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ON THE CATALYTIC SPECIES IN THE HYDROXYMETHYLATION OF PROPYLENE BY IRON PENTACARBONYL - TERTIARY AMINE CATALYST

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Studies on the pressure and temperature dependences of the Reppe's hydroxymethylation of propylene by $Fe(CO)_5$ - tertiary amine catalyst indicated that the catalytic species was hydridotetracarbonyl ferrate, $HFe(CO)_4^-$. The reaction was found to proceed preferably under the condition where the dissociation, $HFe(CO)_4^- \rightleftharpoons HFe(CO)_3^-$ + CO, could occur to form a coordinatively unsaturated species.

The hydroxymethylation of olefins[1] with carbon monoxide and water in the presence of $Fe(CO)_5$ and a tertiary amine under pressure has been generally accepted to proceed catalytically by trinuclear hydridoiron complex, $[HNR_3]^+ \cdot [HFe_3(CO)_{11}]^-$ (I), as an active species according to the proposition by N. v. Kutepow and H. Kindler[2]. In view of the well-established fact that the hydroformylation of olefins is catalyzed by the monomeric hydrocarbonyl of cobalt[3] or rhodium[4], it seems somewhat curious that no attention has been devoted to the function of a corresponding monomeric hydrocarbonyl of iron in the hydroxymethylation.

In the previous papers we reported that under carbon monoxide pressure above 15 kg/cm^2, $Fe(CO)_5$ (or I), tertiary amine and water in alcoholic medium afforded the salt of hydridotetracarbonyl ferrate, $[HNR_3]^+[HFe(CO)_4]^-$ (II), as the predominant species other than $Fe(CO)_5$ at temperatures below 150°C[5], and that the resultant mixture could be used catalytically for the reduction of α,β-unsaturated esters and nitrile at 100°C[6]. In this communication we present several evidences for supporting the idea that the monomeric hydrocarbonyl species (II) is of importance as an active catalyst also in the hydroxymethylation of propylene.

In a 500 ml autoclave equipped with a stirrer and an outlet for sampling, $Fe(CO)_5$ (10 g, 0.05 mol), triethylamine (25.3 g, 0.25 mol), water (14.4 g, 0.8 mol) and methanol (70 ml) were placed. After air in the vessel was displaced with carbon monoxide, a desired pressure of carbon monoxide (6 to 30 kg/cm^2 at room temperature) was introduced and the mixture was heated to the reaction temperature in 1 hr. After establishment of an equilibrium in the formation of II (ca. 76 mol% of the iron species in the mixture at 100°C and 12.5 mol% at 150°C) was checked by ir measurement[5], propylene (10 ml) was added by means of a high pressure liquid injector. The initial pressures at the reaction temperature were maintained by intermittent addition of carbon monoxide during the reaction. When the triethylammonium salt of I (10 g) was used, the amount of triethylamine was reduced to 23.2 g by considering the amount of the ammonium ion in I, and carbon monoxide was introduced to the pressures which correspond to the starting pressure in the case of $Fe(CO)_5$ after the temperature was reached at 100°C. The time course of the formation of n- and iso-butanol was determined by glc with n-propanol as an internal standard. The catalytic nature of the reaction was confirmed by carrying out the reaction at 100°C for 90 hrs (initial pressure of 20 kg/cm^2 and 27 ml of propylene) and holding the starting pressure (36 kg/cm^2) nearly constant to form 2.9 g (0.04 mol) at 21 hr, 4.4 g (0.06 mol) at 29 hr and 6.4 g (0.087 mol) at 90 hr of total butanol, respectively. A gradual decrease of the reaction rate was observed in such a batch procedure, which could be attributable to both consumption of water and accumulation of carbon dioxide due to regeneration process of II.

Since the preliminary experiments showed that carbon monoxide pressure effected markedly on the rate of the butanol formation, dependence of the pressure was examined in the initial stage of the reaction, where other factors influencing to the rate could be minimized, and the result in Fig. 1 was obtained. Fig. 1 clearly indicates that the rate of reaction decreases on increasing carbon monoxide pressure. An approximate estimation of the effect of the pressure on the rate from Fig. 1 afforded the relationship; rate $\propto [P_{CO}]^{-2}$. The similar negative influence of carbon monoxide pressure is well known in the hydroformylation[7]. A leveling of the rate increase on raising the reaction temperature around 150°C in Fig. 2 is well consistent with the behavior of the

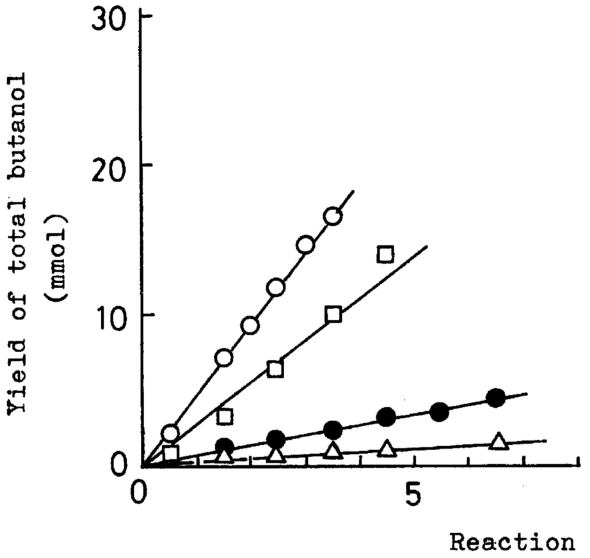

Fig. 1 Effect of carbon monoxide pressure (at 100°C)

○ : 6, □ : 10, ● : 20, △ : 30, the initial pressures at room temperature, kg/cm^2.

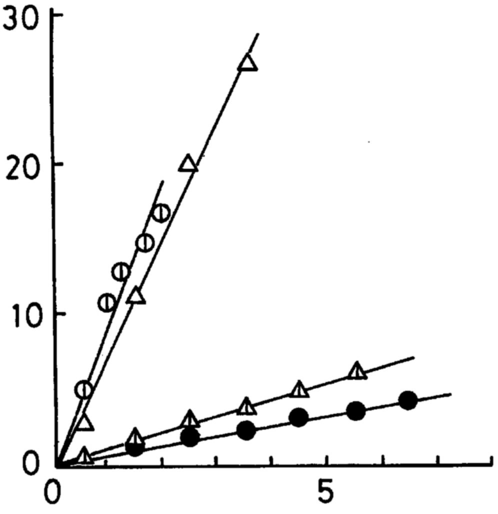

Fig. 2 Effect of reaction temperature at the initial pressure of 20 kg/cm^2

● : 100°C, △ : 125°C, ⦶ : 150°C, △ : Twenty ml of propylene was used at 100°C.

catalytic system observed previously5) that the equilibrium content of II decreased with increasing temperature, but was almost independent on the carbon monoxide pressure ranging from 15 to 100 kg/cm^2. In all cases the trinuclear species could not be detected by ir in the reaction mixture except for those where the pressure was low (6 - 10 kg/cm^2). It has been found5) that under atmospheric pressure II rapidly changes to I with the liberation of hydrogen and carbon monoxide, while I slowly reverts into II at 100°C under carbon monoxide pressure above 20 kg/cm^2. If I formed

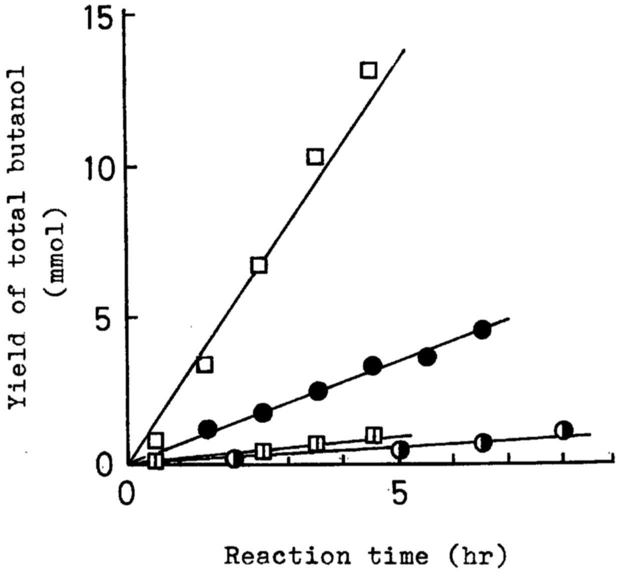

Fig. 3 Effect of ironcarbonyl species (at 100°C)

$Fe(CO)_5$; □ : 10, ● : 20

$[HNEt_3]^+[HFe_3(CO)_{11}]^-$; ◫ : 10, ◑ : 20

(the same as in Fig. 1, kg/cm^2)

from II by the interconversion at lower pressure was an active catalyst rather than II, use of I in place of $Fe(CO)_5$ would give rise to much increase of the reaction rate. However, this was not true as shown in Fig. 3.

All these facts suggest not only that II rather than I is the active catalytic species, but also that I becomes in use as the catalyst after being converted to II. Now it seems conflicting that the reduced pressure favors the formation of the catalytically inactive I on one hand, while it increases the rate of hydroxymethylation on the other. This is reasonably explained by supposing that a prior liberation of carbon monoxide to form a coordinatively unsaturated species is involved in both the processes (Eq. 1).

$$HFe(CO)_4^- \rightleftharpoons HFe(CO)_3^- + CO \qquad 1)$$

Thus, in the absence of olefin the unsaturated species is eventually converted into I, but enters into the hydroxymethylation in the presence of olefin and I is formed to only a limited extent. The observation that the reaction mixture under the most favorable conditions (6 - 10 kg/cm^2) is pink color* and the color gradually fades to faint yellow at higher pressure indicates that the reaction takes place preferably under the condition where a small amount of I is coexisting with II, i.e. the condition being capable of forming the coordinatively unsaturated species.

From all the results in this study, it seems quite probable that the hydroxymethylation of propylene is catalyzed by II and proceeds via the prior dissociation step of II (Eq. 1) to form $HFe(CO)_3^-$, which is in close resemblance with the fact being recognized in the hydroformylation catalyzed by $HCo(CO)_4$[8].

*A characteristic evidence for the existence of I of deep red color.

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