Reinvestigation of the Infrared Spectra of Oxoosmium(VI) Esters by Isotopic Labeling

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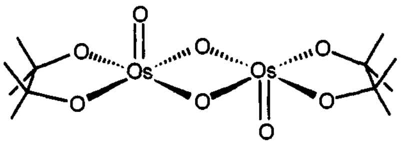
As part of our efforts to probe the mechanism of the osmylation reaction[1] using matrix isolation techniques in concert with infrared spectroscopy,[2] we have reinvestigated the infrared spectrum of the oxoosmium(VI) ester complex of 2,3-dimethyl-2-butene (tetramethylethylene, TME). We have found discrepancies in our interpretation of the isotopic data with the assignments made in the literature.[3] This short note reports our current interpretation of the infrared spectra of oxoosmium(VI) esters.

In a typical experiment, olefin diluted in CCl_4 (M/R = 10/1) and OsO_4 diluted in Ar (M/R = 10/1) were codeposited on a CsI window held at 65-75 K.[4] Warming to temperatures in excess of 180 K resulted in loss of matrix material and formation of a thin film of dimeric oxoosmium(VI) ester $[OsO_2(OCMe_2CMe_2O)]_2$ (**1**) on the window. The infrared spectrum of this film (Figure 1c) is nearly identical with that of an independently prepared sample[5] (KBr pellet; see Figure 2b) and compares favorably with the literature values[3] (Table I) for the reported absorptions. Additional absorptions not mentioned in the literature are reported in Table I.



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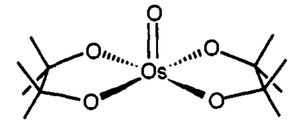

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The spectrum obtained on oxygen-18 substitution is shown in Figure 1a. In general, all bands higher in energy than 1000 cm⁻¹ show negligible isotopic shifts, while those of lower energy all show significant shifts (22–50 cm⁻¹). In particular, the strong band at 1125 cm⁻¹, previously assigned to ν(C–O) of the glycolate, is clearly a strictly hydrocarbon vibration. The strong band at 987 cm⁻¹ shifts 50 cm⁻¹, in good agreement with an absorption involving only osmium and oxygen. The doublet pattern at 987 and 935 cm⁻¹ in the mixed-isotope spectrum (Figure 1b) confirms the presence of only one oxygen in the transition, consistent with a terminal Os═O stretch.

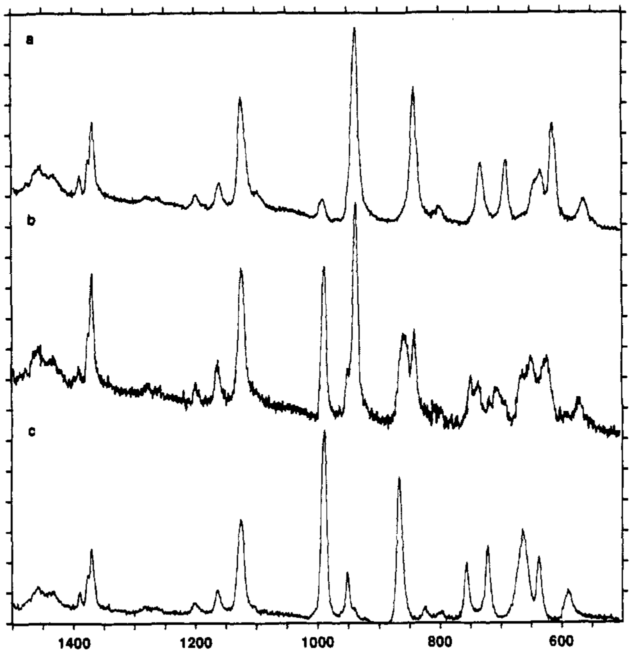

Figure 1. (a) Infrared spectrum $[OsO_2(OCMe_2CMe_2O)]_2$ formed from warming codeposited CCl_4/TME (10/1) and Ar/$Os^{18}O_4$ (~95% oxygen-18; 10/1) to >180 K. (b) Same as (a) but using $Os^{16,18}O_4$ (60% oxygen-18). (c) Same as (a) but using natural-abundance OsO_4.

Table I. Infrared Absorptions (cm⁻¹) for $[OsO_2(OCMe_2CMe_2O)]_2$ (**1**)[a]

film (^{16}O) obsd	film (^{18}O) obsd	film (^{18}O) calcd[d]	KBr pellet	lit. (^{16}O)[b]	lit. (^{18}O)[b]	assgnt[c]
588	563	557	591	588	565	Os_2O_2
636	614	603	634			ring def
663	634	628	661	655	617	Os_2O_2
720	691	682	718			ring def
754	731	714	750			ring def
864	840	819	863	860	839	Os–O–C
949		899	948			
987	937	935	992	982	932	Os═O str
1125	1125	1098[e]	1128	1122	1121	CH_3 def

[a] Bands to the blue of 1130 cm⁻¹ not tabulated. [b] Reference 3. [c] This work. [d] Based on diatomic Os–O. [e] Based on diatomic C–O.

Table II. Infrared Absorptions (cm⁻¹) for $OsO(OCMe_2CMe_2O)_2$ (**2**)[a]

KBr pellet	assgnt	KBr pellet	assgnt
632	ring def	861	Os–O–C
710	ring def	948	
721	ring def	979	Os═O str
736	ring def	1123	CH_3 def
824			

[a] Bands to the blue of 1130 cm⁻¹ not tabulated.

The remaining strong band at 864 cm⁻¹ has been previously assigned to a ν(C–C) of the ligand. The isotopic shift of 24 cm⁻¹ for this band, however, while not sufficient magnitude for a strictly Os–O or C–O vibration, indicates strong oxygen character in this transition. In the mixed-isotopic spectrum (Figure 1b) this band appears as a triplet, attesting to the involvement of two equivalent oxygen atoms in this vibration. We therefore assign this transition to a stretching frequency in the glycolate ring. Of the remaining peaks in the 800–500-cm⁻¹ region, the 754-, 720-, and 636-cm⁻¹ bands are previously unassigned. All three of these bands exhibit

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(2) McGrath, D. V.; Brabson, G. D.; Andrews, L.; Sharpless, K. B. Manuscript in preparation.

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(4) Typical ratios of OsO_4/TME/CCl_4 were approximately 1/1.5/20.

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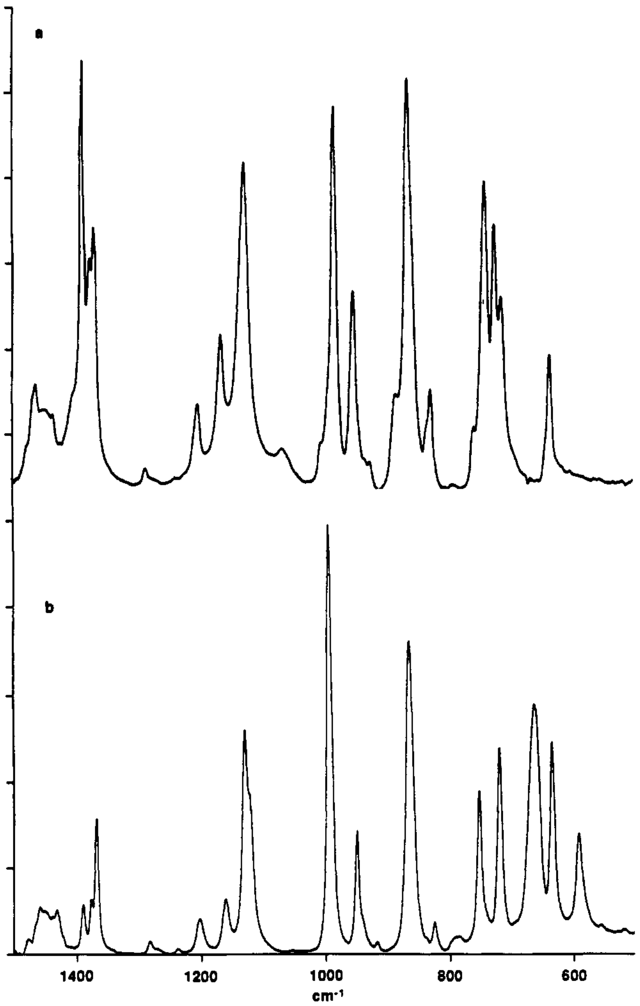

Figure 2. Infrared spectra (KBr pellet) of (a) [$OsO(OCMe_2CMe_2O)_2$] and (b) [$OsO_2(OCMe_2CMe_2O)]_2$ prepared as in ref 5.

isotopic shifts and mixed-isotopic patterns similar to the 864-cm^{-1} band, and hence can be assigned to vibrations in the glycolate ring. Those at lower energy more likely arise from bending motions within the ring rather than stretching motions, as supported by calculations on the monomeric monoglycolate of ethylene.[6]

The original tentative assignment[3] of the band at ca. 660 cm^{-1} to the central Os_2O_2 bridge was based on its necessary absence in the spectrum of the monomeric diester (**2**) (Figure 2a, Table II) as well as its large shift (655 to 617 cm^{-1}) on ^{18}O substitution. This large isotopic shift is based on an incorrect assignment of peaks. We believe the correct correlation to be as shown in Table I (663 to 634 cm^{-1} and 636 to 614 cm^{-1}). The alternative assignment would require an isotopic shift of 49 cm^{-1}, on the basis of our data, for the 663-cm^{-1} band, while the maximum expected shift for an Os–O stretching band at 660 cm^{-1} is 35 cm^{-1}. The observed shift of 29 cm^{-1} is in reasonably close agreement with the expected value. The weak band at 588 cm^{-1} is also tentatively assigned to a ν(Os–O) stretch.[3] This band exhibits a rather large ^{18}O isotopic shift of 25 cm^{-1} (calculated 31 cm^{-1}) and is reassigned to the Os_2O_2 ring.

Our current reassignment of the infrared data for [$OsO_2(OCMe_2CMe_2O)]_2$ should be general for the similar absorptions of other dimeric oxoosmium(VI) esters.[3] We have used it as a basis for the identification of intermediates in the osmylation reaction which we have observed by infrared spectroscopy in low-temperature matrices.[2]

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