Isomerization or CO Dissociation for Metal Carbonyl Substitution Reactions? A Mechanistic Dilemma

ANTHONY J. POË

J. Tuzo Wilson Research Laboratories, Erindale College, University of Toronto, Mississauga, Ont., L5L 1C6, Canada
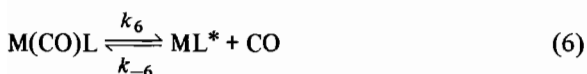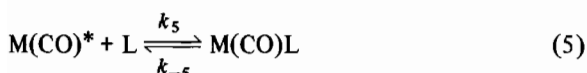
Substitution reactions of metal carbonyls frequently proceed to completion [1–3] according to the rate equation shown in eqn. (1).

$$k_{obs} = ak(\lim)\{[L]/[CO]\}/\{1 + a[L]/[CO]\} \qquad (1)$$

$k(\lim)$ is a limiting first order rate constant, obtained in the absence of CO, and it is independent of the nature or concentration of the entering nucleophile L; a is a constant. When reactions are carried out in the presence of CO, k_{obs} increases with [L] towards the limiting rate constant. A plot of $1/k_{obs}$ *versus* [CO]/[L] is linear with an intercept of $1/k(\lim)$ and a gradient of $1/ak(\lim)$. Such behaviour is usually accounted for by the now classic CO dissociative mechanism shown schematically in eqns. (2) and (3).

$$M(CO) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} M + CO \qquad (2)$$

$$M + L \xrightarrow{k_3} ML \qquad (3)$$

In this case $k(\lim)$ corresponds to k_2 and a to k_3/k_{-2}. This mechanism must surely operate when mononuclear binary carbonyls are involved but it cannot be assumed that it also operates when reactions of more complex metal carbonyls follow eqn. (1). An alternative is shown in eqns. (4)–(7) where it is assumed

$$M(CO) \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} M(CO)^* \qquad (4)$$

$$M(CO)^* + L \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} M(CO)L \qquad (5)$$

$$M(CO)L \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} ML^* + CO \qquad (6)$$

$$ML^* \xrightarrow{k_7} ML \qquad (7)$$

that the substitution goes to completion, even in the presence of CO. $M(CO)^*$ and ML^* are reactive isomers of $M(CO)$ and ML, respectively, and they and $M(CO)L$ are assumed to be present only in low, steady state concentrations throughout the reaction.

The corresponding rate equation is shown, in its convenient inverse form, in eqn. (8). The conditions

$$
\begin{aligned}
1/k_{obs} = {} & (1/k_4) + \{(k_{-4}/k_4 k_5)/[L]\} \\
& + \{(k_{-4}k_{-5}/k_4 k_5 k_6)/[L]\} \\
& + \{(k_{-4}k_{-5}k_{-6}/k_4 k_5 k_6 k_7)[CO]/[L]\} \qquad (8)
\end{aligned}
$$

necessary for k_{obs} to be independent of [L] in the absence of CO are $k_{-4} \ll k_5[L]$, and k_{-5} is not $\gg k_6$, *i.e.* the rate of attack of L on the isomer $M(CO)^*$ must be much greater than the rate of isomerization back to $M(CO)$, and the rate of loss of L from $M(CO)L$ must not be much greater than the rate of loss of CO from the same complex. The condition necessary for CO retardation to occur is $k_7 \ll k_{-6}\cdot[CO]$. Thus it is required that both reactive isomers are attacked by free nucleophiles more quickly than they isomerize to their more stable forms. If these conditions apply then the rate equation is as shown in eqn. (9) which has exactly the same form as that for

$$
\begin{aligned}
k_{obs} = {} & k_4 k_5 k_6 k_7 [L]/\{k_{-4}k_{-5}k_{-6}[CO] \\
& + k_5 k_6 k_7 [L]\} \qquad (9)
\end{aligned}
$$

reversible CO dissociation. However, $k(\lim)$ now corresponds to the rate constant for isomerization of $M(CO)$ and a corresponds to the more complicated ratio $k_5 k_6 k_7/k_{-4}k_{-5}k_{-6}$. Essentially the same equations apply to photochemical reactions except that k_4 is replaced by $\Phi I_a/[M(CO)]$, where Φ is the quantum yield for formation of $M(CO)^*$. The only way that such a mechanism can be distinguished kinetically from reversible CO dissociation is if $k_5[L]$ is not always $\gg k_{-4}$ and/or $k_{-5} \gg k_6$, in which case k_{obs} will increase with [L] to a limiting value even in the absence of CO. On the other hand, eqn. (9) is obtained directly if reactions (5) and (6) are labile equilibria, even when $k_{-5} \gg k_6$.
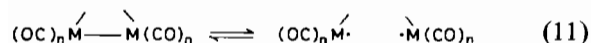
It is not really possible to envisage reasonable forms for reactive isomers of mononuclear binary carbonyls but mononuclear isomers containing vacant coordination sites can easily be created if a ligand is present that can spontaneously migrate to and from a C atom in a CO ligand. Hydride migration has been proposed [4] as a possible rate determining step in substitution of some carbonyl hydrides.

In the case of metal carbonyl clusters, or even simple binuclear carbonyls, isomerization can occur by insertion of a terminal CO ligand into a metal–metal bond and this provides a vacant coordination site as shown in eqn. (10). Attack at the vacant coordination site by L should be very rapid. This type

$$(OC)_n M \!-\! M(CO)_n \rightleftharpoons (OC)_n M \underset{\underset{O}{C}}{\overset{}{\diagup\diagdown}} M(CO)_{n-1} \qquad (10)$$
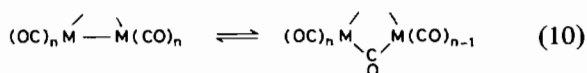
of isomerization has been proposed as an alternative to CO dissociation for the last 20 years for thermal [5, 6] and, more recently for photochemical [7, 8] reactions but it is not always recognized that even detailed CO retardation studies leading to rate equations such as eqn. (1) do not prove the CO dissociative mechanism. It is, however, possible to disprove the CO dissociative mechanism when a rise of k_{obs} with [L] to a limiting value is observed even in the absence of CO [6, 8].

Another possible form of isomerism exists for metal carbonyl clusters. These can undergo homolysis of a metal–metal bond as in eqn. (11). The two 17-

$$(OC)_n M \overset{/}{\underset{\textstyle \diagdown}{\rule{2cm}{0.4pt}}} M(CO)_n \rightleftharpoons (OC)_n \overset{/}{M}\cdot \quad \cdot \overset{\diagdown}{M}(CO)_n \qquad (11)$$

electron metal-centred radicals so produced are connected via the metal atoms in the rest of the cluster and this could in itself prevent overall fragmentation. They could be connected as well by a bridging ligand, or only by a bridging ligand (e.g. $Ph_2PCH_2PPh_2$, $HC(CH_2PPh_2)_3$ etc.) in the case of dimetal carbonyls [9], and this would also help prevent fragmentation. Such 17-electron radicals are known to undergo very rapid associative substitution [10] and geometrical relaxation of the opened cluster might well make re-formation of the closed cluster relatively slow as required. Johnson has recently [11] proposed heterolysis of a metal–metal bond instead of the homolysis shown in eqn. (11) and this would show exactly the same kinetic behaviour.

It must therefore be acknowledged that the usual kinetic criteria accepted for the CO dissociative mechanism are certainly not sufficient to prove that it is operating in reactions of a very wide variety, indeed the vast majority, of metal carbonyls. In the absence of evidence actually disproving the CO dissociative mechanism (a rise of k_{obs} with [L] to a limiting value in the absence of CO), a distinction between the dissociative and isomerization mechanisms, and between the various possible types of isomerization, cannot be made on kinetic grounds alone. Evidence in favour of various forms of isomerization can take the form of detection of intermediates such as $(OC)_n M(\mu\text{-}CO)M(CO)_{n-1}L$ [12], or of the existence [9] or non-existence [7, 8] of scavenging reactions of 17-electron radicals (e.g. by alkyl halides). Isomerization by heterolysis [11] might be indicated by the effects of solvent polarity. In photochemical reactions the occurrence of a CO dissociative process can be demonstrated by the trapping at low temperatures of intermediates that are coordinatively unsaturated (or apparently so) [13].

Other arguments can also be supportive of rate determining isomerization. Thus, substitution of reduced, radical anion, forms of metal carbonyl clusters can be argued [14] to go via metal–metal homolysis since the extra electron is in a metal–metal

antibonding orbital, and the overall negative charge strengthens the M–CO bonds compared to the much less reactive unreduced neutral complexes. Elegant ESR studies have suggested that the symmetrical cluster $Fe_3(CO)_9(\mu_3\text{-}PPh)_2^{\overset{-}{}}$ undergoes P–Fe heterolysis to form $Fe_3(CO)_9(\mu_3\text{-}PPh)(\mu_2\text{-}PPh)^{\overset{-}{}}$ which has the odd electron localized on a single 17-electron Fe centre [15]. The substitution reaction of $Fe_3(CO)_9(\mu_3\text{-}PPh)_2^{\overset{-}{}}$ with $P(OMe)_3$ to form Fe_3-$(CO)_8(\mu_3\text{-}PPh)_2\{P(OMe)_3\}^{\overset{-}{}}$ is clearly shown to go via initial isomerization to $Fe_3(CO)_9(\mu_3\text{-}PPh)(\mu_2\text{-}PPh)^{\overset{-}{}}$ [15].

In spite of these notable but rather scarce examples a wide range of mechanistically ambiguous substitution reactions exists. This applies especially to CO retarded, unimolecular reactions of substituted metal carbonyl clusters where the M–CO and M–M bonds are believed to have comparable strengths [16]. The systematics of substituent effects in these clusters should not, therefore, be discussed only in terms of dissociative rate determining processes [17].

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