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THE EFFECT OF DBU(1,8-DIAZABICYCLO[5.4.0]NDECENE-7) ON THE WATER GAS SHIFT REACTION CATALYZED BY $M_3(CO)_{12}$(M = Ru, Os)

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DBU was found to be an effective cocatalyst for the water gas shift reaction(WGSR) catalyzed by $M_3(CO)_{12}$(M= Ru, Os), especially by $Os_3(CO)_{12}$ under basic conditions. The dianion cluster, $H_2M_4(CO)_{12}{}^{2-}$ was isolated in the DBU-$M_3(CO)_{12}$ catalyst system as bis(triphenylphosphine)iminium salts and was considered to be one of the active species in the reaction.

Recently metal carbonyl clusters have been attracting considerable interest in organometallic and synthetic chemistry because of the intrinsic novel properties and also of the potential ability to activate carbon monoxide.1) Metal carbonyl-base catalyst system has been known to be an effective catalyst for the homogeneous water gas shift reaction(WGSR), and weak organic bases such as trialkylamines were found to provide better activity than Brönsted bases under appropriate conditions.1) Now we wish to report the effect of strong organic base, DBU, in the homogeneous WGSR catalyzed by $M_3(CO)_{12}$ and species of the resulting carbonyl cluster anions in the reaction system.

Typical experimental procedure of the WGSR was as follows. Water(1.0 g), solvent(6.0 ml), metal carbonyl(3 x 10^{-5} mol), and base were placed in a 30 ml autoclave. Air in the autoclave was flushed three times with carbon monoxide, and then 10 kg/cm^2 of carbon monoxide was charged. After the reaction was carried out for 24 h at 150 ± 2 °C except run 2 in Table 1, gaseous products were analyzed by GLC for H_2 and CO. For examination of metal carbonyl anion clusters by IR or by isolation of the present WGSR were summarized in Table 1.

$Os_3(CO)_{12}$ is known to be much less active for the WGSR in basic solution than $Ru_3(CO)_{12}$.1b) As Table 1 shows, however, the activity of $Os_3(CO)_{12}$-DBU-MeOH system was almost comparable with that of $Ru_3(CO)_{12}$. Under the same reaction conditions $Fe(CO)_5$ and $Fe_3(CO)_{12}$ were decomposed to give brownish precipitates. The activity of the Os system decreased both in the low concentration of DBU(run 4 in Table 1) and in the repeated runs cattied out by recharge of CO(10 kg/cm^2). The observed results may suggest that the activity of the Os catalyst is affected 1) by decreasing of basicity of the solution by CO_2 generated in the WGSR, and/or 2) by the

Table 1. The effect of solvent, base and water on the catalytic activity

Run	Solvent	Base	Molar ratio H_2O/base	Activity[a)] Ru	Activity[a)] Os
1	MeOH	DBU	3.25[b)]	180	175
2	MeOH	DBU	3.25[b)]	55[i)]	23[i)]
3	MeOH	DBU	1.62[c)]	212	189
4	MeOH	DBU	8.12[d)]	160	30
5	MeOH	DBU	0.81[e)]	167	154
6	THF	NEt_3	3.10[f)]	206	21
7	MeOH	NEt_3	3.10[f)]	82	trace
8	MeOH	KOH	9.11[g)]	95[j)]	34[j)]
9	MeOH	DBN	2.65[h)]	150	145
10	MeOH	none	-	trace	0

a) The activity means moles of H_2/day/mole of $M_3(CO)_{12}$ (M = Ru, Os). The reaction temperature was 150 ± 2 °C except run 2 (130 ± 2 °C). Experimental error was within ± 10 %.

b) DBU, 17.1 mmol; H_2O, 55.6 mmol. c) DBU, 17.1 mmol; H_2O, 27.8 mmol. d) DBU, 6.84 mmol; H_2O, 55.6 mmol. e) DBU, 17.1 mmol; H_2O, 13.9 mmol. f) NEt_3, 17.9 mmol; H_2O, 55.6 mmol. g) KOH, 6.1 mmol; H_2O, 55.6 mmol. h) DBN, 21.0 mmol; H_2O, 55.6 mmol. i) The reaction temperature was 130 ± 2 °C. j) Decomposition of the complex (partly or totally).

reaction of the active catalyst with MeOH, DBU, or H_2O.

The Ru - DBU catalyst in MeOH had almost the same activity with that of the most active catalyst system, $Ru_3(CO)_{12}$-NR_3-THF reported by Pettit et al.[2)] among known $Ru_3(CO)_{12}$-base systems,[1)] and the activity did not change in repeated runs.

When KOH was used instead of DBU, Ru or Os catalyst decomposed partly or totally. Among other strong organic bases examined, DBN(1,5-diazabicyclo[4.3.0]-nonene-5) also acted as an effective base for the WGSR but 1,8-bis(diethylamino)-naphthalene(pKa = 12.34) was not effective though the basicity is stronger than that of DBU(pKa = 11.5).

In the WGSR catalyzed by $Ru_3(CO)_{12}$ - KOH system, the monoanionic clusters, $HRu_3(CO)_{12}^-$ and $H_3Ru_4(CO)_{12}^-$, were proposed to be active species by Ford and his collaboraters.[1c)] Recently, J.C.Bricker and his coworkers described that the trinuclear combination, $HRu_3(CO)_{11}^-$ - $Ru_3(CO)_{12}$ plays the major role in catalysis of the WGSR in basic solution. However, IR specrum of the reaction mixture in the $Ru_3(CO)_{12}$ - DBU system was proved to be very different from that of Ru - NR_3 and - KOH systems.[1c)] Anionic clusters formed in our reaction systems were isolated by addition of bis(triphenylphosphine)iminium chloride. After purification by column chromatography or recrystallization, the structure of those complexes was

Table 2. The isolated carbonyl clusters from the WGSR system.[a)]

Run	Base	Isolated Complexes[b)]	Found(Calcd), %			Y, mg[c)]	Anions[d)]
			C	H	N		
1	KOH	$[PPN][H_3Ru_4(CO)_{12}]$	44.75 (44.97	2.61 2.59	1.14 1.09)	51.1	$[HRu_3(CO)_{11}]^-$ $[H_3Ru_4(CO)_{12}]^-$
2	DBU	$[PPN]_2[H_2Ru_4(CO)_{12}]$	55.13 (55.45	3.53 3.43	1.54 1.54)	51.3	$[H_2Ru_4(CO)_{12}]^{2-}$
3	KOH	$[PPN][H_3Os_4(CO)_{12}]$	35.39 (35.19	2.01 2.03	0.94 0.85)	80.2	$[HOs_3(CO)_{11}]^-$ $[H_3Os_4(CO)_{12}]^-$
4	NEt_3	$[PPN][HOs_3(CO)_{11}]$	39.44 (39.80	2.20 2.20	1.00 0.99)	101.2	$[HOs_3(CO)_{11}]^-$
5	DBU	$[PPN]_2[H_2Os_4(CO)_{12}]$ $([PPN][H_3Os_4(CO)_{12}])$[e)]	45.61 (46.36	2.86 2.87	1.35 1.29)	69.8	$[H_2Os_4(CO)_{12}]^{2-}$ $[H_3Os_4(CO)_{12}]^-$

a) Reaction conditions were as follows. $M_3(CO)_{12}$ (M = Ru, Os); 0.1 mmol, base; 17.1 mmol, H_2O; 55.6 mmol, and MeOH; 6 ml were used and other conditions were the same as those of Table 1 except the reaction time, 14 h.

b) PPN = bis(triphenylphosphine)iminium cation. The structure of all isolated complexes were also confirmed by IR and NMR.

c) Yields were not optimized.

d) The existence of these anionic clusters was observed in the IR spectrum of each reaction mixture. Starting cluster, $M_3(CO)_{12}$, was not detected in every case.

e) $[PPN][H_3Os_4(CO)_{12}]$ was also isolated (Y. 42.6 mg).

confirmed by direct comparison with authentic samples[4)] and by elemental analysis. The results were summarized in Table 2. In the $Ru_3(CO)_{12}$-DBU-MeOH system, the dianionic cluster, $H_2Ru_4(CO)_{12}^{2-}$ was isolated as a major complex from the reaction mixture.[4a)] The dianion complex is known but the catalytic behavior has not been elucidated, and the dianion has never been found in the WGSR catalyzed by $Ru_3(CO)_{12}$ in the presence of other bases examined before. In the case of the Os system, $H_2Os_4(CO)_{12}^{2-}$ was also isolated along with monoanionic species, $H_3Os_4(CO)_{12}^-$, from the reaction mixture. It is noteworthy that only the Os-DBU system which gave $H_2Os_4(CO)_{12}^{2-}$ was very active for the WGSR among the other Os - base systems.
The catalytic behavior of these dianionic complexes is still not clear but preliminary experiments on reduction of benzaldehyde by anionic ruthenium clusters suggest that $H_2Ru_4(CO)_{12}^{2-}$ is also one of the active species in our WGSR system.[5)]

We are now further investigating these systems in order to gain more mechanistic information in connection with the catalytic behavior of these dianionic clusters.

References

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4) a) $H_2Ru_4(CO)_{12}^{2-}$ and $H_3Ru_4(CO)_{12}^{-}$: K. E. Inkrott and S. G. Shore, *Inorg. Chem.*, 18, 2819(1979); The dianion could be prepared from $H_4Ru_4(CO)_{12}$ by using only a very strong base, KH, under anhydrous condition, because KOH, even in use of a large excess of it, could give not the dianion but only $H_3Ru_4(CO)_{12}^{-}$. We could obtain the dianion easily from DBU and $H_4Ru_4(CO)_{12}$, even in the presence of water.
   b) $HRu_4(CO)_{13}^{-}$, $Ru_4(CO)_{13}^{2-}$, and $Ru_4(CO)_{12}^{4-}$: C. C. Nagel and S. G. Shore, *J. Chem. Soc., Chem. Commun.*, 1980, 530;
   c) $HOs_3(CO)_{11}^{-}$: C. R. Eady, B. F. G. Johnson, J. Lewis, and M. C. Malatesta, *J. Chem. Soc., Dalton Trans.*, 1978, 1358;
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5) Reduction of benzaldehyde by anionic ruthenium clusters was carried out at 125 °C for 3 h, under the following conditions, where only a desired anionic cluster plays as catalyst, since the anionic clusters proved to be interconvertible depending on H_2/CO ratios and base[1a,3,6]: $H_2Ru_4(CO)_{12}^{2-}$-H_2(20 kg/cm^2)-DBU, $H_3Ru_4(CO)_{11}^{-}$-H_2(20 kg/cm^2)-NEt_3, and $HRu_3(CO)_{11}^{-}$-CO(10 kg/cm^2)-H_2O-NEt_3. The extent of the reduction was qualitatively in the following order;
   $H_2Ru_4(CO)_{12}^{2-}$(95%) $>$ $H_3Ru_4(CO)_{12}^{-}$(47%) $\gg$ $HRu_3(CO)_{11}^{-}$(~2%).
   From the result together with those in Table 1 and 2, it is reasonably presumed that the dianion of stronger hydridic character would be also able to produce H_2 in the presence of proton source.
6) F. Wada, M. Shimuta, and T. Matsuda, unpublished results.

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