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KINETICS OF REACTION OF ALKYNES WITH SOME COBALT CARBONYLS*

A.J. POË
Erindale College and the Department of Chemistry, University of Toronto, Toronto (Canada)

Introduction

The reaction of alkynes with octacarbonyldicobalt to form the alkyne-bridged complex $(OC)_3\overline{Co(\mu\text{-}C_2RR')Co}(CO)_3$ is well known and the kinetics in toluene at 25°C were first studied by Tirpack et al. [1] by measurement of carbon monoxide evolution under an atmosphere of carbon monoxide. Rather complex kinetic behaviour was observed owing to the high concentrations of carbonyl and alkynes that were used but a mechanism was proposed (eqns. 1-3) that involved slow production of a reactive form of cobalt carbonyl which could either revert to the stable form or undergo competitive bimolecular reaction with the alkyne to form the intermediate $[Co_2(CO)_7C_2RR']$ with evolution of one carbon monoxide ligand. The kinetics indicated that this intermediate accumulated to a significant extent during the reaction.

$$[Co_2(CO)_8] \rightleftharpoons [Co_2(CO)_8{}^*] \tag{1}$$

$$[Co_2(CO)_8{}^*] + C_2RR' \rightleftharpoons [Co_2(CO)_7C_2RR'] + CO \tag{2}$$

$$[Co_2(CO)_7C_2RR'] \rightarrow (OC)_3\overline{Co(\mu\text{-}C_2RR')Co}(CO)_3 + CO \tag{3}$$

By using lower concentrations of complex Ellgen [2] found that the rate of formation of $[Co_2(CO)_7(C_2RR')]$ ($C_2RR' = C_2Ph_2$, 1-octyne or 2-octyne) could be reduced to such an extent that this intermediate did not accumulate during the reaction and simple pseudo-first-order rate plots were obtainable. Ellgen also pointed out that the stage at which the first carbon monoxide ligand was released could, in principle, only be determined by a study of the dependence of the rate on [CO]. Thus the rate equations for reactions 1-3 and 4-6 are shown in equations 7 and 8 and are not distinguishable in the absence of a [CO]-dependence study. Equations 7 and 8 are in practice indistinguishable if $k_{-2}[CO]/k_3 \gg 1$ and this was unfortunately found to be the case. By reverting to conditions under which $[Co_2(CO)_7C_2RR']$ had been inferred to accumulate Ellgen was, however, able to distinguish the two mechanisms by initial-rate studies and to

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show that the kinetics were consistent with equations 4-6 rather than with equations 1-3.

$$[Co_2(CO)_8] \rightleftharpoons [Co_2(CO)_7] + CO \tag{4}$$

$$[Co_2(CO)_7] + C_2RR' \rightleftharpoons [Co_2(CO)_7C_2RR'] \tag{5}$$

$$[Co_2(CO)_7C_2RR'] \rightarrow [(OC)_3\overline{Co(\mu\text{-}C_2RR')Co}(CO)_3] + CO \tag{6}$$

$$k_{obs} = k_1k_2[C_2RR']/\{k_{-1} + (k_{-1}k_{-2}/k_3)[CO] + k_2[C_2RR']\} \tag{7}$$

$$k_{obs} = k_4k_5[C_2RR']/\{k_{-4}[CO] + (k_{-4}k_{-5}/k_6)[CO] + k_5[C_2RR']\} \tag{8}$$

Ungváry and Markó showed at the same time [3] that the rate of evolution of carbon monoxide from equimolar amounts of 1-heptyne and $[Co_2(CO)_8]$ was proportional to [alkyne] and inversely proportional to [CO]. They proposed reaction 9 as a rapid pre-equilibrium followed by the slow, irreversible reaction 10. It is not clear why the data are not equally well represented by the mechanism in equations 4-6 with $k_{-4}(1 + k_{-5}/k_6)[CO] \gg k_5[C_2RH]$.

$$[Co_2(CO)_8] + C_2RH \rightleftharpoons [Co_2(CO)_7C_2RH] + CO \tag{9}$$

$$[Co_2(CO)_7C_2RH] \rightarrow [(OC)_3Co(\mu\text{-}C_2RH)Co(CO)_3] + CO \tag{10}$$

Indeed Ellgen claimed that the data of Tirpak et al. specifically preclude a mechanism such as in reactions 9 and 10, and an examination of Ungváry and Markó's data shows them to be quite compatible with those of Ellgen under comparable conditions. The reactions of $[Co_2(CO)_8]$ with alkynes are sufficiently fast to make IR spectrophotometric studies of the kinetics very difficult, and CO-evolution was much easier to follow. This means that the evidence for accumulation of the intermediate $[Co_2(CO)_7C_2RR']$ is purely kinetic and needs supplementing, for example, by IR studies.

Reaction of diphenylacetylene with $[Co(CO)_3P\text{-}n\text{-}Bu_3]_2$ and $[(OC)_3\overline{Co(\mu\text{-}GePh_2)(\mu\text{-}CO)Co}(CO)_3]$

We have studied [4] the reaction in decalin of diphenylacetylene with the complex $[Co(CO)_3P\text{-}n\text{-}Bu_3]_2$. This proceeds sufficiently slowly that it can be followed by IR spectrophotometry and an immediate consequence of this was that the initial product was clearly characterizable as $[(CO)_3\overline{Co(\mu\text{-}C_2Ph_2)Co}(CO)_2PBu_3]$, i.e. one carbon monoxide and one tributylphosphine ligand had been displaced rather than two carbon monoxides or two phosphines. The tributylphosphine released in the first stage then reacted with this product to form $[Bu_3P(OC)_2\text{-}\overline{Co(\mu\text{-}C_2Ph_2)Co}(CO)_2PBu_3]$ by a reaction shown [5] to be mixed zero- and first-order in $[PBu_3]$.

The kinetics of the first stage were quite complex and showed that two main reaction paths are followed. One (A) involves an increase to a limiting rate with increasing $[C_2Ph_2]$, and another (B) is first-order in $[C_2Ph_2]$. The limiting rate by path (A) is substantially reduced by carbon monoxide, and appears also to be reduced by the presence of free phosphine. A quantitative study of the latter effect is severely limited by the occurrence of direct attack by phosphine on $[Co(CO)_3PBu_3]_2$ to form more highly-substituted products. The rate data for path (A) showed that reversible dissociation of two ligands (one carbon monoxide and one phosphine) has to occur before attack by the alkyne and subsequent formation of the product. The sequence of dissociation is carbon monoxide followed by phosphine. However, the fact that the limiting rate appeared also to be reduced by free phosphine indicates that a small contribution from the reverse sequence of dissociation also occurs. The rate of reaction by path (B) is also retarded by both carbon monoxide and phosphine but this cannot imply that reversible CO or PBu_3 dissociation is an initial step since these have already been assigned to the kinetically distinct path (A) and are much too slow. The data are, however, consistent with highly reversible formation of an adduct $[Co_2(CO)_6(PBu_3)_2C_2Ph_2]$, either as a steady-state intermediate or in a rapidly established pre-equilibrium lying well to the left. This then reversibly loses first carbon monoxide and then tributylphosphine before final formation of the product. The reverse sequence of dissociation cannot occur to more than a small extent.

We have also studied the kinetics [6] of the reaction [7] of the complex $[(OC)_3\overline{Co(\mu\text{-}GePh_2)(\mu\text{-}CO)Co}(CO)_3]$ with diphenylacetylene to form $[(OC)_3\overline{Co(\mu\text{-}C_2Ph_2)Co}(CO)_3]$, polymeric $(GePh_2)_n$, and free carbon monoxide. This seemed likely to be of interest since the $GePh_2$ bridge is not known to be able to change rapidly and reversibly into a terminal ligand in the way carbon monoxide can and this should have a major effect on the choice of reaction paths open to the system. The reaction goes smoothly in decalin at convenient rates between 50 and 90°C, is first order in [complex] and $[C_2Ph_2]$, and is retarded by carbon monoxide. A mechanism that fits the data (eqns. 11-14) involves slow, highly reversible, production of a reactive form of the complex followed sequentially by reversible addition of diphenylacetylene, reversible loss of carbon monoxide, and irreversible loss of $GePh_2$. An alternative path involving formation of terminally-bonded $GePh_2$ did not accord with the data in some important respects.

$$[(OC)_3\overline{Co(\mu\text{-}GePh_2)(\mu\text{-}CO)Co}(CO)_3] \rightleftharpoons [\text{complex}^*] \tag{11}$$

$$[\text{complex}^*] + C_2Ph_2 \rightleftharpoons [\text{complex}^* \cdot C_2Ph_2] \tag{12}$$

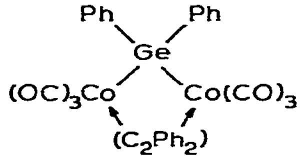
$$[\text{complex}^* \cdot C_2Ph_2] \rightleftharpoons [(\text{complex}^* \text{—} CO)C_2Ph_2] + CO \tag{13}$$

$$[(\text{complex}^* \text{—} CO)C_2Ph_2] \rightarrow [(OC)_3\overline{Co(\mu\text{-}C_2Ph_2)Co}(CO)_3] + GePh_2 \tag{14}$$

The nature of the reactive intermediates

The complex $[Co_2(CO)_8]$ seems to need to lose only one carbon monoxide ligand before attack by alkynes is possible to form the intermediate $[Co_2(CO)_7C_2RR']$, the structure of which is unknown. This is not because kinetically significant amounts of $[Co_2(CO)_6]$ cannot be generated in solution by reversible loss of two carbon monoxide ligands since $[Co_2(CO)_6]$ appears to be a probable intermediate in the reaction of $[Co_2(CO)_8]$ to form $[Co_4(CO)_{12}]$ [8]. In the reaction of $[Co(CO)_3PBu_3]_2$ with diphenylacetylene by one path it is necessary for two ligands (one carbon monoxide and one phosphine) to be removed before attack by the alkyne can occur. It must be presumed that $[Co_2(CO)_5(PBu_3)_2]$ and $[Co_2(CO)_6PBu_3]$ are sterically too bulky for the alkyne to approach closely enough but that such approach is possible if $[Co_2(CO)_5PBu_3]$ is formed. This intermediate probably has quite a stable planar form with two four-coordinate d^8 cobalt atoms such that essentially simultaneous nucleophilic attack on each cobalt by the two orthogonal π-electron pairs of the alkyne can occur if the alkyne approaches the plane of the complex with its C≡C axis perpendicular to the Co—Co bond.

The nature of the $[Co_2(CO)_6(PBu_3)_2C_2Ph_2]$ adduct involved in the other path is again a matter of speculation but a carbonyl-bridged intermediate $[Bu_3P(OC)_3\overline{Co(\mu\text{-}CO)Co}(CO)_2PBu_3]$ has been proposed [9] for the insertion of tin(II) chloride into the cobalt—cobalt bond of $[Co(CO)_3PBu_3]_2$, and $[Bu_3P(OC)_3\text{-}\overline{Co(\mu\text{-}CO)Co}(CO)_2(PBu_3)C_2Ph_2]$ would be a reasonable formulation for the adduct. This type of intermediate, but with a $GePh_2$ bridge in place of the carbonyl bridge, is also suggested for the reaction of $[(OC)_3\overline{Co(\mu\text{-}GePh_2)(\mu\text{-}CO)Co}(CO)_3]$ with diphenylacetylene. This complex has been shown to react with L to form $[(OC)_4Co(\mu\text{-}GePh_2)Co(CO)_3L]$ (L = CO, PPh_3, or PBu_3) at a rate proportional to [L] [10]. Highly reversible ring-opening to form $[(OC)_4Co(\mu\text{-}GePh_2)Co(CO)_3]$ with subsequent attack by L at the vacant coordination site has been proposed. Attack on such an intermediate by diphenylacetylene is also plausible and the relative rate parameters for attack by carbon monoxide, phosphines and diphenylacetylene are quite compatible. The very negative value of $\Delta S^{\neq}$ (—163 kJ mol^{-1}) for formation of the transition state in equation 14 is thought to imply that $[(complex^*—CO)C_2Ph_2]$ should be formulated as I, which is highly structured and which would have a consequently low intrinsic entropy. Although CO-dissociation from $[(OC)_3\overline{Co(\mu\text{-}GePh_2)(\mu\text{-}CO)Co}(CO)_3]$ occurs readily under the conditions of this reaction [10] the product will probably still be in the bridged, cluster form and sterically unsuited to attack by diphenylacetylene. $[Co_2(CO)_7]$, on the other hand, should be able to exist in the non-bridged form $[(OC)_4Co—Co(CO)_3]$ which can more readily form an adduct with an alkyne.



(I)

Although there are common features in the reaction mechanisms of some of these complexes these studies show that reactions that are very similar stoichiometrically can follow substantially different paths when relatively small modifications are made in the complexes, and that a given complex can react by more than one path. This diversity shows both the need for caution in proposing mechanisms for such reactions without detailed kinetic studies, and the mechanistic versatility that must be the cause of the varied and important chemistry of such systems.

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