Short Communication

Kinetic Analysis of the Hydrido-tetracarbonylcobalt(I) Reduction of Aldehydes to Alcohols
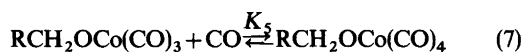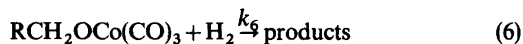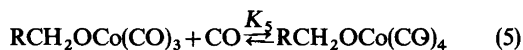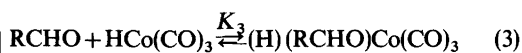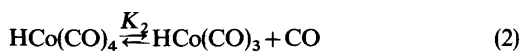
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The details of the mechanisms of very few transition metal complex catalyzed reactions of organic compounds are known with certainty. Hydrogenation of unsaturated organics has been studied most intensively and some detailed mechanisms have been postulated.[1−6] Since the reactions generally involve the formation of reactive intermediates in concentrations too low to be characterized, reaction kinetics offers the most powerful tool for mechanism analysis. Kinetic data have been obtained[7] in a pertinent case, the hydridotetracarbonylcobalt(I) reduction of aldehydes to alcohols, and a mechanism has been proposed based on these data. The mechanism was discussed in some detail in a monograph dealing with the mechanisms of organotransition metal chemistry.[1] The purpose of this communication is to present a kinetic analysis of the proposed mechanism, show that the observed kinetics do not fit that mechanism, and suggest a mechanism consistent with the data.

The rate data[7] give rise to rate law (1). The proposed mechanism is summarized by eqns. (2)−(6). If reactions (2)−(5) can be considered to be in equilibrium, the reactions involving the formation of the reactive intermediate, $RCH_2OCo(CO)_3$ can be summarized as in (7). The·equilibrium assumption then gives rise to rate laws (8) or (9), both of which show that the proposed mechanism results in inverse first order in carbon monoxide rather
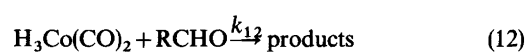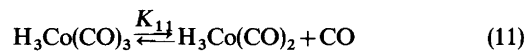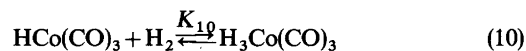
$$Rate = k[RCHO][Co][H_2]/[CO]^2 \qquad (1)$$

$$HCo(CO)_4 \overset{K_2}{\rightleftharpoons} HCo(CO)_3 + CO \qquad (2)$$

$$RCHO + HCo(CO)_3 \overset{K_3}{\rightleftharpoons} (H)(RCHO)Co(CO)_3 \qquad (3)$$

$$(H)(RCHO)Co(CO)_3 \overset{K_4}{\rightleftharpoons} RCH_2OCo(CO)_3 \qquad (4)$$

$$RCH_2OCo(CO)_3 + CO \overset{K_5}{\rightleftharpoons} RCH_2OCo(CO)_4 \qquad (5)$$

$$RCH_2OCo(CO)_3 + H_2 \overset{k_6}{\rightarrow} products \qquad (6)$$

$$HCo(CO)_4 + RCHO \overset{K' = K_2K_3K_4}{\rightleftharpoons} \qquad$$

$$RCH_2OCo(CO)_3 + CO \overset{K_5}{\rightleftharpoons} RCH_2OCo(CO)_4 \qquad (7)$$

$$Rate = k_6K'[HCo(CO)_4][RCHO][H_2]/[CO] \qquad (8)$$

$$Rate = k_6[RCH_2OCo(CO)_4][H_2]/K_5[CO] \qquad (9)$$

than the experimentally observed order, −2. Two limiting cases depend upon the magnitude of K_5. If K_5 is very large, the predominant cobalt containing species will be $RCH_2OCo(CO)_4$ and the kinetics are best described by (9). On the other hand if K_5 is small, the side equilibrium is negligible and the kinetics are described best by (8). The equilibrium approximation may not be strictly valid, however, the analysis does show that the postulated mechanism cannot give rise to the observed kinetics. The fact that the order in [CO] was observed to be an integer, −2, suggests a mechanism involving sequential dissociations of CO from the complex rather than the side equilibrium. A side equilibrium would most likely be accompanied by non-integral reaction orders.

In order to arrive at a mechanism consistent with rate law (1) it is only necessary to change the order in which the complexes react with hydrogen and the aldehyde. Thus, if reaction (2) is followed by reactions (10)−(12), the kinetics would be expected to conform to those observed,[7] and give rate law (1). This mechanism implies that the octahedral com-

$$HCo(CO)_3 + H_2 \overset{K_{10}}{\rightleftharpoons} H_3Co(CO)_3 \qquad (10)$$

$$H_3Co(CO)_3 \overset{K_{11}}{\rightleftharpoons} H_3Co(CO)_2 + CO \qquad (11)$$

$$H_3Co(CO)_2 + RCHO \overset{k_{12}}{\rightarrow} products \qquad (12)$$

plex formed in (10) must dissociate to give the
square pyramid and CO in (11) in order to provide a
coordination site for the aldehyde in (12). Reaction
(12) would then involve several steps including a
catalyst regeneration.

The mechanism of the hydridotetracarbonyl-
cobalt(I) reduction of aldehydes has been discussed
in connection with that for the commercially im-
portant hydroformylation reaction.[8] The analysis
presented here indicates that the analogy does not
exist since the two processes follow different kinetic
patterns.

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