significant and might imply that, although the zero field populations are the same at all times (exponential decay), they are not equal. Such a situation can arise when there is anisotropic energy transfer occurring in the crystal.[8]

Of the three spin components at zero field only the T_x substate does not have the symmetry of a pure π-electron state of the molecule. The $n\pi^*$ state has strong (one-center) spin-orbit coupling only with π states. Therefore, we have found evidence indicating in this instance that the chemistry of the triplet state[7] is controlled by the singlet admixture in the various substates. A simple spin orbit coupling calculation yields $k_y \approx k_z$ and our result can be used along with eq 2 to show that k_x is $\sim 10^{-3}$ of k_y or k_z. Thus the effect reported here is substantial.

We are presently pursuing zero field approaches to measuring the chemistry of different spin substates as well as a detailed structural analysis of dimethyl-*s*-tetrazine that will allow a more complete picture of the contributions from each spin substate to the relative reactivity of the triplet state.

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References and Notes

(1) S. A. Rice in "Excited States", Vol. II, E. C. Lim, Ed., Academic Press, New York, N.Y., 1975.
(2) M. Leung and M. A. El-Sayed, *J. Am. Chem. Soc.*, **97**, 669 (1975).
(3) R. M. Hochstrasser and D. S. King, *J. Am. Chem. Soc.*, **97**, 4760 (1975).
(4) R. M. Hochstrasser and D. S. King, *J. Am. Chem. Soc.*, **98**, 5443 (1976).
(5) R. M. Hochstrasser, D. S. King, and A. B. Smith, III, *J. Am. Chem. Soc.*, **99**, 3923 (1977).
(6) D. S. King, C. T. Denny, R. M. Hochstrasser, and A. B. Smith, III, *J. Am. Chem. Soc.*, **99**, 271 (1977).
(7) The quantum yield of the photochemical dissociation has not been measured for direct triplet excitation. It was shown in ref 3 that the yield was not qualitatively different from that of the singlet state which is known to be near unity. Strictly speaking (83 μs)$^{-1}$ represents the sum of the rates of the photochemical reaction and any intersystem to the ground state that does not result in reaction.
(8) (a) R. M. Hochstrasser in "International Review of Science", Physical Chemistry Series Two, A. D. Buckingham, Ed., Butterworth, London-Boston, 1976; (b) R. M. Hochstrasser in "Energy Transfer", R. Levine and J. Jortner, Ed., Wiley, New York, N.Y., 1976.

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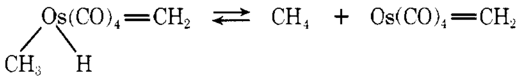
Mechanism of Reductive Elimination. 3.[1] Methyl Radical Elimination from *cis*-Dimethyltetracarbonylosmium

Sir:

Reported work on the decomposition of polymethyl transition-metal compounds, while extensive, has rarely offered definitive conclusions. For example, many workers have suggested the involvement of methyl radicals[2-6] on the basis of observed methane formation. However, the process of α elimination, which has been suggested by many workers[2a,c] and for which reasonable evidence has recently been published,[7] offers an alternative pathway for elimination of methane from two methyl ligands: it would leave a coordinated methylene carbene *without* a methyl radical intermediate. Such a mechanism has recently been proposed for the thermal decomposition of $(CH_3)_2Co[P(OCH_3)_3]_4^+$.[8]

We have therefore investigated in detail the formation of methane from $Os(CO)_4(CH_3)_2$.[9,10] Despite the extraordinary thermal stability of this compound (considerable undecomposed material can be recovered after 1 week at 162.5 °C), methane elimination is irreversible once it occurs. The presence of 0.2 atm of CH_4 has no significant effect on the rate of decomposition (gas phase) of $Os(CO)_4(CH_3)_2$, nor is any H found in $Os(CO)_4(CD_3)_2$ recovered after partial decomposition in the presence of 1 equiv of CH_4. Thus neither a *reversible* α elimination nor any other reversible process is occurring.



$$(CH_3)(H)Os(CO)_4{=}CH_2 \rightleftarrows CH_4 + Os(CO)_4{=}CH_2$$

It is much harder to demonstrate that methane formation is *not* occurring *irreversibly* from an intermediate formed by α elimination. As such a process would give only CH_4 and CD_4 from $Os(CO)_4(CH_3)_2$ and $Os(CO)_4(CD_3)_2$, respectively, a mixture of those two compounds was decomposed at 162.5 °C. All possible isotopically substituted methanes (CH_4, CH_3D, CH_2D_2, CHD_3, CD_4) were formed.[11] These results offer no support for an irreversible process via α elimination, but they do not disprove it. The observation of CH_2D_2 suggests instead that methane is attacked during the decomposition process.

Other observations confirm this inference. CD_3H is observed[12] in the methane atmosphere resulting from both the partial decomposition of $Os(CO)_4(CD_3)_2$ in the presence of 1 equiv of CH_4, described above, and the decomposition of $Os(CO)_4(CH_3)_2$ in the presence of 1 equiv of CD_4.

These results require the irreversible formation of methane via a species capable of reacting with it and suggest the intermediacy of a methyl radical.[13,14] Solvent attack is thus predicted when the reaction is run in solution. Indeed, CD_3H is formed upon thermolysis of $Os(CO)_4(CD_3)_2$ in a wide variety of solvents at 162.5 °C:[15] mesitylene, dodecane, di-*n*-pentyl ether, phenetole, *sec*-butylbenzene, 2-octanone, acetophenone, and 1,2,3,4-tetramethylbenzene. Some CD_4 is also formed, e.g., $CD_4/CD_3H = 0.18$ in di-*n*-pentyl ether.

The isotopic selectivity k_H/k_D, required to demonstrate that the intermediate is in fact a methyl radical, thus cannot be determined from a single experiment in which solvent H and solvent D compete for the intermediate; some of the CD_4 will be the result of attack by the intermediate on the starting material, not on the solvent. A solution to this problem is suggested by the following general rate equations

$$d[CD_4]/dt = k_D[I][R\text{-}D] + \text{rate of formation of } CD_4 \text{ directly from } Os(CO)_4(CD_3)_2 \quad (1)$$

$$d[CD_3H]/dt = k_H[I][R\text{-}H] \quad (2)$$

where R-D and R-H are deuterated and nondeuterated solvent and I is the reactive intermediate, presumably (but not necessarily) arising from a process first order in $Os(CO)_4(CD_3)_2$. If temperature (162.5 °C), initial concentration of $Os(CO)_4(CD_3)_2$ (0.03 M), and reaction time (20% completion) are held constant, then [I] and the "rate of formation of CD_4 directly from $Os(CO)_4(CD_3)_2$" are constant, and for a series of reactions with different mole fractions of deuterated solvent

$$[CD_4]/[CD_3H] = k_D/k_H([R\text{-}D]/[R\text{-}H]) + \text{a constant} \quad (3)$$

Thus from the slope of a plot of $[CD_4]/[CD_3H]$ against $[R\text{-}D]/[R\text{-}H]$, k_H/k_D can be obtained.[16]

Results from the thermolysis of $Os(CO)_4(CD_3)_2$ in mixtures of n-$C_{12}H_{26}$ and n-$C_{12}D_{26}$ are shown in Figure 1. The value of k_H/k_D which results, 5.3 ± 0.9, provides quantitative verification of our hypothesis that methyl radicals are involved. Similar selectivities (the numbers quoted have been extrapo-

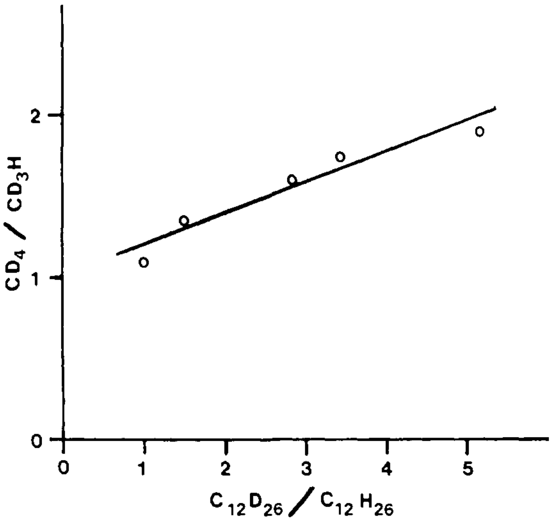


Figure 1. Plot of the CD_4/CD_3H ratio from the thermolysis of $Os(CO)_4(CD_3)_2$ in dodecane as a function of the n-$C_{12}D_{26}/n$-$C_{12}H_{26}$ ratio.

lated to 162.5 °C when necessary) have been reported for known methyl radicals attacking C_2H_6/C_2D_6 ($k_H/k_D = 5.6$)[17] and for the attack of deuteriomethyl radicals on secondary H and D in propane ($k_H/k_D = 5.2$).[18] Such isotope effects are known to be almost identical whether the reaction is conducted in solution or in the gas phase;[19] they are also virtually independent of the isotopic labeling of the methyl radical ($\cdot CD_3$ or $\cdot CH_3$).[17]

Although methane, via methyl radicals, is clearly the principal product (from 0.8 to 1.2 equiv, depending upon conditions) of the thermolysis of $Os(CO)_4(CH_3)_2$, small amounts of other products are formed. Acetone (0.2 equiv) can be detected from thermolysis in a sealed tube; the addition of 5.5 equiv of triphenylphosphine increases this yield (to 0.7 equiv) and acetone becomes the principal product. It is possible that this acetone results from simple intramolecular reductive elimination, and that the increase represents the accelerating effect of an external nucleophile,[20] but the dominance of the methyl radical path prevents investigation of this possibility: the acetone recovered from thermolysis of mixtures of $Os(CO)_4(CH_3)_2$ and $Os(CO)_4(CD_3)_2$ contains all possible combinations of hydrogen and deuterium.

In the presence of Ph_3P, as above, the principal inorganic product is $Os(CO)_3L_2$. Otherwise a number of clusters, unstable under the reaction conditions and therefore present in small steady-state concentrations, can be isolated in low yield,[21] along with some $Os_3(CO)_{12}$.

The fact that the primary process in the thermal decomposition[22] of $Os(CO)_4(CH_3)_2$ is Os-C bond cleavage contrasts with the smooth dinuclear elimination that we have observed in $Os(CO)_4H_2$[23] and $Os(CO)_4(H)CH_3$.[1] Together these results prompt the hypothesis that dinuclear elimination can only occur when hydride ligands are present or available. The fact that dinuclear elimination does not occur with the dimethyl compound $Os(CO)_4(CH_3)_2$ probably results from the inaccessibility of a methyl-bridged transition state—an inaccessibility also mirrored by the fact that methyl bridges between transition metals are extremely rare in stable compounds.[24] $Os(CO)_4(CH_3)_2$, in short, represents a case where both simple intramolecular reductive elimination and dinuclear elimination are so energetically unfavorable that the only decomposition pathway available under forcing conditions is metal-carbon bond homolysis.

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References and Notes

(1) Part 2: S. J. Okrasinski and J. R. Norton, *J. Am. Chem. Soc.* **99,** 295 (1977).

(2) Examples of such studies are the thermolysis of $(C_5H_5)Pt(CH_3)_3$[3] and the photolysis of $(C_5H_5)_2M(CH_3)_2$ (M = Ti, Zr, Hf).[4] In a few cases, such as the thermolysis of $(C_5H_5)_2Ti(CH_3)_2$[5] and the photolysis of the monomethyl $CH_3Au(PPh_3)$,[6] spectroscopic evidence for the formation of odd-electron species has been obtained. For comments on the difficulty of providing definitive evidence of homolytic M–C bond cleavage, see in particular (a) R. R. Schrock and G. W. Parshall, *Chem. Rev.* **76,** 243 (1976), as well as the discussions of metal alkyls in other reviews such as (b) M. C. Baird, *J. Organomet. Chem.*, **64,** 289 (1974), and (c) P. J. Davidson, M. F. Lappert, and R. Pearce, *Chem. Rev.*, **76,** 219 (1976).

(3) K. W. Egger, *J. Organomet. Chem.*, **24,** 501 (1970).

(4) H. Alt and M. D. Rausch, *J. Am. Chem. Soc.*, **96,** 5936 (1974).

(5) G. A. Razuvaev, V. N. Latyaeva, and L. I. Vyshinskaya, *Dokl. Akad. Nauk SSSR*, **159,** 383 (1964).

(6) P. W. N. M. Van Leeuwen, R. Kaptein, R. Huis, and C. F. Roobek, *J. Organomet. Chem.*, **104,** C44 (1976).

(7) N. J. Cooper and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 208, 761 (1974).

(8) E. L. Muetterties and P. L. Watson, *J. Am. Chem. Soc.*, **98,** 4665 (1976).

(9) (a) F. L'Eplattenier, *Inorg. Chem.*, **8,** 965 (1969); (b) F. L'Eplattenier and C. Pelichet, *Helv. Chim. Acta*, **53,** 1091 (1970); (c) R. D. George, S. A. R. Knox, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 972 (1973). Although ref 9b states that ethane is formed on thermolysis of $Os(CO)_4(CH_3)_2$ under high CO pressure, we have been unable to detect ethane under any of the conditions that we have employed.

(10) We find the most convenient synthesis to be the treatment of a suspension of $Na_2Os(CO)_4$ in tetraglyme with excess methyl tosylate; the only component of significant volatility is the product $Os(CO)_4(CH_3)_2$. Use of methyl-d_3 tosylate permits easy preparation of $Os(CO)_4(CD_3)_2$.

(11) Confirmed by high-resolution mass spectrometry.

(12) The formation of CD_3H is noted as this is the most accurately measured isotopically mixed methane.

(13) Other interpretations of the gas phase data are certainly possible as considerable amounts of solid secondary products are formed. However, the reaction of methyl radicals with methane at this temperature and pressure is compatible with known rate constants.[14]

(14) See Table 3 in J. A. Kerr, "Free Radicals", Vol. I, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, p 15.

(15) A control experiment (thermolysis of $Os(CO)_4(CH_3)_2$ in n-$C_{12}H_{26}$ under CD_4) demonstrates that methane is not attacked when the reaction is carried out in the liquid phase.

(16) This approach was suggested by that of W. A. Pryor, D. L. Fuller, and J. P. Stankey, *J. Am. Chem. Soc.*, **94,** 1632 (1972).

(17) J. R. McNesby, *J. Phys. Chem.*, **64,** 1671 (1962), and references therein.

(18) W. M. Jackson, J. R. McNesby, and B. deB. Darwent, *J. Chem. Phys.*, **37,** 1610 (1962).

(19) W. A. Pryor, "Free Radicals", McGraw-Hill, New York, N.Y., 1966, p 163.

(20) P. S. Braterman, R. J. Cross, and G. B. Young, *J. Chem. Soc., Chem. Commun.*, 627 (1975), and references therein.

(21) Mass spectrometry of these compounds and of their detuerated analogues, prepared from $Os(CO)_4(CD_3)_2$, tentatively shows their empirical formulas to be $Os_4(CO)_{12}C_3H_4$, $Os_4(CO)_{14}C_2H_4$, and $Os_4(CO)_{14}C_3H_6$.

(22) Preliminary results suggest the same process occurs photochemically: photolysis (Hanovia 450W) of $Os(CO)_4(CH_3)_2$ in hexane through quartz yields methane and no ethane.

(23) J. Evans and J. R. Norton, *J. Am. Chem. Soc.*, **96,** 7577 (1974).

(24) See comments in J. Holton, M. F. Lappert, G. R. Scollary, D. G. H. Ballard, R. Pearce, J. L. Atwood, and W. E. Hunter, *J. Chem. Soc., Chem. Commun.*, 425, 480 (1976). Substituted alkyl bridges have, however, recently been reported in paramagnetic Mn dimers: R. A. Andersen, E. Carmona-Guzman, J. F. Gibson, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 2204 (1976).

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Synthesis of α-Peroxylactones by Direct Oxygenation of Ketenes. Evidence for an Intermediate

Sir:

α-Peroxylactones possess inherent interest as high energy content molecules and importance as intermediates in chemiluminescent systems;[1] yet useful synthetic methods for pre-