route as in Scheme II, to yield the corresponding dehydrogenation products. No isotope effect was found with CH_2D_2, which yields products $OsCH_2^+$:$OsCHD^+$:$OsCD_2^+$ in nearly the statistical 1:4:1 ratio. The same mechanism is probably operative in the reaction of OsO^+, although CH_4 differs from NH_3 in that it does not yield any H_2O loss. The reaction of OsO_2^+ with CH_4 is analogous to that with NH_3, but the secondary reaction 26 results in predominant loss of H_2, in contrast to the analogous reaction 20, in which only H_2O loss is observed. No H_2O loss is seen in the secondary reaction 28. Possible mechanisms for the reactions of OsO_2^+, $OsOCH_2^+$, and $OsOC_2H_4^+$ are illustrated in Scheme IV.

There is a clear trend away from H_2O loss as the extent of hydrocarbon ligation increases. OsO_2^+ reacts only to lose H_2O; $OsOCH_2^+$ yields H_2O in the minor pathway; $OsOC_2H_4^+$ yields little or no H_2O. The simplest explanation is that hydrocarbon ligands donate electron density to the metal. Electron donation will increase the ionicity of the metal–oxygen bond, making it stronger.[48] Another contribution to the OsO_2^+ reactivity may be the "spectator oxo" effect, in which a "spectator" oxo or imido ligand compensates for loss of metal–ligand bonds by forming a triple bond to the metal center.[49]

Regardless of the particulars of the reaction mechanisms, the thermochemistry raises some intriguing possibilities for gas-phase catalysis. Especially interesting is the apparent formation of C_2H_4 and C_3H_6 complexes. (The failure to form C_4 complexes suggests an especially stable structure for $OsOC_3H_6^+$, such as an allyl hydride.) Derived thermodynamic limits leave ample leeway for reactions 70–72 to be exothermic (i.e., $-\Delta H° > 0$), and catalytic

$$OsOCH_2^+ + O_2 \rightarrow OsO_2^+ + CH_2O \qquad (-\Delta H° < 54 \pm 14 \text{ kcal/mol}) \quad (70)$$

$$OsOC_2H_4^+ + O_2 \rightarrow OsO_2^+ + CH_3CHO \qquad (-\Delta H° < 50 \pm 13 \text{ kcal/mol}) \quad (71)$$

$$OsOC_3H_6^+ + O_2 \rightarrow OsO_2^+ + CH_3CH_2CHO \qquad (-\Delta H° < 38 \pm 13 \text{ kcal/mol}) \quad (72a)$$

$$OsOC_3H_6^+ + O_2 \rightarrow OsO_2^+ + CH_3COCH_3 \qquad (-\Delta H° < 44 \pm 13 \text{ kcal/mol}) \quad (72b)$$

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(45) Chong, A. O.; Oshima, K.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 3420.

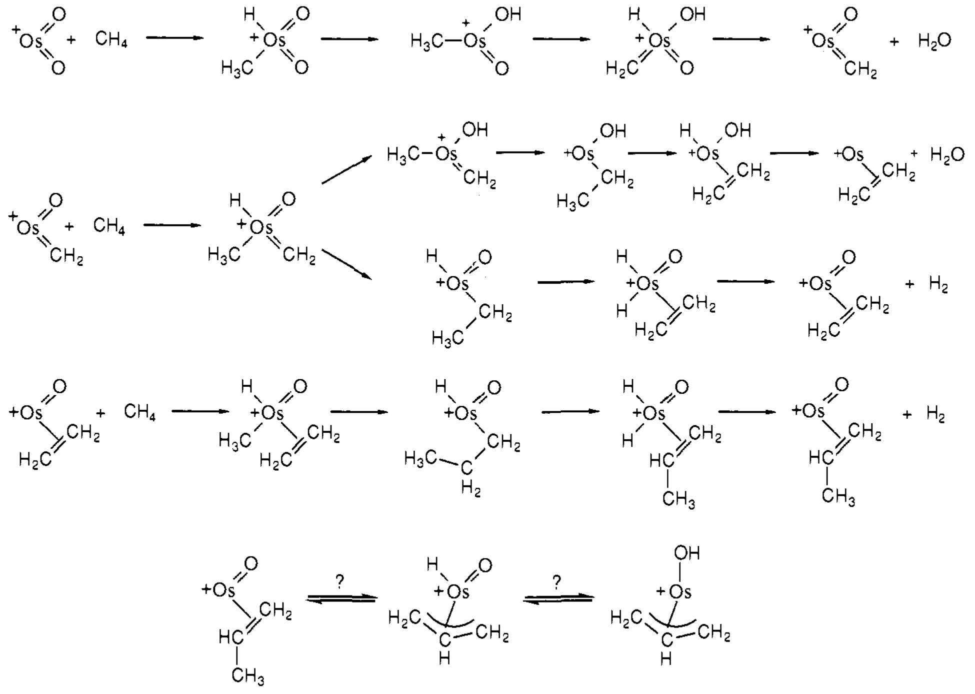
(46) Graselli, R. K. *Appl. Catal.* **1985**, *15*, 127.

(47) (a) Schilling, J. B.; Goddard, W. A., III; Beauchamp, J. L. *J. Phys. Chem.* **1987**, *91*, 5616. (b) Schilling, J. B.; Goddard, W. A., III; Beauchamp, J. L. *J. Am. Chem. Soc.* **1987**, *109*, 5565.

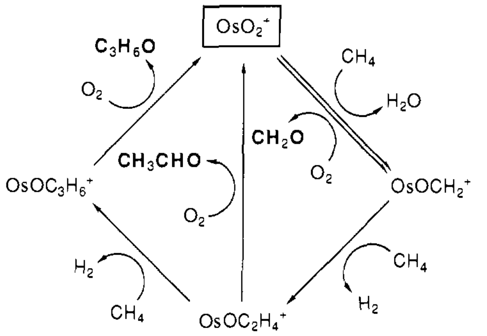
(48) Preliminary results of our Hartree–Fock calculations indicate that the Os–O bond is substantially ionic in OsO_n^+ as well as in neutral OsO_n.

(49) Rappé, A. K.; Goddard, W. A., III *J. Am. Chem. Soc.* **1982**, *104*, 3287.

Scheme IV



Scheme V



cycles converting CH_4 to a number of partially oxidized compounds may be possible, as illustrated in eq 70–72 and Scheme V. Work is currently in progress to explore the viability of these cycles. We are encouraged by reports by Squires et al. that O_2 can oxidize the ligands in gas-phase organometallic anions.[50]

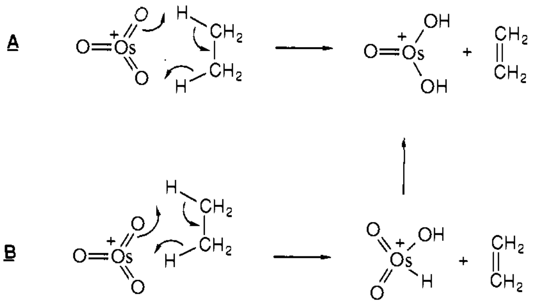
Reaction with CH_3CHO. As mentioned in the Results section, CH_3CHO reacts with Os^+ to give $OsCH_2^+$ as the only product. With acetaldehyde-d_1, CH_3CDO, the product methylidene complexes are formed in a statistical 1:1 ratio of $OsCH_2^+$:$OsCHD^+$. This suggests the intermediacy of a methylidene dihydride species in which α-hydrogen shifts are reversible, allowing scrambling.

This reaction constitutes clear evidence for reversible α-migrations to and from carbon; preliminary results with $H_2{}^{18}O$ suggest that such reversibility is also possible to and from oxygen.

Reactions with Heavier Hydrocarbons. With some exceptions, reactivity is very similar among the heavier hydrocarbons examined: ethylene, ethane, propane, and butane. Os^+ and OsO^+ both react by extensive dehydrogenation. With propane, C–C bond cleavage is also observed. Unfortunately, the limited detail available precludes any confidence in choosing from among the many possible mechanisms.

With minor exceptions, a single oxo ligand has little effect on Os^+ chemistry. As mentioned previously, this is also the case with V^+, and, as with V^+, the lack of qualitative change is probably due to the strength of the metal–oxo bond. Subsequent oxygens, however, completely change the reactivity.

Scheme VI



In reactions with C_2H_4, C_2H_6, and C_3H_8, only single dehydrogenation generally occurs with OsO_2^+ and OsO_3^+, with loss of hydrocarbon rather than H_2. Two possible mechanisms are outlined in Scheme VI, using the reaction between OsO_3^+ and C_2H_6 as an example. The reactivity of OsO_3^+ argues against oxidative addition to the metal center. Reaction 39, in which OsO_2^+ and propane yield $OsOC_3H_4^+$, H_2, and H_2O, does not appear to follow either mechanism. As usual, OsO_4^+ reacts only by hydrogen atom abstraction.

Reactions with Silane. These reactions are dominated by complete dehydrogenation of SiH_4 to yield the corresponding silicides. This is in marked contrast to reactions of first-row transition-metal atomic ions with SiH_4.[51] Single dehydrogenation is the only exothermic reaction observed with these metals, and some ions, including the osmium congener Fe^+, are unreactive.

OsO_3^+ is again unreactive, consistent with a requirement for initial oxidative addition, and OsO_4^+ again reacts only by hydrogen atom abstraction. Among the other ions, however, the ligands have no effect on the chemistry; all the $OsO_nSi_m^+$ (n = 0–2, m = 0–2) react by double dehydrogenation to the corresponding silicides. One exception is reaction 52b of OsO_2^+ to form silanol (or 2 H_2 + SiO). The formation of the higher $OsO_nSi_m^+$ suggests that the SiO moiety may be present as a ligand, as an electropositive analogue of CO. More knowledge of the structures of reactants and products is needed to devise mechanisms for the dehydrogenation. The only real clue is that the reactive $OsO_nSi_m^+$

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(50) (a) Wang, D.; Squires, R. R. *Organometallics* **1987**, *6*, 905. (b) Squires, R. R. *Chem. Rev.* **1987**, *87*, 623.

(51) Kang, H.; Jacobson, D. B.; Shin, S. K.; Beauchamp, J. L.; Bowers, M. T. *J. Am. Chem. Soc.* **1986**, *108*, 5668.

must have the metal in an oxidation state less than +7 in order for oxidative addition of SiH_4 to be reasonable.

Formation of metal silicides is of heightened interest because of the applications of these materials in the electronics industry.[52] MSi_x layers with $x > 2$ are particularly desirable in this context.

Reactions with Methylsilane. This system displays reactivity similar to silane in some cases and similar to ethane in others. As with the silane reactions, it is difficult to assign structures for the products in this system. In sharp contrast to the reactions of SiH_4, however, the products formed from CH_3SiH_3 are very sensitive to the ligands present on osmium. OsO_3^+ is unreactive, suggesting that oxidative addition is an essential first step for CH_3SiH_3, as with SiH_4 but not C_2H_6. OsO_2^+ either demethanates or is reduced to the monoxide; OsO^+ gives double and triple dehydrogenation; Os^+ reacts both by demethanation and dehydrogenation; $OsSi^+$ reacts by loss of CH_4 and H_2 to give the disilicide. The 1,1-dehydrogenation product that would be expected based upon reactions of first-row transition-metal ions[51] was not observed. The diversity of these reactions dramatically demonstrates the possible sensitivity of the chemistry of gas-phase, ionic metal complexes to the number and character of ligands.

Conclusions

Ion-molecule reactions of the osmium and oxo osmium ions OsO_n^+ (n = 0–4) with a variety of hydrocarbons and small molecules have been found to yield a wealth of chemical information. In many cases, mechanistic details have been inferred from the patterns of reactivity. Oxidative addition appears to be the initial step in many reactions, as suggested by the lack of reactivity of OsO_3^+ (formally Os^{+7}) in these systems. Isotopic labeling experiments provide strong evidence for rapidly reversible α-hydrogen shifts to and from carbon and possibly oxygen. OsO_4^+ is an oxygen-centered cation radical and exhibits H atom abstraction reactions closely analogous to the organic cation radical CO_2^{+}.[41]

Reactions of OsO_n^+ (n = 1–3) with H_2 appear to be $[2_s + 2_s]$ cycloadditions. High kinetic efficiencies indicate low barriers for this process, consonant with ab initio predictions for H_2 addition to metal methylidene complexes. Ab initio studies of metal oxo systems would be helpful in corroborating (or contradicting) this mechanism as well as clarifying the role of the net positive charge.

Reductions with CO and SO_2 are proposed to proceed through a transition state with Dewar–Chatt–Duncanson bonding *through* a coordinated oxygen atom. An ab initio evaluation of this proposal would also be welcome.

Another intriguing process observed is facile formation of mono-, di-, and trisilicides from SiH_4; such a process may have implications for silicide technology in the electronics industry. Oxo-silicide complexes may contain SiO coordinated to Os^+ in a manner similar to the archetypal CO ligand. Finally, there is the strong possibility that OsO_2^+ will catalytically oxidize methane to aldehydes in the presence of a terminal oxidant such as O_2. Investigations into this process as well as other reactions of oxometal ions are currently underway.

Acknowledgment. We gratefully acknowledge the support of donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation under Grant CHE-87-11567. K.K.I. thanks the National Science Foundation for graduate fellowship support during part of the term of this study. We also thank E. S. Uffelman for helpful suggestions.

Appendix

The following discussion is intended to clarify the reasoning behind the choice of literature values for the thermochemical quantities presented in the upper part of Table V.

The $\Delta H_f(OsO_{4,(g)})$ value is based on von Wartenberg's measurement of $\Delta H_f(OsO_{4,(c)}) = -93.4 \pm 1.4$ kcal/mol[53] and a value for $\Delta H_{vap}(OsO_4) = 12.5 \pm 1$ kcal/mol. The latter value is a simple average of those reported by von Wartenberg (13.5)[53] and by Ogawa (11.6).[54] $\Delta H_f(Os_{(g)})$ was taken to be an average of the values reported by Parrish and Reif (187.4 ± 0.9 kcal/mol)[55] and by Carrera et al. (189.0 ± 1.4).[56] IP(OsO_4) is the average of values reported from photoelectron studies by Diemann and Müller (12.39 eV),[37a] Burroughs et al. (12.35),[37b] and Foster et al. (12.32).[37d]

IP(OsO_3) is more problematic; the cited experimental value of 12.3 ± 1 eV comes from the electron impact measurement by Grimley et al.[32] They also measured IP(OsO_4) to be 12.6 ± 1 eV. If their error is assumed to be systematic, then their difference in ionization potentials is reliable. Estimating an error limit of 0.1 eV yields the listed value for IP(OsO_3).

From spectroscopic data, Albertson has estimated IP(Os) to be roughly 8.7 eV.[57] Subsequently, van Kleef and Klinkenberg reviewed the available spectroscopic data to conclude that Albertson had based his estimate upon an erroneous assignment. They suggested IP(Os) to be "about" 8.5 ± 0.1 eV.[58] In a recent and more comprehensive study of metal ionization potentials, Rauh and Ackermann determined IP(Os) = 8.28 eV by electron impact, as corrected for excited states of the neutral atoms.[59] We have chosen a value of 8.3 ± 0.1 eV to reflect this apparently more accurate value.

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(52) (a) Murarka, S. P. *Solid State Technol.* **1985**, *28*, 181. (b) Brors, D. L.; Fair, J. A.; Monnig, K. A.; Saraswat, K. C. In *Proceedings of the 9th International Conference on Chemical Vapor Deposition*; Robinson, McD., Cullen, G. W., van den Brekel, C. H. J., Blocher, J. M., Jr., Rai-Choudhury, P., Eds.; The Electrochemical Society: Pennington, NJ, 1984; pp 275–286.

(53) von Wartenberg, H. *Ann. Chem.* **1924**, *440*, 97.

(54) Ogawa, E. *Bull. Chem. Soc. Jpn.* **1931**, *6*, 302.

(55) Parrish, M. B.; Reif, L. *J. Chem. Phys.* **1962**, *37*, 128.

(56) Carrera, N. J.; Walker, R. F.; Plante, E. R. *J. Res. Nat. Bur. Stand.* **1964**, *68A*, 325.

(57) Albertson, W. *Phys. Rev.* **1934**, *45*, 304.

(58) van Kleef, Th. A. M.; Klinkenberg, P. F. A. *Physica* **1961**, *27*, 83.

(59) Rauh, E. J.; Ackermann, R. J. *J. Chem. Phys.* **1979**, *70*, 1004.