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Preliminary communication

REDUCTION OF CARBON DIOXIDE BY ANIONIC RUTHENIUM CARBONYL CLUSTERS

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Summary

Carbon dioxide has been found to react with ruthenium carbonyl cluster tetra- and hexa-anions such as $K_4[Ru_4(CO)_{12}]$, $Na_6[Ru_4(CO)_{11}]$, $Na_4[Ru_6(CO)_{17}]$ and $Na_6[Ru_6(CO)_{16}]$ to give carbon monoxide and carbonate by electron transfer from cluster anions. The Ru cluster anions are converted into the corresponding di- and tetra-anions. $Ca[Ru_3(CO)_{11}]$ also reacts with CO_2 to give $Ru_3(CO)_{12}$ in low yield. Other Ru cluster dianions, e.g. $K_2[Ru_4(CO)_{13}]$, $K_2[H_2Ru_4(CO)_{12}]$ and $Na_2[Ru_6(CO)_{18}]$ are unchanged under CO_2 atmosphere.

Considerable research effort has been expended in the activation of carbon oxides by transition metals because of the great potential for using not only carbon monoxide but carbon dioxide as chemical feedstocks. Recently, Maher and Cooper [1] have reported an unusual carbon dioxide reduction using electron transfer from mononuclear transition-metal dianions. Shore and co-workers [2—5] have developed unique syntheses of ruthenium carbonyl clusters and their anions. However, the reactions of these cluster anions with carbon dioxide are not known. We wish to report here the reduction of carbon dioxide by anionic ruthenium carbonyl clusters such as $K_4[Ru_4(CO)_{12}]$, $Na_6[Ru_4(CO)_{11}]$, $Na_4[Ru_6(CO)_{17}]$, $Na_6[Ru_6(CO)_{16}]$ and $Ca[Ru_3(CO)_{11}]$.

Treatment of a suspension of $K_4[Ru_4(CO)_{12}]$ in tetrahydrofuran (THF) with gaseous CO_2 at ambient temperature resulted in immediate formation of a dark red-brown solution. Solution IR spectra showed that the $[Ru_4(CO)_{13}]^{2-}$ dianion was the only carbonyl-containing product produced in significant quantities. After removal of the solvent under vacuum, the residue was extracted with diethyl ether to leave a 70% yield of K_2CO_3 [6]. Removal of the ether left an 89% yield of $K_2[Ru_4(CO)_{13}]$ [7]. The reaction

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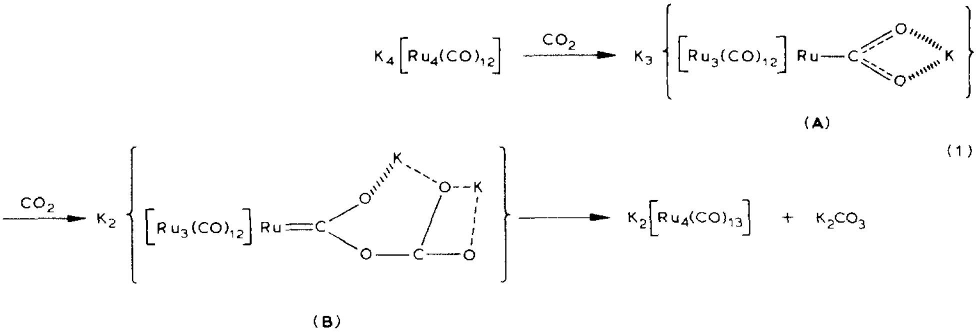
is equally facile when the tetraanion is introduced as the sodium salt, suggesting that the reaction is insensitive to the nature of the counterion. When the resulting dark red-brown solution obtained from the reaction of $K_4[Ru_4(CO)_{12}]$ and CO_2 was acidified with excess H_2SO_4, the sole ruthenium-containing product was $H_2Ru_4(CO)_{13}$ (>93% yield), further confirming that the $[Ru_4(CO)_{12}]^{4-}$ tetraanion was converted into the $[Ru_4(CO)_{13}]^{2-}$ dianion. However, a THF solution of $K_2[Ru_4(CO)_{13}]$, when treated further with gaseous CO_2 (purity >99.99%) in the temperature range 25—70° C remained unchanged over a period of 24 h. At higher temperature (>80° C) and for a prolonged period (>8 h), partial decomposition of the dianion to an unidentified precipitate was observed. When the dianionic $[Ru_4(CO)_{13}]^{2-}$ was treated with a large excess of CO_2 of 95% purity at ambient temperature for a prolonged period (>9 h), a monoanionic $[HRu_4(CO)_{13}]^-$ was formed, possibly owing to the reaction of the dianion with traces of water contaminated in CO_2.

The higher anion, $Na_6[Ru_4(CO)_{11}]$, also reacted with excess CO_2 to give the dianion $Na_2[Ru_4(CO)_{13}]$ via the $Na_4[Ru_4(CO)_{12}]$ tetraanionic intermediate. When a suspension of $Na_6[Ru_4(CO)_{11}]$ in THF was treated with two equivalents of CO_2, besides the $Na_4[Ru_4(CO)_{12}]$ tetraanion, some $Na_2[Ru_4(CO)_{13}]$ dianion was also formed (<30% yield). Prolonged stirring resulted in decrease of dianion concentration.

Similarly, the hexanuclear ruthenium tetraanion, $Na_4[Ru_6(CO)_{17}]$, also reduces CO_2 with an appreciably slower rate, giving a solution of the dianionic $Na_2[Ru_6(CO)_{18}]$ in 70% yield at ambient temperature over a period of 3 h. The acidification of the resultant solution gave $H_2Ru_6(CO)_{18}$. Further treatment of $Na_2[Ru_6(CO)_{18}]$ with CO_2 at ambient temperature resulted in no reaction over a period of 24 h. The hexaanionic $Na_6[Ru_6(CO)_{16}]$ cluster also reacts with CO_2 to give the dianionic cluster $Na_2[Ru_6(CO)_{18}]$ via the $Na_4[Ru_6(CO)_{17}$ tetraanionic intermediate.

The reduction of CO_2 by the trinuclear ruthenium dianion, $Ca[Ru_3(CO)_{11}]$, is very sluggish. At a temperature range of 25—60° C, less than 15% $Ru_3(CO)_{12}$ was formed over a period of 24 h. The prolonged reaction only resulted in a slight increase of formation of $Ru_3(CO)_{12}$. However, under similar conditions, treatment of the dianion $K_2[H_2Ru_4(CO)_{12}]$ with CO_2 did not give $H_2Ru_4(CO)_{13}$.

The mechanism of these reactions is probably similar to that proposed by Maher and Cooper [1] for the reduction of CO_2 by mononuclear metal dianions. This involves a two-intermediate sequence in which initial nucleophilic



(1)

attack on a CO_2 molecule forms a carboxylate anionic intermediate (A), followed by attack on a second molecule of CO_2 giving a C_2O_4 ligand-containing intermediate (B), which would collapse to give $K_2Ru_4(CO)_{13}$ as shown in eq. 1.

The reduction of CO_2 by the trinuclear dianionic $Ca[Ru_3(CO)_{11}]$, in contrast to tetranuclear and hexanuclear dianions, e.g. $K_2[Ru_4(CO)_{13}]$, $K_2[H_2Ru_4(CO)_{12}]$ and $Na_2[Ru_6(CO)_{18}]$, is probably driven by the higher negative charge density on each Ru atom and the strength of the calcium-to-oxygen bond formed in the intermediates. Further experiments on other Group VIII metal clusters and the reaction with carbon disulfide will be investigated.

References

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6 Identified by comparison of the IR spectrum of a Nujol mull with that of an authentic sample.
7 Identified by comparison of the IR and NMR spectra with those of an authentic sample.