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Mechanism of Reactions of Group 7 Decacarbonyl Dimers

Sir:

Obviously there remain questions regarding the mechanism of reactions of the group 7 metal carbonyl dimers.[1] I would like to use this opportunity to clarify the questions relating to *substitution* reactions of the decacarbonyls. My discussion will proceed in the following three areas: (1) Simple ligand substitution reactions of the decacarbonyls need not proceed by the same mechanism as reactions of the decacarbonyls with O_2, I_2, etc., or $M_2(CO)_8L_2$ with additional ligand where the products are mononuclear and require cleavage of the M–M bond. (2) Reactions of the dimers with O_2 do not lend themselves to detailed kinetic analysis, and the deviations from first-order behavior observed by Poë do not require homolytic fission of the M–M bond. (3) There is no evidence inconsistent with CO dissociation for ligand substitution on the decacarbonyls, and the product distribution for ligand substitution cannot be accounted for by a radical mechanism.[2]

Poë has discussed reactions of three different types without distinguishing between them.[1] This greatly complicates meaningful discussion of the mechanisms. In ligand substitution of the decacarbonyls, which we addressed in our previous paper,[2] the reaction is first order in $M_2(CO)_{10}$ and the product is $M_2(CO)_9L$ or $M_2(CO)_8L_2$ (eq 1). The kinetics of these

$$\begin{aligned} M_2(CO)_{10} + L &\rightarrow M_2(CO)_9L + CO \\ M_2(CO)_{10} + 2L &\rightarrow M_2(CO)_8L_2 + 2CO \end{aligned} \tag{1}$$

reactions have been studied by three different research groups and are summarized in Table I. There is no evidence for a dependence other than first order in the metal decacarbonyl.[2-6] In the thermal decompositions that Poë has studied,[3-8] no soluble products are observed and deviations from first-order behavior are seen at temperatures higher than those used for substitution reactions.

$$M_2(CO)_{10} + O_2 \rightarrow \text{oxides} \tag{2}$$

I will discuss the decomposition reactions in more detail below but see no reason to consider the mechanism of reaction of O_2 to be the same as that for reaction with phosphines and phosphites.[9] It is possible that O_2 could induce radical reactions on $M_2(CO)_{10}$. This has long been recognized in organic chemistry, as the following quotation shows.[10]

> "Since the oxygen molecule itself is a diradical with the electronic structure
>
> $$\cdot\ddot{\underset{..}{O}}-\ddot{\underset{..}{O}}\cdot$$
>
> it is no surprise to find that the majority of these processes [oxidations with oxygen] are free radical reactions...."

The third type of reaction that Poë discusses in the preceding paper is of $M_2(CO)_8L_2$ with additional ligand.[11-15]

$$M_2(CO)_8L_2 + L \rightarrow [M(CO)_3L_2] \rightarrow \text{no organometallic product} \tag{3}$$

The rates of these reactions show a very strong dependence on the ligand L and deviations from first-order behavior, but again no soluble products are isolated. These reactions do not pertain to the mechanism of reaction of the unsubstituted dimers, since the mechanism of reaction often changes with the degree of substitution. A good example is $Ir_4(CO)_{12}$, which is substituted by PPh_3 in a ligand-*dependent* reaction, while $Ir_4(CO)_{11}PPh_3$ undergoes further substitution in a ligand-*independent* reaction.[16] Deviations from first-order behavior in reactions of types 2 and 3 provide no useful information regarding reactions of type 1, which are very clean kinetic reactions and first order in $M_2(CO)_{10}$.

Poë bases much of his argument for homolytic fission on thermal decompositions in the presence of O_2 at high temperature.[3-8] For these reactions he observes deviations from first-order behavior, which he has analyzed by detailed kinetic treatment.[3-8] Following is a quotation from Poë's paper dealing with reaction of $Mn_2(CO)_{10}$ and $MnRe(CO)_{10}$ with O_2.[8]

> "At 110 °C, decomposition reactions under both air and pure oxygen gave first-order plots that were linear for about 80% reaction, the rate constants being the same, and equal to those for the substitution reactions with triphenylphosphine. At 125 °C the reaction under air is slower than that under pure oxygen but the latter still has the same rate as the substitution reaction. Above 125 °C the reactions under air and pure oxygen become increasingly slow compared with the limiting rate shown by the substitution reactions so that only the latter follow good Arrhenius behavior."

The key feature is that deviations from first-order behavior occur, but these are not half-order reactions. For these oxygen decomposition reactions Poë has used decalin as his solvent.[3-8] Decalin is known to undergo oxidation to decalin peroxide by O_2 at conditions very similar to those employed by Poë.[17]

$$C_{10}H_{18} + O_2 \xrightarrow{110\ °C} C_{10}H_{18}O_2 \tag{4}$$

Poë has observed oxidized solvent as a product in the reactions that deviate from first-order behavior but has never investigated the role of solvent oxidation in the mechanism.[3-8] Even if decalin peroxide does not interfere with the decomposition of $M_2(CO)_{10}$ (reaction 2), oxidation of the decalin may deplete the concentration of O_2 in solution. At low concentration of

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(8) Fawcett, J. P.; Poë, A. J.; Sharma, K. R. *J. Am. Chem. Soc.* **1976**, *98*, 1401.
(9) Other mechanisms are possible for reactions of the dimers. Neither CO dissociation nor homolytic fission can apply to reaction of the decacarbonyls with Cl_2 or Br_2 since these reactions occur rapidly at room temperature.
(10) Walling, C. "Free Radicals in Solution": Wiley: New York, 1957; p 398.
(11) Fawcett, J. P.; Jackson, R. A.; Poë, A. *J. Chem. Soc., Chem. Commun.* **1975**, 733.
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Table I. Ligand Substitution on the Decacarbonyls of Group 7

$M_2(CO)_{10}$	L	product	kinetics (order in $M_2(CO)_{10}$)	ref
$Mn_2(CO)_{10}$	PPh_3, $P(OPh)_3$, etc.	$Mn_2(CO)_9L$ and $Mn_2(CO)_8L_2$	1st order, several $t_{1/2}$	3
$Mn_2(CO)_{10}$	PPh_3	$Mn_2(CO)_9PPh_3$ and $Mn_2(CO)_8(PPh_3)_2$	1st order, $3t_{1/2}$	4
$Re_2(CO)_{10}$	PPh_3	$Re_2(CO)_8(PPh_3)_2$	1st order, 2-$3t_{1/2}$	5
$Tc_2(CO)_{10}$	PPh_3	$Tc_2(CO)_9PPh_3$ and $Tc_2(CO)_8(PPh_3)_2$	1st order, $3t_{1/2}$	6
$MnRe(CO)_{10}$	PPh_3	$(CO)_5MnRe(CO)_4PPh_3$	1st order, $3t_{1/2}$	6
$MnRe(CO)_{10}$	PPh_3, $P(OPh)_3$, PBu_3	$(CO)_5MnRe(CO)_4L$ and $MnRe(CO)_8L_2$	1st order, $3t_{1/2}$	2

O_2 would give exactly the characteristics noted in the preceding quotation and would account for the pressure dependence of O_2.[3-8] Poë has never commented on the equilibrium concentration of O_2 in decalin at these high temperatures.

In the preceding two paragraphs I have argued that ligand substitution reactions on $M_2(CO)_{10}$ are different from the other reactions which Poë has discussed in the preceding paper and that the thermal decompositions are experimentally difficult to interpret. I would now like to again present the evidence for CO dissociation and against homolytic fission in ligand substitutions on $MnRe(CO)_{10}$.[2] The rate law and dependence on the nucleophilicity of the entering ligand are analogous to those observed for substitutions on $Cr(CO)_6$ and $Mo(CO)_5Am$, which occur by ligand dissociations of an interchange type.[2,18-20] Inhibition of the rate by CO is also consistent with a CO-dissociative mechanism. The conclusive evidence against a radical mechanism is the product distribution. No homodimetallic complexes are observed (even as intermediates)[2] during the course of the reaction of $MnRe(CO)_{10}$ with phosphines and phosphites. For the observed product distribution to be obtained by homolytic fission of the Mn–Re bond, the manganese isomer, $L(CO)_4MnRe(CO)_5$, would have to rearrange to the rhenium isomer, $(CO)_5MnRe(CO)_4L$, under the reaction conditions.[2,21] This reaction does not occur.

$$L(CO)_4MnRe(CO)_5 \nrightarrow (CO)_5MnRe(CO)_4L \qquad (5)$$

The failure of this isomerization to occur under the reaction conditions rules out the radical mechanism for thermal ligand substitution.[21] The failure to observe homodimetallic complexes also rules out the radical mechanism in the absence of an unusual selectivity in recombination of radicals. In recent experiments of the 17-electron species $\cdot CpFe(CO)PPh_3$ with $Mn_2(CO)_{10}$, we observed eight products from radical recombinations during the course of the room-temperature reaction, suggesting that there is little selectivity in radical recombinations.[22,23] This is consistent with the observations that a variety of 17-electron complexes undergo recombinations at diffusion-controlled rates.[24]

In this paper I have tried to clarify the issue of reaction mechanisms of the group 7 carbonyl dimers. I have shown (1) the simple substitution reactions are different from the other reactions that Poë has studied, (2) there are substantial *experimental* problems that could lead to the poor kinetics seen in the decomposition reactions, and (3) there is *no* evidence that is inconsistent with a CO-dissociative process for the thermal ligand substitution reactions of the group 7 decacarbonyls.

Note Added in Proof. Substitution reactions on $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ occur between 100–120 and 130–150 °C, respectively. Recent work has shown that reaction to $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ does not lead to $MnRe(CO)_{10}$ at 130 °C.[27] We have confirmed this failure to react at 150 °C under a CO atmosphere in toluene. In 48 h no $MnRe(CO)_{10}$ was seen and no decomposition of $Mn_2(CO)_{10}$ or $Re_2(CO)_{10}$ was observed. These observations show that $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ cannot both undergo substitution reactions by metal–metal bond homolysis.

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(21) Both the manganese and the rhenium isomers grow in absorbance, reach a constant absorbance, and then decrease at the end of the substitution reaction, while the bissubstituted complex continues to grow throughout the reaction. If a radical mechanism is occurring, then the formation reactions must be equilibria (the growth and then decrease in concentration mandate a further reaction of $(CO)_5MnRe(CO)_4L$ and $L(CO)_4MnRe(CO)_5$, which requires Mn–Re bond fission for the radical mechanism) to give this behavior:

$$\cdot Re(CO)_4L + \cdot Mn(CO)_5 \rightleftarrows (CO)_5MnRe(CO)_4L$$
$$\cdot Mn(CO)_4L + \cdot Re(CO)_5 \rightleftarrows L(CO)_4MnRe(CO)_5$$

For the observed relative amounts of manganese and rhenium isomers to be obtained, the first equilibrium must lie to the right and the second to the left.[2] With the assumption that the 17-electron species undergo rapid ligand transfer,[22-26] the manganese isomer must rearrange to the rhenium isomer under the reaction conditions for a homolytic fission mechanism to operate. There was no trace of $(CO)_5MnRe(CO)_4L$ observed in the isomerization.

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Response to Preceding Correspondence

Sir:

Atwood has not addressed the fundamental question of why, if decomposition under O_2 occurs by a path quite different from substitution, clean substitution of $MnRe(CO)_{10}$ still occurs even under O_2 and at the same rate as substitution or decomposition individually. He also states that decomposition reactions occurring at least-than-limiting rates are "not half order". On the contrary for $Mn_2(CO)_{10}$ they vary continuously from first order down to clear half order as $[O_2]$ decreases and $[Mn_2(CO)_{10}]$ increases. The orders were determined from the dependence of initial rates on initial concentrations, i.e., under conditions where interference from products would be expected to be minimal and where any depletion of $[O_2]$ has had no time to occur. With allowance for the acknowledged complexity of the decomposition reactions, the quantitative agreement with the homolytic fission mechanism has to be considered excellent. Since the decomposition and substitution reactions must proceed by the same rate-limiting step, it is surely incumbent on those who favor the CO-dissociative mechanism to present

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