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Applications of Homogeneous Water-gas Shift Reaction. III. A Further Study of the Hydrocarbonylation. A Highly Selective Formation of Diethyl Ketone from Ethene, CO, and H_2O

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The hydrocarbonylation of ethene with CO and H_2O produces diethyl ketone with a high selectivity of 99±1%(propanal 1±1%); a $Co_2(CO)_8$–phosphine system is used as an efficient catalyst, which is also active for the homogeneous water-gas shift reaction. The effects of the reaction parameters(CO pressure, temperature, and ethene and H_2O concentrations) on the selectivity and activity are examined for the $Co_2(CO)_8$–1,2-bis(diphenylphosphino)ethane (diphos) system; the selectivity to yield the ketone is fairly high under the variety of conditions studied here. Evidence suggests that the active species which catalyze the water-gas shift reaction participate in the hydrocarbonylation of ethene.

Diethyl ketone(3-pentanone) is produced under normal oxo conditions using a transition-metal catalyst;[1] it was previously reported that a maximum molar ratio of the ketone to propanal up to *ca.* 3 was achieved using $Co_2(CO)_8$ as the catalyst.[2,3]

In preceding papers[4,5] we described the hydrocarbonylation of propene with CO and H_2O, using a $Co_2(CO)_8$-phosphine catalyst system, to yield a mixture of dipropyl ketones(4-heptanone+2-methyl-3-hexanone+2,4-dimethyl-3-pentanone) as primary products.[6] Therefore, the hydrocarbonylation of ethene has become of great interest to us, because a selective and efficient industrial route to obtain diethyl ketone may be realized.

In the present study, optimum conditions are explored for the ketone formation and the catalytic behavior of hydrocarbonylation is discussed further.

Experimental

Materials. The ethene (Research Grade), phosphine, dioxane, and acetone were obtained commercially and used without further purification.

Reaction Procedure. The hydrocarbonylation reactions were carried out in a 100-ml stainless-steel autoclave in which $Co_2(CO)_8$, phosphine, H_2O, and solvent had been placed. The vessel was sealed and degassed by three 10 kg/cm^2 pressurization/depressurization cycles with CO. Into the vessel both ethene and CO were introduced. The vessel was heated with stirring to a definite reaction temperature for a certain reaction period and then cooled down to room temperature.

Analytical Methods. The liquid products were analyzed at 100 °C by means of a gas chromatograph equipped with FID using a 6-m column packed with polyethylene glycol adipate. The infrared and ^{1}H-NMR spectra of the catalyst solutions were recorded on a Hitachi type 215 spectrometer and a Hitachi type R-40 spectrometer respectively.

Results and Discussion

Time Course of Diethyl Ketone Formation. A typical example of the reaction is shown in Fig. 1, where the molar ratio ethene/$Co_2(CO)_8$ of 150/2 was used. At 165 °C, the selectivity of the ketone was as high as 97±1% (propanal 3±1%, 32:1 ratio). An induction period of about 1 h preceded the onset of catalysis; this is roughly the same as that observed in the formation of dipropyl ketones.[4]

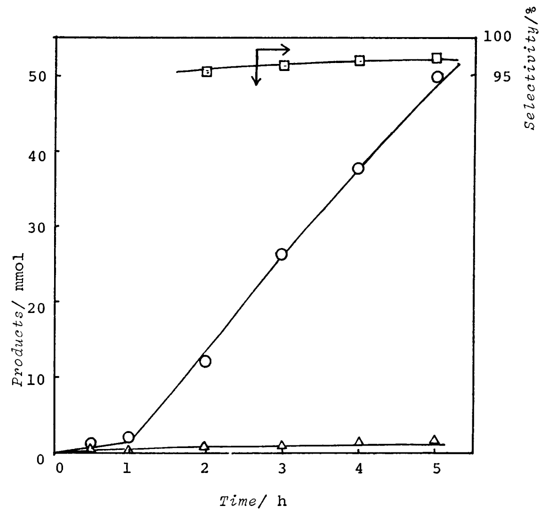


Fig. 1. Cobalt-catalyzed hydrocarbonylation as a function of time.

$Co_2(CO)_8$ 2 mmol, diphos 2 mmol, dioxane 50 ml, H_2O 60 mmol, CO 70 kg/cm^2(const.), temp. 165 °C, ethene 150 mmol.

—○— Diethyl ketone, —△— propanal, —□— selectivity; [diethyl ketone]$_t$/([diethyl ketone]$_t$+[propanal]$_t$), t: time.

No trace of propanoic acid was detected under the conditions described here. Moreover, neither the hydrogenation of propanal to 1-propanol[7] nor aldol condensation occurred, partly because the amount of propanal formed was too small.

The extremely high selectivity suggests that the cobalt-catalyzed hydrocarbonylation of ethene may have some industrial importance. Thus, the optimum conditions were explored in detail in the hope of developing a feasible industrial process.

Effect of Reaction Parameters. Table 1 shows the effect of the phosphorus ligand on the selectivity(S) and activity(r^{max}). The S value was slightly affected by both the phosphine structure(Runs 1—6) and the ratio of diphos to $Co_2(CO)_8$(Runs 7—10), although excess amounts of diphos decreased the S value (Run 7). The use of an equimolar amount of H_2 (60 mmol) instead of H_2O drastically decreased the S value (Run 12). The use of MeOH (60 mmol) resulted in a decrease in the activity r^{max} (Run 13).

The selectivity and activity were examined as a function of the ethene([C_2']) and H_2O([H_2O]) concentration as well as of the CO pressure (Table 2). The S value slightly increased with the increase in ethene from 75 to 190 mmol. The r^{max} value increased with the initial increase in [C_2'], but reached a maximum at *ca.* 150 mmol and decreased thereafter (Runs 1—4). The S value slightly increased with the increase in CO pressure(P_{CO}), while r^{max} reached a maximum at *ca.* 100 kg/cm² of P_{CO}. Excess water reduced the S value (Run 9). The S value decreased with the increase in reaction temperature, but it was still high at 180 °C (Fig. 2). The use of acetone as a solvent resulted in a decrease in the activity, especially at 135 °C.

Thus, the selectivity to diethyl ketone is fairly high under the variety of conditions studied here. However, the mode of the influence of these parameters on the activity r^{max} is similar to that observed in the case of propene.[4]

TABLE 1. HYDROCARBONYLATION OF ETHENE USING CO-H_2O CATALYZED BY $Co_2(CO)_8$-PHOSPHINE SYSTEM
$Co_2(CO)_8$: 2 mmol, phosphine: 1.5 mmol, dioxane: 50 ml, ethene: 150 mmol, H_2O: 60 mmol, CO: 70 kg/cm² (initial), temp: 180 °C (Runs 1—6), 165 °C (Runs 7—13).

Run No.	Added phosphine	Rate[a) r_k^{max} mmol h^{-1}	r_a^{max} mmol h^{-1}	S[b) (−)
1	$Ph_2PCH_2PPh_2$	14.9	0.29	98.1
2	$Ph_2P(CH_2)_2PPh_2$	22.9	0.55	97.6
3	$Ph_2PC{\equiv}CPPh_2$	13.0	0.61	95.5
4	$Ph_2P(CH_2)_3PPh_2$	21.6	0.3	98.6
5	$Ph_2As(CH_2)_2PPh_2$	4.6	0.26	94.6
6	PPh_3	16.4	0.17	99.0
7	$Ph_2P(CH_2)_2PPh_2$ (2.5 mmol)	6.0	1.4	81.1
8	$Ph_2P(CH_2)_2PPh_2$ (2.0 mmol)	12.4	0.44	96.6
9	$Ph_2P(CH_2)_2PPh_2$ (1.5 mmol)	13.2	0.13	99.0
10	$Ph_2P(CH_2)_2PPh_2$ (1.0 mmol)	7.5	0.21	97.3
11	None	2.2	1.2	64.7c)
12d)	$Ph_2P(CH_2)_2PPh_2$ (2.0 mmol)	12.8	15.5	45.2
13e)	$Ph_2P(CH_2)_2PPh_2$ (2.0 mmol)	1.2	—	—

a) r^{max}: the slope of the linear portion of the maximum rate region (see Fig. 1). The suffix 'k': diethyl ketone, 'a': propanal. b) $S=\frac{r_k}{r_k^{max}+r_a^{max}}$. c) The decomposition of $Co_2(CO)_8$ occurs.[4] d) H_2: 60 mmol, CO: 90 kg/cm² (initial). e) CH_3OH: 60 mmol, CO: 50 kg/cm² (initial), ethene: 185 mmol.

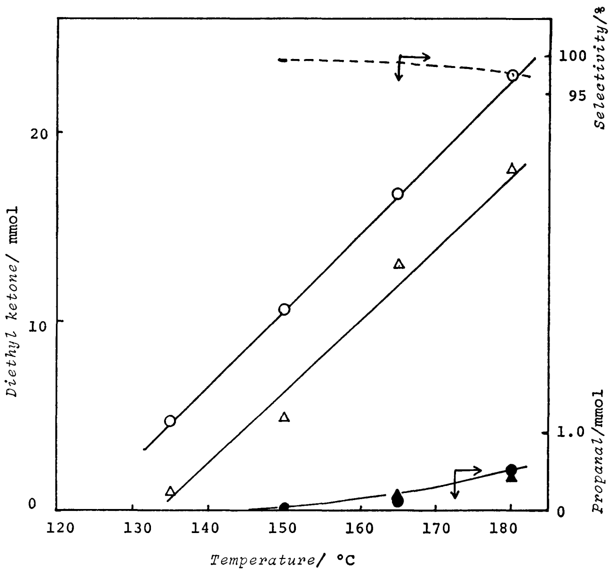
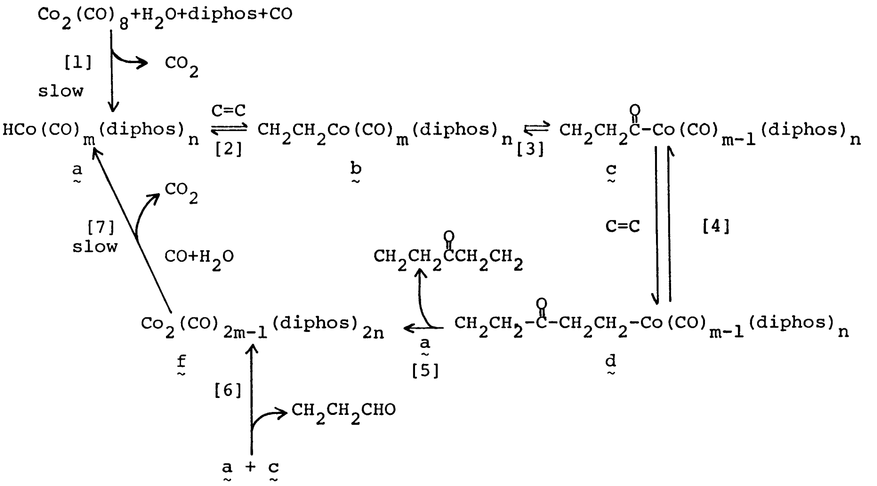


Fig. 2. Effect of temperature.
$Co_2(CO)_8$ 2 mmol, diphos 1.5 mmol, H_2O 60 mmol, dioxane 50 ml, CO 80 kg/cm² (initial), ethene 150 mmol.
Dioxane solution; —○— [r_k^{max}], —●— [r_a^{max}].
Acetone solution; —△— [r_k^{max}], —▲— [r_a^{max}].
---- Selectivity [S].
Notations: See footnote of Table 1.

TABLE 2. EFFECT OF REACTION PARAMETERS
$Co_2(CO)_8$: 2 mmol, diphos: 2 mmol, dioxane: 50 ml, temp: 165 °C.

Run No.	[Ethene] mmol	P_{CO}[a) kg cm^{-2}	[H_2O] mmol	Rate[b) r_k^{max} mmol h^{-1}	r_a^{max} mmol h^{-1}	S (−)
1	74	70	60	12.0	0.5	96.0
2	111	70	60	12.5	0.17	98.6
3	150	70	60	13.2	0.13	99.0
4	185	70	60	12.5	0.06	99.5
5	150	50	60	7.6	0.07	99.1
6	150	90	60	19.6	0.13	99.3
7	150	120	60	17.3	0.09	99.5
8	150	70	120	11.4	0.1	99.0
9	150	70	180	13.6	0.28	97.9

a) Initial pressure. b) See footnote of Table 1.



Scheme 1. A possible reaction scheme of the hydrocarbonylation of ethene with CO and H_2O.

The Nature of Catalytically Active Species. The active species responsible for the hydrocarbonylation of ethene may be assumed to be $HCo(CO)_m(diphos)_n$, as in the case of propene.[4,8] In fact, an induction period of *ca.* 1 h was also observed for the diethyl ketone formation (Fig. 1) and the catalytic behavior was generally similar (Tables 1 and 2 and Fig. 2).

A catalyst solution[8] consisting of $Co_2(CO)_8$, diphos, H_2O, and dioxane, which is active in the water-gas shift reaction, has a characteristic ^{1}H-NMR resonance at δ -17.2.[9,10] Some experiments were performed in order to elucidate the NMR behavior in connection with the catalytic properties. The results may be summarized as follows.

(1) In the absence of CO, a stoichiometric reaction of the water-gas shift catalyst solution with ethene occurred, even at room temperature, to give diethyl ketone[11] selectively. The intensity of the ^{1}H-NMR resonance of the solution decreased significantly after the 3 h-reaction.[12]

(2) The NMR spectrum exhibited no resonance on a short-time (5 min) treatment of a solution ($Co_2(CO)_8$ (4 mmol), diphos (4 mmol), and dioxane (5 ml) with both CO (70 kg/cm^2) and H_2O (60 mmol) at 165 °C; this is in contrast to the reaction of a matured solution[8] (see Fig. 1).

(3) No NMR resonance could be observed during the catalytic hydrocarbonylation of ethene at 165 °C under a CO pressure of 80 kg/cm^2, indicating a rapid consumption of the active species.

(4) The NMR spectrum of a solution in the absence of diphos or H_2O showed no resonance in either case.

(5) When an acetone solution consisting $Co_2(CO)_8$, diphos, and H_2O was treated at 135 °C for 3 h under CO(70 kg/cm^2), its ^{1}H-NMR spectrum exhibited a resonance at δ -17.2, although it was weak in comparison with that of the dioxane solution prepared under the same conditions[13] (see Fig. 2).

Thus, the active species which catalyze the water-gas shift reaction can be expected to participate in the hydrocarbonylation of ethene and to exhibit the ^{1}H-NMR resonance at δ -17.2.

A possible reaction scheme is illustrated in Scheme 1:[14,15] The species, **a**, formed during the course of the water-gas shift reaction[1] is trapped by ethene to form a alkyl cobalt complex, **b**, [2]; CO insertion [3] and succeeding ethene addition to **c**[4] give a 2-propyonylethyl cobalt complex, **d**, and the reaction of **a** with **d** produces diethyl ketone[5].[16] Step [6] accounts for the aldehyde formation, though it may be disregarded because of the high selectivities of the ketone formation. (Figs. 1 and 2 and Tables 1 and 2). The resulting complex, **f**, is converted into **a** by the WGSR pathway[7] again, and thus the catalytic cycle is completed.

Reactions 2—6 proceed rapidly, even under mild conditions, as has been mentioned above((1) and (2)). Reactions 1 and 7, on the other hand, proceed only at a relatively high temperature (120 °C or above (2), Figs. 1 and 2).

Although there is no direct evidence that the ^{1}H-NMR peak is due to $HCo(CO)_m(diphos)_n$, the present reaction scheme of the cobalt-catalyzed hydrocarbonylation using CO and H_2O seems to be probable.

References

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2) M. Dokiya and K. Bando, *Kogyo Kagaku Zasshi*, **71**, 1866 (1968).

3) Better yields can be obtained by using a heterogeneous catalyst, according to the patent literature.[1]

4) K. Murata and A. Matsuda, *Bull. Chem. Soc. Jpn.*, **54**, 249 (1981).

5) K. Murata and A. Matsuda, *Chem. Lett.*, **1980**, 11.

6) K. Murata, A. Matsuda, K. Bando, and Y. Sugi, *J. Chem. Soc., Chem. Commun.*, **1979**, 785.

7) Under the conditions given in Fig. 1, propanal (10 mmol) introduced independently can be hydrogenated to yield 1-propanol (2 mmol) in a 4 h-reaction.

8) A standard sample of the catalyst solution which is subjected to the ^{1}H-NMR analysis was prepared as follows: in a stainless-steel autoclave (50 ml volume) were mixed 4 mmol of $Co_2(CO)_8$, 4 mmol of diphos, 30 mmol of H_2O, and 5 ml of dioxane. The vessel was then sealed, and CO (70 kg/cm^2, room temp) was introduced. After the vessel had been heated to 165 °C with stirring for 3 h, an aliquot sample was quickly withdrawn from the vessel at 0 °C.

9) K. Murata and A. Matsuda, *Bull. Chem. Soc. Jpn.*, **54**, 245 (1981).

10) C. Ungermann, V. Landis, S. A. Moya, H. Cohen, H. Walker, R. G. Pearson, R. G. Rinker, and P. C. Ford, *J. Am. Chem. Soc.*, **101**, 5922 (1979).

11) The product was identified by gas chromatography.

12) When the solution was allowed to react with ethene at 50 °C for 4 h, no ^{1}H-NMR peak was observed at δ -17.2.

13) In these cases, the pH values of the acetone and dioxane solutions were 2.5 and 1.5 respectively. Further investigations concerning the pH effects on the activity are in progress.

14) The participation of the acyl cobalt complex, **c**, has already been described in a previous paper on the hydrocarbonylation of propene.$^{4)}$

15) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 4023 (1961); J. A. Bertrand, C. L. Aldrige, S. Husebye, and H. B. Jonassen, *J. Org. Chem.*, **29**, 790 (1964).

16) There is an alternative route: the acyl complex, **c**, reacts with alkyl complex, **b**, to yield the ketone and dimeric cobalt complex, **f**.