

Studies of the Organic Reaction of Metal Carbonyl. VII.* The Acceleration Effect of the Addition of Inorganic Compounds on the Reaction of Olefin Oxide with Cobalt Hydrocarbonyl

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Previous work¹⁾ in this laboratory has shown that the reaction of olefin oxide with cobalt hydrocarbonyl is accelerated by the addition of even a relatively small amount of such organic compounds as alcohol, ketone, ether and esters.

In the present paper, the effects of the addition of various inorganic compounds will be examined for this type of reaction. The results obtained in this investigation indicate that some inorganic compounds, such as cuprous oxide and halide, silver oxide and aluminum chloride, also have an acceleration effect on this reaction.

Experimental

Reaction Procedures.—The reactions of olefin oxide with cobalt hydrocarbonyl were carried out in the way which has been described in a previous paper.²⁾ Into a 100 ml. four-necked flask, fitted with a 50 ml. dropping funnel, a stirrer and a rubber stopple and connected with a 500 ml. gas buret, various amounts of inorganic compounds were introduced, and the air in the system was replaced with carbon monoxide. By the use of a syringe, 50 ml. of a 0.09 M cobalt hydrocarbonyl solution in toluene or in *n*-hexane and various amounts of organic compounds were put into the flask. To this system, 0.5 ml. of propylene oxide (1.6 mol./mol. cobalt hydrocarbonyl) was then introduced, after which the reaction mixture was agitated at 0°C for several hours.

Analytical Procedures.—The reaction products (ethyl β -hydroxybutyrate and ethyl γ -chloro- β -hydroxybutyrate) were analyzed by gas chromatography and by means of infrared spectra which were taken on a Shimadzu model IR-27 infracord spectrophotometer. The details were given in the previous paper.²⁾

Materials.—All of the materials used in this study were commercial products.

Results and Discussion

The Reaction of Propylene Oxide with Cobalt Hydrocarbonyl in the Presence of Various Inorganic Compounds.—All reactions were carried out at 0°C and under one atmosphere of carbon monoxide, and with the mole ratio*

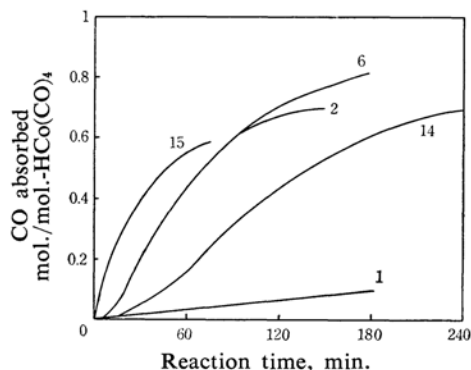


Fig. 1. CO absorption vs. time plots for the reaction of propylene oxide in the presence of inorganic additives.

Number: Exp. No.

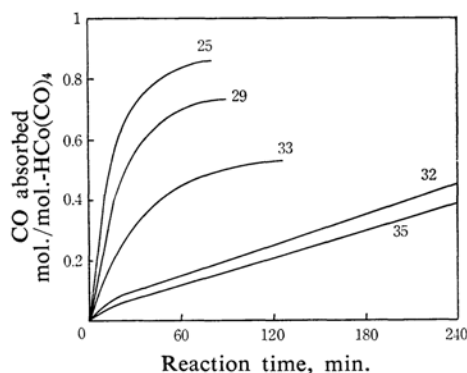


Fig. 2. CO absorption vs. time plots for the reaction of propylene oxide in the presence of inorganic additives.

Number: Exp. No.

* Part VI: Y. Takegami, C. Yokokawa, Y. Watanabe, H. Masada and Y. Okuda, This Bulletin, 38, 787 (1965).

1) Y. Takegami, C. Yokokawa and Y. Watanabe, This Bulletin, 37, 934 (1964).

2) Y. Takegami, C. Yokokawa, Y. Watanabe and H. Masada, *ibid.*, 37, 672 (1964).

* Mole of propylene oxide per mole of cobalt hydrocarbonyl used.

of propylene oxide fixed at 1.6. Under these conditions, the reaction without additives proceeds very slowly (Exp. 1 in Table I).²⁾ The results of the reactions which were carried out in the presence of inorganic additives are summarized in Figs. 1 and 2 and in Tables I—III. The values of the gas absorption rate at the early stage of the reactions relative to the absorption rate of Exp. 1 are shown as a measure of the acceleration effect.

As the gas absorption curves in Fig. 1 show, the gas absorption rate was highly promoted by the addition of a relatively small amount

of cupric and cuprous chloride; the gas absorption rate at the early stage of the reaction was about twenty times as large as that of Exp. 1, which was carried out without additives. The amount of cupric chloride necessary for this acceleration effect seemed to be about 0.05 mol. or less, since the gas absorption rates of Exps. 3—5 (0.1, 0.2 and 0.8 mol. of cupric chloride were added respectively) were comparable to that of Exp. 2. Cuprous chloride also had an effect similar to that of cupric chloride, as Exps. 6—9 and curve 6 show. In all of these reactions, an induction period of

TABLE I. THE REACTION OF PROPYLENE OXIDE WITH COBALT HYDROCARBONYL IN THE PRESENCE OF CUPRIC AND CUPROUS HALIDE AT 0°C

Exp. No.	Additives mol./mol. $\text{HCo}(\text{CO})_4$		Reaction* ¹ time, min.	CO absorbed		Product ester* ³ mol./mol.- $\text{HCo}(\text{CO})_4$
				mol./mol.- $\text{HCo}(\text{CO})_4$	Relative rate* ²	
1	None		180	0.10	1	0.1
2	CuCl_2	0.05	140	0.70	20	0.50
3	CuCl_2	0.10	110	0.70	20	0.50
4	CuCl_2	0.20	160	0.77	20	0.60
5	CuCl_2	0.80	180	0.70	20	0.4
6	CuCl	0.05	210	0.81	20	0.5
7	CuCl	0.20	180	0.86	20	0.5
8	CuCl	0.20	150	0.75	20	0.4
9	CuCl	0.40	180	0.89	20	0.5
10	CuI	0.20	170	0.75	20	0.4
11	CuCN	0.20	260	0.75	15	0.5
12	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	0.20	180	0.73	15	0.4
13* ⁴	CuCl	1.2	400	0.92	—	—

*¹ Other reaction conditions: 1.6 mol. of propylene oxide per mole of cobalt hydrocarbonyl used, under one atmosphere of carbon monoxide. The speed of stirring was 900 r. p. m.

*² The relative value of the gas absorption rate at the early stage of the reaction to the rate of Exp. 1.

*³ Ethyl β -hydroxy-*n*-butyrate.

*⁴ Without propylene oxide.

TABLE II. THE REACTION OF PROPYLENE OXIDE IN THE PRESENCE OF VARIOUS METAL COMPOUNDS

Exp. No.	Additives mol./mol.- $\text{HCo}(\text{CO})_4$		Reaction* ¹ time, min.	CO absorbed		Ester* ³ mol./mol.- $\text{HCo}(\text{CO})_4$
				mol./mol.- $\text{HCo}(\text{CO})_4$	Relative rate* ²	
14	AgCl	0.20	300	0.72	9	0.4
15	AlCl_3	0.2	80	0.60	30	0.3
16	SnCl_4	0.2	320	0.47	5	0.2
17	KCl	0.2	90	0.05	1	—
18	$\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$	0.1	60	0.03	1	—
19	ZnCl_2	0.2	240	0.1	1	—
20	FeCl_3	0.2	60	0.03	1	—
21	NiCl_2	0.2	60	0.04	1	—
22	PdCl_2	0.2	300	0	—	0.
23	TiCl_4	0.2	150	0	—	—

*¹ Other reaction conditions: 1.6 mol. of propylene oxide, under one atmosphere of carbon monoxide.

*² The relative value of the gas absorption rate to the rate of Exp. 1.

*³ β -Hydroxy-*n*-butyrate.

TABLE IIIa. THE REACTION OF PROPYLENE OXIDE IN THE PRESENCE OF CUPROUS AND CUPRIC OXIDE AT 0°C

Exp. No.	Additives mol./mol. $\text{HCo}(\text{CO})_4$		Reaction* time, min.	CO absorbed		Ester* mol./mol.- $\text{HCo}(\text{CO})_4$
				mol./mol.- $\text{HCo}(\text{CO})_4$	Relative rate* ²	
24	Cu_2O	0.001	120	0.73	40	0.4
25	Cu_2O	0.005	80	0.85	75	0.5
26	Cu_2O	0.05	60	0.70	72	0.5
27	Cu_2O	0.10	60	0.50	72	0.3
28	CuO	0.005	120	0.67	27	0.4
29	CuO	0.02	100	0.73	55	0.4
30	CuO	0.10	60	0.67	55	0.4
31	CuO	0.20	50	0.60	60	0.4
32	Cu powder	0.1	420	0.66	4	0.4
33	Ag_2O	0.10	130	0.53	27	0.3
34	Al_2O_3	0.10	120	0.07	1	—
35* ⁴	Cu_2O	0	420	0.50	3	0.3
36* ⁴	CuCl	0	300	0.35	2	—

TABLE IIIb. THE REACTION IN *n*-HEXANE

37	Cu_2O	0.05	150	0.45	14	0.3
38	CuCl	0.10	200	0.57	5	—
39* ⁵	None		250	0.78	—	0.6

*¹ Other condition: 1.6 mol. of propylene oxide and under one atmosphere of carbon monoxide.

*² The relative value of the gas absorption rate to Exp. 1.

*³ β -Hydroxy-*n*-butyrate.

*⁴ 25 ml. of toluene refluxed with cuprous oxide and chloride was added respectively.

*⁵ 6.2 mol. of propylene oxide. The rate of the gas absorption in *n*-hexane is about one-fourth that in toluene.¹⁾

about 5 min. was observed. As the main product in these reactions, ethyl β -hydroxy-*n*-butyrate* was obtained.

Accordingly, it may be concluded that the carbonylation of propylene oxide, i.e. the formation of β -hydroxy-*n*-butyrylcobalt carbonyl, is promoted by the addition of cupric or cuprous chloride.

Gas absorption was observed in the reaction system of cobalt hydrocarbonyl and cuprous chloride (Exp. 13). The gas chromatography, however, gave no indication of the presence of an organic product, and the amount of the gas evolved by treatment with iodine was comparable to the sum of the amount of the gas absorbed and that to be expected from the cobalt hydrocarbonyl used, indicating that the gas absorption is due to the formation of cuprous carbonyl chloride. This interpretation is supported by the facts that a 0.1 *N* hydrogen chloride-cuprous chloride aqueous solution readily absorbs carbon monoxide and that the gas absorbed was evolved by the treatment with iodine. However, the formation of cuprous carbonyl chloride seemed to be independent

of its acceleration effect, since no gas absorption was observed in the reaction system of cobalt hydrocarbonyl and cupric chloride.

Cuprous iodide and cyanide and cupric chloride dihydrate had an acceleration effect almost equal to that of cuprous and cupric chloride (Exps. 10–12).

Silver chloride also had an effect which was smaller than that of cuprous chloride, and it had a longer induction period (about 15 min.) (Exp. 14 and curve 14). Aluminum trichloride had a larger acceleration effect than cuprous chloride and had no induction period (Exp. 15 and curve 15).

The reaction system of cobalt hydrocarbonyl and aluminum trichloride gradually caused gas to evolve, with a color change from yellow to pale green, suggesting that the aluminum chloride decomposed the cobalt hydrocarbonyl.

Tin tetrachloride seemed to have a relatively small acceleration effect (Exp. 16). However, zinc chloride, nickel chloride, ferric chloride, potassium chloride and magnesium chloride-dihydrate had no effect at all on this reaction (Exps. 17–21). The addition of palladium chloride and titanium chloride caused the color of the reaction system to change rapidly from yellow to brown black and green brown

* Obtained from the corresponding acylcobalt carbonyl by cleavage with iodine and ethyl alcohol.

respectively, without gas absorption or evolution, and it gave no ethyl β -hydroxy-*n*-butyrate as a product, suggesting that some reaction other than the carbonylation reaction of propylene oxide occurred (Exps. 22 and 23).

Cuprous and cupric oxide had an acceleration effect similar to that of their chlorides, but the effects of these oxides are several times larger than that of the chlorides (Table III). When more than 0.005 mol. of cuprous oxide or more than 0.02 mol. of cupric oxide was added, the rates of the gas absorption were, respectively, about seventy and sixty times as large as that of the standard run (curves 25 and 29 in Fig. 2). However, the acceleration effect decreased with the decrease in the amount of cuprous and cupric oxide, as Exps. 24 and 28 show. This indicates the following relation: 0.001 mol. < enough cuprous oxide for this reaction < 0.005 mol. and 0.005 mol. < enough cupric oxide < 0.02 mol.

Copper powder also had a promoting effect, one which seems to be about one-fifth that of cuprous chloride (Exp. 32 and curve 32). Silver oxide had a promoting effect about three times as large as that of silver chloride (Exp. 33). On the other hand, aluminum oxide had no effect on this reaction (Exp. 34).

These inorganic additives are insoluble in toluene. Even 0.005 mol. of cuprous oxide (3.5 mg. in 50 ml. of toluene) seemed not to dissolve in the reaction solution. From the standpoint of solubility, the inorganic additives differ from the organic additives, which are very soluble in toluene. It may reasonably be considered that the inorganic additives are effective for the reaction as the solid state. This consideration is supported by the following fact: when 25 ml. of toluene,* refluxed with cuprous oxide or chloride for one hour, was used in the reaction after the separation of the solid phase, only a relatively small acceleration effect was observed (Exps. 35 and 36).

As has been mentioned above, various compounds of copper and silver, but not aluminum chloride, significantly promote the carbonylation reaction of propylene oxide, suggesting that compounds of metals which belong to Periodic Group Ib have an acceleration effect on this type of reaction. This acceleration effect may be attributed to the formation of some active complex from propylene oxide and the inorganic additives. This theory is supported by the fact that the inorganic additives have no effect on the reaction of styrene or ethyl acrylate with cobalt hydrocarbonyl.

Cuprous oxide and chloride have also an effect in *n*-hexane (Exps. 37 and 38), but the effect in this solvent seems to be one-fourth that of the reaction in toluene (cf. Exps. 6 and 26). Without additives, however, the reaction in *n*-hexane seems to proceed about one-fourth as fast as in toluene (Exp. 39), suggesting that this reaction is highly influenced by the solvent. However, the additives seem to be effective in the reaction independently of the solvent.

The Reactions of Propylene Oxide and Epichlorohydrin in the Presence of Inorganic and Organic Additives.—As has previously been reported,¹⁾ the reaction of olefin oxide with cobalt hydrocarbonyl is remarkably promoted by the addition of various organic compounds, such as ethyl alcohol and tetrahydrofuran. The effect of the combination of the inorganic additives described above with organic additives has, therefore, been examined, the results are summarized in Tables IV and V and in Fig. 3.

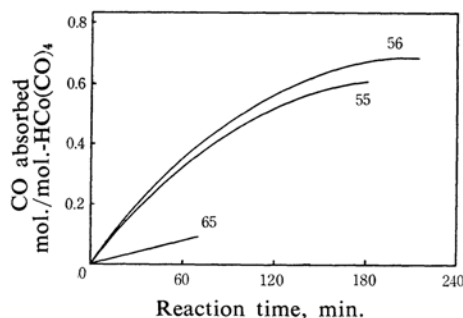


Fig. 3. CO absorption vs. time plots for the reaction of epichlorohydrin in the presence of cuprous oxide or ethyl alcohol. Number: Exp. No.

As Exps. 41 and 42 clearly show, the reaction of propylene oxide is further promoted by the combination of cuprous chloride with ethyl alcohol, suggesting that such a combination has a synergistic effect.

The combination of cuprous chloride with various organic additives, such as tetrahydrofuran (30*¹), acetone (25*¹), ethyl acetate (12*¹) and ethyl ether (6*¹), also has a synergistic effect (Exps. 45 and 48). Cupric chloride and cuprous oxide in combination with ethyl alcohol have also a synergistic effect (Exps. 50 and 52). However, the combination of cuprous chloride with cupric chloride has no synergistic effect (Exp. 51). Ethylene chlorohydrin (10) has no synergistic effect, even when combined with cuprous oxide (75) (Exp. 53).

The relative rates of the reactions with 2.0 mol. of ethyl alcohol (Exp. 44) and with 2.0

* 25 ml. of a 0.18 M cobalt hydrocarbonyl solution in toluene was diluted with 25 ml. of this refluxed toluene in the experiment.

*¹ The relative values of the gas absorption rate when only these compounds were added to the reaction system.

TABLE IV. THE REACTION OF PROPYLENE OXIDE IN THE PRESENCE OF INORGANIC AND ORGANIC ADDITIVES AT 0°C

Exp. No.	Additives mol./mol. $\text{HCo}(\text{CO})_4$				Reaction* ¹ time, min.	CO absorbed		Ester* ³ mol./mol.- $\text{HCo}(\text{CO})_4$
						mol./mol.- $\text{HCo}(\text{CO})_4$	Relative rate* ²	
40	CuCl	0.10,	EtOH	0.5	100	0.82	30	0.50
41	CuCl	0.10,	EtOH	1.0	50	0.85	80	0.5
42			EtOH	1.0	90	0.77	40	0.50
43	CuCl	0.10,	EtOH	2.0	50	0.83	120	0.5
44			EtOH	2.0	90	0.93	120	0.5
45	CuCl	0.10,	Tetrahydro- furan	3.0	50	0.70	60	—
46	CuCl	0.10,	Acetone	3.0	80	0.78	50	0.6
47	CuCl	0.10,	Ethyl acetate	3.0	70	0.78	38	0.5
48	CuCl	0.10,	Ether	2.0	70	0.70	30	0.4
49	CuCl	0.10,	Ethylene chlorohydrin	3.0	60	0.45	23	0.2
50	CuCl_2	0.1,	EtOH	1.0	80	0.89	55	0.7
51	CuCl	0.1,	CuCl_2	0.1	110	0.70	20	0.4
52	Cu_2O	0.01,	EtOH	1.0	60	0.80	90	0.6
53	Cu_2O	0.01,	Ethylene chlorohydrin	3.0	120	0.65	55	0.5

*¹ Other conditions: 1.6 mol. of propylene oxide and under one atmosphere of carbon monoxide.

*² The relative value of the gas absorption rate to Exp. 1.

*³ β -Hydroxy-*n*-butyrate.

TABLE V. THE REACTION OF EPICHLOROHYDRIN WITH COBALT HYDROCARBONYL IN THE PRESENCE OF CUPROUS OXIDE AND ETHYL ALCOHOL AT 0°C

Exp. No.	Additives mol./mol. $\text{HCo}(\text{CO})_4$				Epichloro- hydrin	Reaction* ¹ time, min.	CO absorbed		Ester* ³ mol./mol.- $\text{HCo}(\text{CO})_4$
							mol./mol.- $\text{HCo}(\text{CO})_4$	Relative rate* ²	
55			EtOH	1.0	14.5	180	0.61	1	0.4
56	Cu_2O	0.1			14.5	220	0.67	1	0.3
57	Cu_2O	0.2			14.5	200	0.70	1	0.3
58	Cu_2O	0.1,	EtOH	2.0	14.5	120	0.60	1.4 (2.0* ⁴)	0.2
59	Cu_2O	0.1,	EtOH	3.0	14.5	160	0.76	2.1 (3.0)	0.6
60	Cu_2O	0.1,	EtOH	4.0	14.5	140	0.66	2.9 (4.0)	0.3
61	Cu_2O	0.1,	EtOH	8.0	14.5	90	0.57	6.3 (10)	0.5
62	Cu_2O	0.1,	EtOH	8.0	5.8	120	0.54	2.6 (4.0)	—
63	Cu_2O	0.1,	EtOH	8.0	8.7	70	0.53	4.0 (6.0)	—
64	Cu_2O	0.1,	EtOH	8.0	11.6	60	0.55	5.1 (8.0)	0.3
65	None				14.5	70	0.1	—	—

*¹ Other condition: Under one atmosphere of carbon monoxide.

*² The value of the gas absorption rate relative to the rate of Exp. 55.

*³ γ -Chloro- β -hydroxy-*n*-butyrate.

*⁴ The relative values of the gas absorption rate when cuprous oxide is absent.

mol. of ethyl alcohol and 0.10 mol. of cuprous chloride (Exp. 43) are comparable. This may be interpreted as follows: under the reaction conditions (the apparatus, the speed of stirring, etc.) used, the maximum rate of gas absorption seems to be about 120 of the relative value.

The results with epichlorohydrin are summarized in Table V and Fig. 3, in which the values of the gas absorption rates relative to that of Exp. 55, carried out in the presence

of 1.0 mol. of ethyl alcohol at a 14.5 mol. ratio*² of epichlorohydrin, are shown as a measure of the acceleration effect.

As the results in Fig. 3 show, cuprous oxide also had an acceleration effect on this reaction (Exp. 56). The effect of cuprous oxide is almost comparable to that of 1.0 mol. of ethyl alcohol. The main product of these reactions

*² Mole of epichlorohydrin per mole of cobalt hydrocarbonyl used.

has been proved to be γ -chloro- β -hydroxy-*n*-butyrate.²⁾ Thus, the carbonylation reaction is similarly promoted by the addition of cuprous oxide as ethyl alcohol.

However, the combination of cuprous oxide with ethyl alcohol has a retardation effect on this reaction. As Exps. 58—64 show, the relative values of the gas absorption rate in the presence of both cuprous oxide and ethyl alcohol decreased to about two thirds of those in the presence of ethyl alcohol alone. Thus, the equation^{*3} of the gas absorption rate at the early stage of the reaction, obtained in the presence of ethyl alcohol alone, may be corrected by the combination of ethyl alcohol with cuprous oxide as follows:

$$\text{Rate} = 0.6 - 0.7 k \times$$

$$[\text{epichlorohydrin}] [\text{ethyl alcohol}]$$

In the light of the above equation, cuprous oxide seems to lose its own acceleration effect and to retard some of the active complex formation of ethyl alcohol with epichlorohydrin.

Summary

The reaction of olefin oxide with cobalt hydrocarbonyl in the presence of inorganic

(and organic) additives has been investigated.

1) The addition of relatively small amounts of various compounds of copper and silver promote the carbonylation of propylene oxide. The order of the promoting effect of these compounds is Cu_2O , $70 > \text{CuO}$, $60 > (\text{AlCl}_3, 30) > \text{Ag}_2\text{O}$, $27 > \text{CuCl}_2$, CuCl and CuI , $20 > \text{CuCN}$, $15 > \text{AgCl}$, $9 > \text{Cu}$ powder, $4 > \text{None}$, 1 (the numbers indicating the relative rates of the gas absorption at the early stage of the reaction). Among these, cuprous oxide has the largest effect. The amount of cuprous oxide necessary for this effect is only about 0.005 mol./mol. $\text{HCo}(\text{CO})_4$. β -Hydroxy-*n*-butyrate has been the main reaction product obtained. On the other hand, chlorides of zinc, nickel, ferric, potassium, magnesium, palladium and titanium have no promoting effect on the reaction.

2) The combination of cuprous halide (and oxide) with various organic additives, which also have a promoting effect,¹⁾ has a synergistic effect on the reaction of propylene oxide.

3) The reaction of epichlorohydrin is also promoted by the addition of cuprous oxide. However, in this case cuprous oxide combined with ethyl alcohol has a retardation effect.

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^{*3} When only ethyl alcohol is present, the gas absorption rate at the early stage of the reaction is represented as follows:¹⁾ $\text{Rate} = k[\text{epichlorohydrin}][\text{ethylalcohol}]$.