# Correspondence

## Kinetics and Mechanisms of Reactions of Dimetal Decacarbonyls

*Sir:*

In a recent paper by Sonnenberger and Atwood (S&A)[1] it was claimed, "By a careful reinvestigation of the kinetics of the substitution reactions of MnRe(CO)$_{10}$ we have shown that the previously accepted mechanism

$$MnRe(CO)_{10} + L \rightarrow MnRe(CO)_9L + CO \quad (1)$$

involving homolytic fission of the metal–metal bond is incorrect...." It was further suggested that the homolytic fission mechanism was also incorrect for the homonuclear dimeric complexes Mn$_2$(CO)$_{10}$, Tc$_2$(CO)$_{10}$, and Re$_2$(CO)$_{10}$, and instead it was concluded that CO dissociation was the rate-determining step. We wish to point out that the kinetic study reported (a) did essentially no more than repeat, with identical results, some work that had already been published several years ago[2] and (b) provided no kinetic evidence pertinent to the mechanistic question. The only new kinetic results reported were those that showed that the rates of reaction 1, previously shown[2] to be independent of the *concentration* of L when L = PPh$_3$, were also independent of the *nature* of L when L = PPh$_3$, P(OPh)$_3$, and P-*n*-Bu$_3$. Additional evidence offered against the homolytic fission mechanism was based on the nature of the observed products and the absence of others. Again we had shown[3] that the product of reaction 1 (L = PPh$_3$) was (OC)$_5$MnRe(CO)$_4$(PPh$_3$) and had also shown that the other isomer (PPh$_3$)(OC)$_4$MnRe(CO)$_5$ could be identified in solution,[3] though it was not isolated. No homonuclear dimeric products were observed in either study.[1–3]

The very positive kinetic evidence for homolytic fission as the rate-determining step in oxidation and substitution reactions of MnRe(CO)$_{10}$[4] and other[2–9] complexes has been presented in detail elsewhere. The essential feature is the decrease below unity and toward 0.5 of the order with respect to [complex] for reactions that proceed at rates less than the limiting ones. This arises because the slower reactions involve a competition between the second-order recombination of the metal-centered radicals and first-order or pseudo-first-order substitution or oxidation of the radicals. That substitution and oxidation reactions involve the same initial rate-determining process is shown by the general identity, often over wide temperature ranges, of rates of substitution, oxidative decomposition under atmospheres of pure O$_2$, oxidations with halogeno compounds such as C$_2$H$_2$Cl$_4$ and I$_2$ (at low [I$_2$]) to form mononuclear halogenocarbonyl complexes, and substitution

reactions under O$_2$.[2,7,9–13] If the substitution and oxidative decomposition reactions proceeded by completely different mechanisms, then not only would different rates be expected but reactions with substituting ligands under O$_2$ would proceed at rates that would be the sum of the rates of substitution and decomposition observed separately. Results for the decomposition reactions therefore are capable of providing crucially important information about the mechanism of substitution as well.[14]

In particular, the reaction of MnRe(CO)$_{10}$ with O$_2$ shows a dependence on [O$_2$] that is in extremely good quantitative agreement with the homolytic fission mechanism (Figure 4B in ref 4). It is very difficult to reconcile this with postulated nonequilibrium concentrations of O$_2$ in the solutions. Reactions were generally carried out under continuous streams of appropriate O$_2$–N$_2$ mixtures, and there seems to be no reason to suppose that Henry's law would not apply and that, if it did not, there would be a coincidental agreement with the quite precise and restrictive predictions based on the homolytic fission mechanism. Depletion of O$_2$ during reaction would have led to a progressive decrease in the gradients of the first-order plots throughout the reactions. Quite the reverse occurred, the first-order plots *increasing* in gradient throughout reactions that involved low values of [O$_2$].

This type of evidence has been obtained for all the decacarbonyls including MnRe(CO)$_{10}$.[2,4,5,9] An important qualitative feature of the reaction of MnRe(CO)$_{10}$ with PPh$_3$ under O$_2$ is that not only is (OC)$_5$MnRe(CO)$_4$(PPh$_3$) formed in high yield at the same rate as under Ar but large amounts of OPPh$_3$ are also produced.[2] This is very suggestive of the participation of radical intermediates. No attempt to refute these data, or to explain them in terms of a CO-dissociative mechanism, was made by S&A.[1]

The facts that the substitution rates of MnRe(CO)$_{10}$ in the absence of CO are independent of the nature of the entering ligands[1] and of their concentration[2] are equally consistent with homolytic fission or CO dissociation as the rate-determining step. This is simply because all subsequent reactions are very rapid and do not contribute toward the kinetics. The fact that the rates are reduced by CO is also not diagnostic of the dissociative mechanism. This has been shown conclusively for the analogous reaction (2),[6,8] which is retarded in the presence

$$Mn_2(CO)_8(PPh_3)_2 + P(OPh)_3 \rightarrow$$
$$Mn_2(CO)_8(PPh_3)P(OPh)_3 + PPh_3 \quad (2)$$
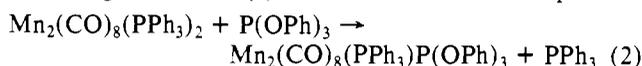
of free PPh$_3$ and yet proceeds via initial homolytic fission. The kinetic data for this particular reaction show that substitution 3 proceeds by an associative mechanism. We have shown[9,15]

$$\cdot Mn(CO)_4(PPh_3) + P(OPh)_3 \rightleftharpoons$$
$$Mn(CO)_4P(OPh)_3 + PPh_3 \quad (3)$$
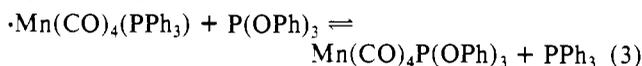
that reaction 4 also proceeds entirely by an associative

(1) Sonnenberger, D.; Atwood, J. D. *J. Am. Chem. Soc.* **1980**, *102*, 3484.
(2) Fawcett, J. P.; Poë, A. J. *J. Chem. Soc., Dalton Trans.* **1976**, 2039.
(3) Fawcett, J. P.; Poë, A. J.; Twigg, M. V. *J. Organomet. Chem.* **1973**, *61*, 315.
(4) Fawcett, J. P.; Poë, A. J.; Sharma, K. R. *J. Am. Chem. Soc.* **1976**, *98*, 1401.
(5) Fawcett, J. P.; Poë, A. J.; Twigg, M. V. *J. Organomet. Chem.* **1973**, *41*, C17.
(6) Fawcett, J. P.; Jackson, R. A.; Poë, A. J. *J. Chem. Soc., Chem. Commun.* **1975**, 733.
(7) Chowdhury, D. M.; Poë, A. J.; Sharma, K. R. *J. Chem. Soc., Dalton Trans.* **1977**, 2352.
(8) Fawcett, J. P.; Jackson, R. A.; Poë, A. J. *J. Chem. Soc., Dalton Trans.* **1978**, 789.
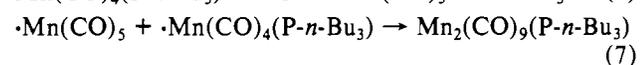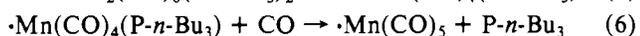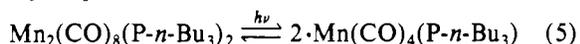(9) Fawcett, J. P.; Poë, A. J.; Sharma, K. R. *J. Chem. Soc., Dalton Trans.* **1979**, 1886.

(10) Fawcett, J. P.; Poë, A. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1302.
(11) Jackson, R. A.; Poë, A. J. *Inorg. Chem.* **1978**, *17*, 997.
(12) Haines, L. 1. B.; Hopgood, D.; Poë, A. J. *J. Chem. Soc. A* **1968**, 421.
(13) Haines, L. I. B.; Poë, A. J. *J. Chem. Soc. A* **1969**, 2826.
(14) The reason examples of less than limiting rates are more readily found for oxidative decomposition must be that reaction of the intermediate radicals with O$_2$ is slower than substitution so that it competes less successfully with radical recombination.
(15) Fox, A.; Malito, J.; Poë, A. J. "Abstracts of Papers", Second Chemical Congress of the North American Continent, Las Vegas, 1980; American Chemical Society: Washington, D.C., 1980; INOR 313; *J. Chem. Soc., Chem. Commun.*, in press. Poë, A. J. *Transition Met. Chem.*, in press.

$$\cdot Re(CO)_5 + PPh_3 \rightleftharpoons \cdot Re(CO)_4(PPh_3) + CO \qquad (4)$$

mechanism contrary to what has been argued elsewhere.[1,16] Inhibition of the overall substitution (1) by CO, i.e., the group being replaced, is therefore in no way inconsistent with initial homolytic fission. Consequently the kinetics of the *substitution* reactions of $MnRe(CO)_{10}$ studied by us and by S&A do not provide evidence either way for the CO-dissociative or homolytic fission mechanisms and were not claimed to do so by us.[2]

The nonkinetic arguments presented by S&A are based essentially on the absence of any evidence for formation of $Mn_2(CO)_{10}$ or $Re_2(CO)_8L_2$ among the products of reaction 1. This point is basically related to the relative rates of combination of the various radicals involved. Meyer et al.[17] have shown that $\cdot Mn(CO)_5$ radicals dimerize with rate constants close to those characteristic of diffusion control. Nevertheless these dimerization processes can successfully be competed with by substitution[16] and halogen-abstraction reactions,[18,19] and their actual rates are obviously very dependent on the steady-state concentrations of the radicals. The question of the selectivity of radical combination was considered for the reactions of $MnRe(CO)_{10}.$[4] We commented that the data for the decomposition reactions implied that, for the particular steady-state concentrations pertaining, the rate of recombination of $\cdot Mn(CO)_5$ and $\cdot Re(CO)_5$ had to exceed the rates of formation of the homonuclear dimetal carbonyls. In the case of the substitution reactions the rate of substitution of $PPh_3$ into $\cdot Re(CO)_5$ has to exceed that into $\cdot Mn(CO)_5$, and the rate of combination of $\cdot Mn(CO)_5$ and $\cdot Re(CO)_4(PPh_3)$ has to exceed those of the other possible radical combinations.[2] The arguments made by S&A are essentially that these inferences are unreasonable. Our position is that not enough evidence is available to make this judgement and that it is certainly not a sound basis for discarding or ignoring the very positive kinetic evidence for homolytic fission.[2,4–9] There are, moreover, several cases that suggest that the inferences can indeed be justified.

Flash photolysis of $MnRe(CO)_{10}$ leads to $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ in equal amounts.[20] This stoichiometry is not "statistical" but is inevitable because for every dimerization of one type of radical an equal amount of dimerization of the other must occur. The crucial point is the photochemical *yield* of these products, and it has been commented[4] that this seems to be significantly lower than that of $MnRe(CO)_{10}$ from a mixture of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}.$[20] A low yield of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ from $MnRe(CO)_{10}$ could readily be accounted for if the initial photoproducts $\cdot Mn(CO)_5$ and $\cdot Re(CO)_5$ preferentially recombine. The fact that the product of reaction 2 is the mixed complex and not $Mn_2(CO)_8[P-(OPh)_3]_2$ shows that, again under the particular steady-state conditions pertaining, $\cdot Mn(CO)_4(PPh_3)$ and $\cdot Mn(CO)_4P-(OPh)_3$ combine more rapidly than $\cdot Mn(CO)_4P(OPh)_3$ dimerizes.[6,8] Finally, the photochemical reaction of $Mn_2-(CO)_8(P-n-Bu_3)_2$ with CO forms mainly $Mn_2(CO)_9(P-n-Bu_3)$ and little $Mn_2(CO)_{10}.$[16] This reaction is believed,[16] we think correctly, to proceed via reactions 5–7 so the combination of
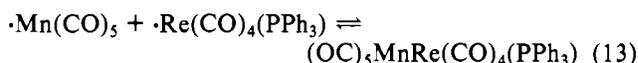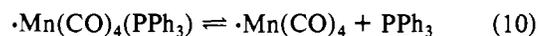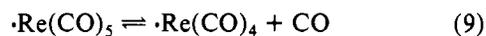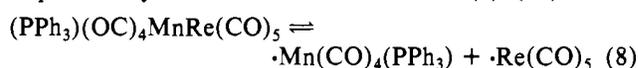
$$Mn_2(CO)_8(P-n-Bu_3)_2 \xrightarrow{h\nu} 2 \cdot Mn(CO)_4(P-n-Bu_3) \qquad (5)$$

$$\cdot Mn(CO)_4(P-n-Bu_3) + CO \rightarrow \cdot Mn(CO)_5 + P-n-Bu_3 \qquad (6)$$

$$\cdot Mn(CO)_5 + \cdot Mn(CO)_4(P-n-Bu_3) \rightarrow Mn_2(CO)_9(P-n-Bu_3) \qquad (7)$$

$\cdot Mn(CO)_5$ and $\cdot Mn(CO)_4(P-n-Bu_3)$ must be more rapid than

the dimerization of $\cdot Mn(CO)_5$; i.e., there is pronounced selectivity of radical combination in this system under these conditions.

The implication that $\cdot Re(CO)_5$ undergoes substitution more rapidly than $\cdot Mn(CO)_5$ is also not unreasonable in view of the associative nature of the former reaction at least.[15]

The homolytic fission mechanism is also consistent with the observation that isomerization of $(PPh_3)(OC)_4MnRe(CO)_5$ to $(OC)_5MnRe(CO)_4(PPh_3)$ is extremely slow. It would have to proceed by a series of reactions such as (8)–(13). This

$$(PPh_3)(OC)_4MnRe(CO)_5 \rightleftharpoons$$
$$\cdot Mn(CO)_4(PPh_3) + \cdot Re(CO)_5 \qquad (8)$$

$$\cdot Re(CO)_5 \rightleftharpoons \cdot Re(CO)_4 + CO \qquad (9)$$

$$\cdot Mn(CO)_4(PPh_3) \rightleftharpoons \cdot Mn(CO)_4 + PPh_3 \qquad (10)$$

$$\cdot Re(CO)_4 + PPh_3 \rightleftharpoons \cdot Re(CO)_4(PPh_3) \qquad (11)$$

$$\cdot Mn(CO)_4 + CO \rightleftharpoons \cdot Mn(CO)_5 \qquad (12)$$

$$\cdot Mn(CO)_5 + \cdot Re(CO)_4(PPh_3) \rightleftharpoons$$
$$(OC)_5MnRe(CO)_4(PPh_3) \qquad (13)$$

seems highly unlikely, and the fact that decomposition is observed rather than isomerization is not surprising. A direct interchange reaction between $\cdot Mn(CO)_4(PPh_3)$ and $\cdot Re(CO)_5$ also seems highly improbable. In the presence of added $PPh_3$ reaction 4 would ensure that substitution to form $MnRe-(CO)_8(PPh_3)_2$ would occur in preference to isomerization and this is exactly what occurs.[2]

The suggestion[1] that the CO-dissociative mechanism is followed also by $Mn_2(CO)_{10}$, $Tc_2(CO)_{10}$, and $Re_2(CO)_{10}$ again takes no account of the positive kinetic evidence in favor of homolytic fission.[2,4,9] In the case of $Mn_2(CO)_{10}$ there is evidence that substitution may proceed partly by CO dissociation[14] but the evidence that homolytic fission is the major path is very strong.[4,5] Thermal decomposition under Ar is half order in $[Mn_2(CO)_{10}]$ over very wide ranges of concentration and temperature, exactly as expected for highly reversible formation of $\cdot Mn(CO)_5$ racicals.[4] The overall reaction is not inhibited appreciably by CO below ca. 150 °C, a fact hardly consistent with a CO-dissociative mechanism but consistent with decomposition of the $\cdot Mn(CO)_5$ radicals by some form of reaction with the solvent. This is an aspect of the reaction that clearly requires further study. Above ca. 150 °C the reaction does become inhibited by CO, which shows that CO dissociation from $\cdot Mn(CO)_5$ does become important under those conditions but is a relatively slow, high-energy process. Reactions in the presence of various amounts of $O_2$ are quantatively in excellent agreement with the homolytic fission mechanism and a bimolecular reacton between $O_2$ and $\cdot Mn-(CO)_5$.

We therefore maintain that there is a substantial body of positive kinetic evidence in favor of reversible homolytic fission of all these dimetal decacarbonyls and against a CO-dissociative mechanism as a mechanism for decomposition or substitution. This evidence has to be refuted or reinterpreted, rather than being ignored,[1] when any case is being made for a totally different mechanism. Attempts[1] to refute these conclusions by kinetic studies that repeat work done under conditions incapable of providing a distinction between the mechanisms are not helpful. Arguments based on perceived difficulties with the homolytic fission mechanism in terms of nonappearance of certain products are more appropriate to these columns than to papers in the *Journal of the American Chemical Society* and should be tested by further investigations of reactions of the 17-electron, five-coordinate radicals with particular emphasis on their selective combination. The evidence in favor of unselective combination of radicals (see above) is not uniformly positive by any means.

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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)$_8$L$_2$ 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)$_9$L or M$_2$(CO)$_8$L$_2$ (eq 1).  The kinetics of these

$$M_2(CO)_{10} + L \rightarrow M_2(CO)_9L + CO$$
$$M_2(CO)_{10} + 2L \rightarrow M_2(CO)_8L_2 + 2CO \quad (1)$$
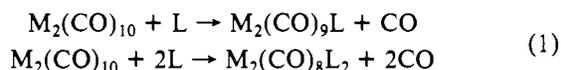
reactions have been studied by three different research groups and are summarized in Table I.  There is no evidence for a dependence other than first order in the metal decacarbonyl.[2-6] In the thermal decompositions that Poë has studied,[3-8] no soluble products are observed and deviations from first-order behavior are seen at temperatures higher than those used for substitution reactions.

$$M_2(CO)_{10} + O_2 \rightarrow oxides \quad (2)$$
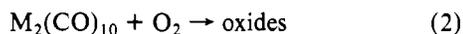
I will discuss the decomposition reactions in more detail below but see no reason to consider the mechanism of reaction of O$_2$ to be the same as that for reaction with phosphines and phosphites.[9]  It is possible that O$_2$ could induce radical re-actions on M$_2$(CO)$_{10}$. This has long been recognized in organic chemistry, as the following quotation shows.[10]

"Since the oxygen molecule itself is a diradical with the electronic structure

$$\cdot\ddot{O}-\ddot{O}\cdot$$

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)$_8$L$_2$ with additional ligand.[11-15]

$$M_2(CO)_8L_2 + L \rightarrow [M(CO)_3L_2] \rightarrow$$
$$no\ organometallic\ product \quad (3)$$
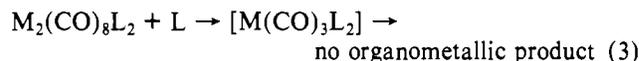
The rates of these reactions show a very strong dependence on the ligand L and deviations from first-order behavior, but again no soluble products are isolated. These reactions do not pertain to the mechanism of reaction of the unsubstituted dimers, since the mechanism of reaction often changes with 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]

$$C_{10}H_{18} + O_2 \xrightarrow{110\ °C} C_{10}H_{18}O_2 \quad (4)$$
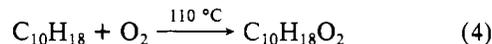
Poë has observed oxidized solvent as a product in the reactions that deviate from first-order behavior but has never investigated the role of solvent oxidation in the mechanism.[3-8]  Even if decalin peroxide does not interfere with the decomposition of M$_2$(CO)$_{10}$ (reaction 2), oxidation of the decalin may deplete the concentration of O$_2$ in solution. At low concentration of

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(2) Sonnenberger, D.; Atwood, J. D. *J. Am. Chem. Soc.* **1980**, *102*, 3484.
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(9) Other mechanisms are possible for reactions of the dimers. Neither CO dissociation nor homolytic fission can apply to reaction of the deca-carbonyls with Cl$_2$ or Br$_2$ since these reactions occur rapidly at room temperature.
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