Registry No. 1, 98088-31-4; 2, 109744-92-5; 3, 109744-93-6; 4, 109744-94-7; 5, 109744-95-8.

Supplementary Material Available: Tables of fractional coordinates, bond distances, bond angles, anistropic thermal parameters, and hydrogen atom coordinates and isotropic thermal parameters (5 pages); a listing of structure factor amplitudes (56 pages). Ordering information is given on any current masthead page.

---

(10) Fe–P bond distances in low-valent carbonyliron complexes usually fall in the range of 2.17–2.35 Å. See, e.g.: (a) Knoll, K.; Huttner, G.; Wasiucionek, M.; Zsolnai, L. *Angew. Chem.* 1984, *96*, 708; *Angew. Chem., Int. Ed. Engl.* 1984, *23*, 739. (b) Lal De, R.; Vahrenkamp, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* 1986, *B41*, 273. (c) Arif, A. M.; Cowley, A. H.; Pakulsky, M. *J. Am. Chem. Soc.* 1985, *107*, 2553. (d) Huttner, G.; Mohr, G.; Friedrich, G.; Schmid, H. G. *J. Organomet. Chem.* 1978, *160*, 59. (e) Williams, G. D.; Geoffroy, G. L.; Whittle, R. R.; Rheingold, A. L. *J. Am. Chem. Soc.* 1985, *107*, 729.

Competitive H–O and H–C Bond Activation in the Reaction of CH_3OH with $(OC)_3Mn^-$

Richard N. McDonald* and Michael T. Jones

Department of Chemistry, Kansas State University
Manhattan, Kansas 66506

Received April 28, 1987

Summary: The activation of the H–O and H–C bonds in CH_3OH are shown to be competitive in the reaction with $(OC)_3Mn^-$ by product studies and kinetic deuterium isotope effects.

Three oxidative addition pathways involving the H–C,[1] H–O,[2,3] and C–O bonds[3] have been suggested for the reactions of coordinatively unsaturated transition-metal complexes with alcohols. We wish to report the results of product studies and kinetic deuterium isotope effects for the reaction of the 14-electron complex $(OC)_3Mn^-$ with CH_3OH which support intermolecular H–C and H–O oxidative addition as the two competitive channels.

Our gas-phase studies are carried out in a previously described flowing afterglow (FA) apparatus in a fast flow of helium buffer gas (P_{He} = 0.7 torr, $\bar{v}$ = 57 m s^{-1}, 298 K).[4] A mixture containing major signals of $(OC)_3Mn^-$ (*m/z* 139) and $(OC)_4Mn^-$ (*m/z* 167) and a small signal of $(OC)_5Mn^-$ (*m/z* 195) is produced by dissociative electron attachment of energetic electrons with $Mn_2(CO)_{10}$.[5] Neither $(OC)_4Mn^-$ or $(OC)_5Mn^-$ react with CH_3OH, H_2O, or alkanes.

Addition of gaseous CH_3OH to the fast helium flow containing $(OC)_3Mn^-$ produced a fast decay of the signal for $(OC)_3Mn^-$ (*m/z* 139) and generated two product ions at *m/z* 143 and 169 (Table I and eq 1). The ion at *m/z* 143 is the (adduct – CO)$^-$ analogous to the product formed by the oxidative addition of H_2O to $(OC)_3Mn^-$.[5,6] Although $(OC)_2Mn(H)(OH)^-$ [5] undergoes *one* H/D exchange when allowed to react with D_2O,[7] *no* H/D exchange was observed between the *m/z* 143 ion and D_2O or CH_3OD, indicating the absence of the HO ligand. The *m/z* 143 ion reacted with SO_2 to yield $(O_2S)Mn(H)(OCH_3)^-$ (*m/z* 151) by loss of both CO ligands which implies multiple Mn-to-O bonding in *m/z* 143 with the CH_3O ligand serving as a multielectron donor.[5] The product ion at *m/z* 169 (eq 1b) is the (adduct – H_2)$^-$ analogous to the olefin product ions generated by dehydrogenation of alkanes by $(OC)_3Mn^-$.[8] Reaction of the *m/z* 169 ion with SO_2 yields $(OC)_3Mn(SO_2)^-$ (*m/z* 203) with exclusive loss of H_2CO suggesting that H_2O is η^2-bound in the ion at *m/z* 169.[6]

$$\underset{m/z\ 139}{(OC)_3Mn^-} + CH_3OH \xrightarrow{0.29} \underset{m/z\ 143}{(OC)_2Mn(H)(OCH_3)^-} + CO \qquad (1a)$$

$$\underset{m/z\ 139}{(OC)_3Mn^-} + CH_3OH \xrightarrow{0.71} \underset{m/z\ 169}{(OC)_3Mn(H_2CO)^-} + H_2 \qquad (1b)$$

The reactions of $(OC)_3Mn^-$ with various deuteriated methanol molecules were examined to determine the source of H_2 in the major product channel 1b and the kinetic deuterium isotope effects on both product forming channels. The elimination of HD in the reactions of $(OC)_3Mn^-$ with CH_3OD and CD_3OH yielding $(OD)_3Mn(H_2CO)^-$ (*m/z* 169) and $(OC)_3Mn(D_2CO)^-$ (*m/z* 171), respectively, establish the origin of H_2 in channel 1b as the H–O bond and a H–C bond in the CH_3OH molecule (Table I).

The kinetic and product data for the reactions of $(OC)_3Mn^-$ with CH_3OH, CH_3OD, CD_3OH, and CD_3OD are given in Table I. Although the errors in the reproducibility of the rate constants and product channel branching fractions are significant, we have calculated the rate constants for the separate product forming channels by using the average k_{total} and average branching fractions. The good agreement in the two values each obtained for k_{CH_3} and k_{CD_3} in these experiments strongly suggests that the initial intermolcular oxidative addition of the H–C and D–C to $(OC)_3Mn^-$ is rate limiting in channel 1b and that the intramolecular migration of H or D from oxygen to the metal is fast and does not contribute to the rate. A similar conclusion was reached for the inter- and intramolecular steps in the related dehydrogenation of alkanes by $(OC)_3Mn^-$.[8] With use of the average of the two values for k_{CH_3} and k_{CD_3}, $k_{CH_3}/k_{CD_3} \approx 2.4$.

The rate constant k_{OD} derived in the reactions of $(OC)_3Mn^-$ with CH_3OD and CD_3OD will have the larger error since these channels involve the smallest product ion signal intensities. However, the good agreement in the two results in Table I support $k_{OD} \approx 4.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} in these reactions. Thus, $k_{OH}/k_{OD} \approx 7$ is calculated for channel 1a involving oxidative addition of the H–O bond

---

(1) *Chem. Eng. News* 1985, 53 describes the paper of Professor R. G. Bergman given at the PAC CHEM 1984 meeting, and private communications with Professor Bergman. Products of exclusive H–C oxidative addition were observed or inferred by J. C. Hayes and P. O. Stoutland when mixtures of $[c\text{-}C_5(CH_3)_5][(CH_3)_3P]Ir(H)_2$ in *tert*-butyl alcohol or ethanol were irradiated in the condensed phase.

(2) Lane, K. R.; Squires, R. R. *J. Am. Chem. Soc.* 1985, *107*, 6403.

(3) McElvany, S. W.; Allison, J. *Organometallics* 1968, *5*, 416, 1219.

(4) (a) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* 1985, *107*, 4123. (b) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *Ibid.* 1980, *102*, 6491.

(5) McDonald, R. N.; Chowdhury, A. K.; Jones, M. T. *J. Am. Chem. Soc.* 1986, *108*, 3105.

(6) The reverse of the present oxidative addition reactions involving selective reductive elimination of CH_3OH from $(Me_3P)_2(Cl)(OC)Rh(H)(OCH_3)$ and of H_2CO from $(Me_3P)_2(Cl)(OC)Rh(H)(CH_2OH)$ was recently proposed: Milstein, D. *J. Am. Chem. Soc.* 1986, *108*, 3525.

(7) We believe that the *fast, single* H/D exchange observed in the reaction of $(OC)_2Mn(H)(OH)^-$ with D_2O occurs on the HO ligand via a four-centered intermediate or transition state. If $(OC)_2Mn(H)(OH)^-$ had oxidatively added D_2O, the possible products could be the starting complex ion containing one and two deuteriums (*m/z* 144 and 145) formed by retroaddition along with the HD elimination product $(OC)_2Mn(OH)(OD)^-$; $(OC)Fe(H)(OH)^{\bullet-}$ slowly added H_2O to yield $(OC)Fe(OH)_2^{\bullet-}$.[5] $(OC)_2Mn(H)(OH)^-$ failed to react with H_2O ($k < 10^{-13}$ cm^3 molecule^{-1} s^{-1}) under these same reaction conditions.[5]

(8) McDonald, R. N.; Jones, M. T. *J. Am. Chem. Soc.* 1986, *108*, 8097.

0276-7333/87/2306-1991$01.50/0

Table I. Summary of Kinetic and Product Data for the Reactions of $(OC)_3Mn^-$ with CH_3OH, CH_3OD, CD_3OH, and CD_3OD

neutral substr	product ions	fractn of product ion signal[a]	k_{total},[b] $cm^3\ molecule^{-1}\ s^{-1}$	calcd rate consts of separate product forming channels[c]
CH_3OH	$(OC)_2Mn(H)(OCH_3)^-$	0.29	$(1.2 \pm 0.1) \times 10^{-10}$	3.5×10^{-11} (k_{OH})
	$(OC)_3Mn(H_2CO)^-$	0.71		8.5×10^{-11} (k_{CH_3})
CH_3OD	$(OC)_2Mn(D)(OCH_3)^-$	0.05	$(1.0 \pm 0.2) \times 10^{-10}$	5.0×10^{-12} (k_{OD})
	$(OC)_3Mn(H_2CO)^-$	0.95		9.5×10^{-11} (k_{CH_3})
CD_3OH	$(OC)_2Mn(H)(OCD_3)^-$	0.54	$(8.4 \pm 0.2) \times 10^{-11}$	4.5×10^{-11} (k_{OH})
	$(OC)_3Mn(D_2CO)^-$	0.46		3.9×10^{-11} (k_{CD_3})
CD_3OD	$(OC)_2Mn(D)(OCD_3)^-$	0.11	$(4.2 \pm 0.2) \times 10^{-11}$	4.6×10^{-12} (k_{OD})
	$(OC)_3Mn(D_2CO)^-$	0.89		3.7×10^{-11} (k_{CD_3})

[a] Errors in these relative integrated product ion signals are ±0.03 from two runs for each substrate molecule. [b] Errors are maximum deviations from the average of two runs for each substrate molecule. Generally, our reproducibility of rate constants is ≤±10%. [c] Obtained by multiplying the average value of k_{total} by the fraction of the product ion ignal for that reaction channel; in units of $cm^3\ molecule^{-1}\ s^{-1}$.

in methanol to $(OC)_3Mn^-$. The large value for this kinetic isotope effect suggests that the hydroxyl hydrogen is transferred as a proton in a symmetrical Mn···H···O transition state with probably weaker development of the Mn···O bond.[9]

The data clearly establish the two product forming channels in eq 1 as discrete processes involving competitive intermolecular oxidative addition of the H–O and the H–C bonds of CH_3OH to $(OC)_3Mn^-$ yielding the excited isomeric negative ions **1** and **2**, respectively. Multiple bonding

$$\underset{\mathbf{1}}{[(OC)_3Mn(H)(OCH_3)^-]^*} \qquad \underset{\mathbf{2}}{[(OC)_3Mn(H)(CH_2OH)^-]^*}$$

($Mn{=}OCH_3$)[5] in **1** is expected to yield the excited 18-electron ion which then dissociates a CO ligand to yield the product ion at *m/z* 143 (eq 1a). Structure **2** is believed to undergo fast intramolecular β-hydrogen migration from oxygen to manganese producing $[(OC)_3Mn(H)_2(H_2CO)^-]^*$ which then reductively eliminates H_2 giving the major product ion at *m/z* 169 (eq 1b).

The increase in the rate constant for H–C bond oxidative addition of CH_3OH to $(OC)_3Mn^-$ compared to that with secondary CH bonds in alkanes (D^0(2° C–H) ≈ D^0($HOCH_2$–H))[10] is largely due to the increased number of collisions of $(OC)_3Mn^-$ with CH_3OH since CH_3OH has a significant dipole moment.[11] The doubling of the rate constant k_{OH} for the methanol H–O bond oxidative addition to $(OC)_3Mn^-$ compared to the analogous reaction with H_2O[5] probably is the result of the lower H–O bond dissociation energy ($D^0(CH_3O\text{–}H) = 104 \pm 1\ kcal\ mol^{-1}$,[12] $D^0(HO\text{–}H) = 119.3 \pm 0.3\ kcal\ mol^{-1}$)[13] and the associated increased acidity ($\Delta H^0_{acid}(CH_3OH) = 379\ kcal\ mol^{-1}$, $\Delta H^0_{acid}(H_2O) = 391\ kcal\ mol^{-1}$)[14] of CH_3OH. We believe that it is the similarity of the two separate rate constants for H–C and H–O activation that allows for observation of both reaction channels in the present study. This appears not to be the case with the iridium complex of Bergman et al.[1] and the Lane and Squires $HCr(CO)_3^-$ anion.[2,15]

Acknowledgment. We wish to thank the National Science Foundation for support of this research and Professor Allison and Dr. McElvany for a preprint of their paper.

Registry No. $(OC)_3Mn^-$, 101953-17-7; methanol, 67-56-1.

---

[9] Bierbaum et al. (Bierbaum, V. M.; Filley, J.; DePuy, C. H.; Jarrold, M. F.; Bowers, M. T. *J. Am. Chem. Soc.* **1985**, *107*, 2818) report $k_H/k_D = 5.5$ for the elimination reaction of H_2N^- with $(C_2H_5)_2O$ ($\rightarrow NH_3 + C_2H_4 + C_2H_5O^-$).

[10] O'Neal, H. E.; Benson, S. W. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2. $D^0(HOCH_2\text{–}H) = 95.9\ kcal\ mol^{-1}$.

[11] Ion–molecule collision rate constants are calculated by using the *average dipole orientation* theory (Su, T.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 1); for reactions with $(OC)_3Mn^-$, $k_{ADO}(c\text{-}C_5H_{10}) = 1.0 \times 10^{-9}\ cm^3\ molecule^{-1}\ s^{-1}$ and $k_{ADO}(CH_3OH) = 1.7 \times 10^{-9}\ cm^3\ molecule^{-1}\ s^{-1}$.

[12] (a) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rogers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279. (b) Engelking, P. C.; Ellison, G. B.; Lineberger, W. C. *J. Chem. Phys.* **1978**, *69*, 1826 report $\Delta H_f°(CH_3O) = 0.7 \pm 1.0\ kcal\ mol^{-1}$.

[13] "JANAF Thermochemical Tables", *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* **1971**, *NSRDS-NBS 37*.

[14] Bartmess, J. E.; McIver, R. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 2.

[15] Our results from the fast reaction of $(OC)_3Cr^{\cdot-}$ with CH_3OH showed the large oxophilicity of this chromium complex by producing 98% of the complex $(OC)_2Cr(H)(OCH_3)^{\cdot-}$.

Structural Characterization of a Linear [Au···Pt···Au] Complex, $Au_2Pt(CH_2P(S)Ph_2)_4$, and Its Oxidized Linear Metal–Metal Bonded [Au–Pt–Au] Product, $Au_2Pt(CH_2P(S)Ph_2)_4Cl_2$

H. H. Murray, David A. Briggs, Guillermo Garzón, Raphael G. Raptis, Leigh C. Porter, and John P. Fackler, Jr.*

Department of Chemistry and Laboratory for Molecular Structure and Bonding
Texas A&M University, College Station, Texas 77843

Received April 27, 1987

Summary: The reaction of the lithiated ylide anion $[Li][CH_2P(S)Ph_2]$ with $Au(C_4H_8S)Cl$ in a 2:1 ratio gives $[Li][Au(CH_2P(S)Ph_2)_2]$, characterized as the $[PPN][Au(CH_2P(S)Ph_2)_2]$ (**1**) salt. The reaction of **1** with *cis*-$Pt(Cl)_2(SEt_2)_2$ in a 2:1 ratio gives the neutral linear trinuclear complex $Au_2Pt(CH_2P(S)Ph_2)_4$ (**2**). The reaction of **1** with K_2PtCl_4 in a 1:1 ratio gives $Au_2Pt(CH_2P(S)Ph_2)_4Cl_2$ (**3**), a novel complex containing linear Cl–Au–Pt–Au–Cl bonding. This same molecular product is obtained (crystallographically identified) upon reaction of **2** with $PhICl_2$. Oxidation of **2** with CCl_4 or with Cl_2 in CCl_4 also gives **3** (identified spectroscopically by NMR) a ong with other yet to be identified species. We report here the X-ray crystal structures. **1**: $[PPN][Au(CH_2P(S)Ph_2)_2]$, *C*2/*c* (No. 15), *a* = 18.047 (7) Å, *b* = 13.262 (4) Å, *c* = 22.788 (8) Å, β = 90.91 (3)°. **2**: $Au_2Pt(CH_2P(S)Ph_2)_4$, *I*4 (No. 82), *a* = 17.348 (17) Å. **3**: $Au_2Pt(CH_2P(S)Ph_2)_4Cl_2{\cdot}C_2H_{10}O$, *P*2₁/*c* (No. 14), *a* = 18.989 (3) Å, *b* = 13.024 (2) Å, *c* = 24.191 (4) Å, β = 96.08 (1)°.

The oxidative addition of halogen or other oxidants[1] to

0276-7333/87/2306-1992$01.50/0 © 1987 American Chemical Society