Effects of Organic Bases on the Rate of the Oxo Reaction of Methylacrylate[1]

By Ryoji IWANAGA

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When cobaltic oxide suspended in benzene is treated with synthesis gas under high pressure at about 100°C in the presence of a small amount of dicobalt octacarbonyl as an initiator, carbon monoxide and hydrogen are readily absorbed and cobalt carbonyl is formed. This reaction is considered to be catalyzed by cobalt hydrocarbonyl, which is produced from dicobalt octacarbonyl and which increases in amount as the reaction proceeds.

We have previously[2] found that the rate of this reaction is remarkably accelerated by the presence of a small amount of pyridine. Studying the mechanism of this reaction, it has occurred to the author that this effect of pyridine on the rate of the formation of cobalt carbonyl may be applied to the oxo reaction for the purpose of increasing the rate.

We have, therefore, examined the rate of the oxo reaction of methylacrylate in benzene in the presence of an amount of pyridine equimolar to cobalt of dicobalt octacarbonyl added as catalyst. It was consequently found that the rate of this oxo reaction is thereby about doubled.

To obtain information on the mechanism of this pyridine effect, we have studied the rate of the oxo reaction by adding various amounts of pyridine. In addition, the effects of various other aliphatic and aromatic amines on the rate were investigated.

Wender et al. previously[3] reported that the treatment of a solution of dicobalt octacarbonyl in pyridine with synthesis gas at 120°C and 230 atm. results in the conversion of all of the cobalt to the pyridinium salt of cobalt hydrocarbonyl, $[C_5H_5NH]^+ [Co(CO)_4]^-$, and that the oxo reaction of a mixture of 2, 3-dimethylbutene-1 and -2 at 135°C and 230 atm. of synthesis gas was completely inhibited in the presence of triethylamine. The author has also observed that the oxo reaction of methylacrylate is suppressed in the presence of a large amount of pyridine or other amines.

Thus, the effect of pyridine in increasing the rate of oxo reaction appears only in the presence of a small amount of pyridine. Therefore, in the case of the examination of the effects of other amines, an amount of them equi-molar to the cobalt of dicobalt octacarbonyl added as catalyst was used.

Furthermore, to elucidate the mechanisms of the effects of pyridine and other amines on the rate of oxo reaction, the initial rate of the formation of the cobalt carbonyl anion was measured in this paper.

Experimental

Rate of the Formation of Cobalt Carbonyl from Cobaltic Oxide.—Fine powders of 16.6 g. (100 mmol.) of cobaltic oxide and a 180 ml. benzene solution containing 0.47 g. (6 mmol.) or 0.16 g. (2 mmol.) of pyridine were put into a 600 ml. stainless steel rocking autoclave, and then 20 ml. of a benzene solution containing 1.71 g. (5 mmol.) of dicobalt octacarbonyl were slowly pipetted into the solution. The autoclave was immediately sealed, placed in an electrically heated jacket, flushed and pressured with 1 : 1 synthesis gas to 200 kg./cm^2 at room temperature, and heated. After the temperature had risen to 110°C, the rocking was started, and the temperature was controlled at 110 ± 1°C. The

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[1] R. Iwanaga, T. Fujii and T. Yoshida, presented in part at the 9th Meeting of the Chemical Society of Japan, Kyoto, April, 1956.

[2] T. Yoshida, R. Iwanaga and H. Mori, U. S. Pat. 2848304 (1958).

[3] I. Wender, H. W. Sternberg and M. Orchin, *J. Am. Chem. Soc.*, 75, 3041 (1953).

rate of the reaction was estimated by the pressure decrease in the autoclave.

Rates of the Oxo Reaction of Methylacrylate in Benzene in the Presence of Pyridine or Other Amines.—Pyridine and other amines were obtained in the best commercial grades available. These were treated with anhydrous sodium sulfate for 24 hr. and then distilled. The middle fractions consistent with the boiling points described in the literature were then collected in dry flasks, protected from any atmospheric moisture, and were used immediately. Methylacrylate and benzene were treated in the same way.

A solution of 148 ml. benzene containing 30.0 g. (348 mmol.) of methylacrylate and 0.60 g. (1.74 mmol.) of dicobalt octacarbonyl was put into a 300 ml. stainless steel rocking autoclave, and 2 ml. of a benzene solution containing pyridine or other amines to be tested were pipetted slowly into the solution in the autoclave. The autoclave was immediately filled with 1 : 1 synthesis gas to 200kg./cm² and heated as described above. After the temperature of the solution had reached a temperature a little lower than the temperature to be tested, the rocking was started and the reaction temperature was controlled at 100 ± 1°C or 120 ± 1°C. The rocking was continued until the pressure decrease stopped.

Rates of the Formation of the Cobalt Carbonyl Anion from Dicobalt Octacarbonyl in the Presence of Amines in the Oxo Condition.—The methods described in the preceding paper[4] were in general followed, except that a crystal of dicobalt octacarbonyl was added to a toluene solution of pyridine or of triethylamine after the pressure and temperature had been raised to the reaction condition. Namely, 100 ml. of a toluene solution containing 198 mg. (2.5 mmol.) of pyridine or 254 mg. (2.5 mmol.) of triethylamine were put into a 300 ml. stainless steel rocking autoclave, and, on the other hand, 0.87 g. of dicobalt octacarbonyl crystal was put into a 10 ml. beaker, which was set rigidly with a stainless steel wire on the inside of the cover of the autoclave in order to keep dicobalt octacarbonyl separate from the pyridine or triethylamine until the pressure and temperature had been raised to the reaction condition. The autoclave was then sealed, flushed and pressured to about 70 kg./cm² with 1 : 1 synthesis gas. After the temperature of the system had been raised to 100°C and the pressure had been adjusted to 100 kg./cm², the autoclave was turned upside down and the rocking was started immediately so that the dicobalt octacarbonyl crystal could be dissolved into the solution. About 2 ml. aliquots of the reaction solution were withdrawn directly into a nitrogen atmosphere from the autoclave through a high pressure coil of tube in the course of the reaction, and the cobalt hydrocarbonyl in the aliquot was analyzed by the methylene blue method.

Results and Discussion

Figure 1, which illustrates the pressure decrease in the autoclave during the production

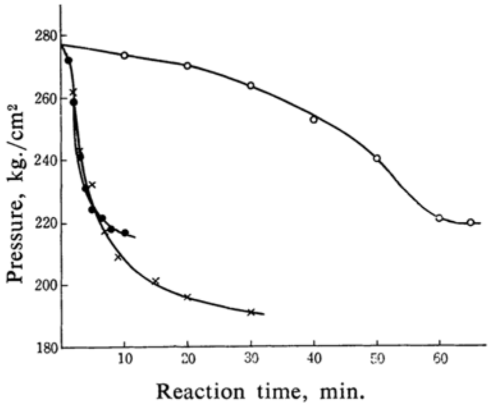

Fig. 1. Effect of pyridine on the rate of formation of cobalt carbonyl from cobaltic oxide.
—○— In absence of pyridine
—●— In presence of pyridine
—×— In presence of pyridine and kieselguhr

of cobalt carbonyl from cobaltic oxide in benzene, shows that the rate of gas absorption is much higher in the presence of pyridine than when pyridine is absent. After about 62% of the cobaltic oxide was digested, the gas absorption stopped. The stopping was due to the coagulation of powders of cobaltic oxide in the water which was produced during the reaction in a separated phase from the benzene solution. When about 5 g. of dry kieselguhr were added as a absorbent of the water, this reaction could proceed until the cobaltic oxide had been digested completely.

In view of the fact that the production of cobalt carbonyl from cobaltic oxide in the absence of cobalt carbonyl under high pressure synthesis gas did not take place until the temperature had been raised to 150°C, whereas in the presence of cobalt carbonyl it took place immediately even at temperatures below 100°C, and the fact the the rate of gas absorption increased with time, as is shown in Fig. 1, it is likely that cobalt carbonyl itself is the catalyst for the production of cobalt carbonyl. Therefore, the author visualizes the reaction as occurring in the following steps:

$$\begin{aligned}&Co_2O_3 + 6HCo(CO)_4\\&\quad \rightarrow 2Co + 3Co_2(CO)_8 + 3H_2O \qquad (1)\end{aligned}$$

$$2Co + 8CO \rightarrow Co_2(CO)_8 \qquad (2)$$

$$Co_2(CO)_8 + H_2 \rightarrow 2HCo(CO)_4 \qquad (3)$$

On the other hand, as illustrated in Table III, the initial rate of the formation of the cobalt carbonyl anion from dicobalt octacarbonyl under a high pressure synthesis gas and at an elevated temperature is greatly increased in the presence of pyridine or triethylamine.

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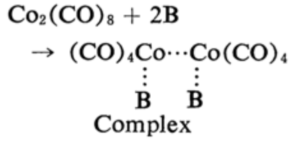
[4] R. Iwanaga, This Bulletin, 35, 778 (1962).

In a number of papers it has been shown that Lewis bases react with dicobalt octacarbonyl under mild conditions according to the equation,

$$2x\mathrm{B} + 3\mathrm{Co_2(CO)_8} \rightarrow 2[\mathrm{Co(B)}_x][\mathrm{Co(CO)_4}]_2 + 8\mathrm{CO} \quad (4)$$

When B is pyridine or triethylamine, this homomolecular disproportionation occurs similarly. However, under a high pressure of synthesis gas, no carbon monoxide is liberated and all the cobalt in the system is present in the forms of cobalt hydrocarbonyl, cobalt carbonyl anion and dicobalt octacarbonyl, even in the presence of amines. Therefore, it is considered that the effect of pyridine on increasing the rate of the production of cobalt carbonyl may be due to an acceleration of the rate of the reaction (Eq. 3) by a formation of an intermediate complex and a subsequent rapid formation of cobalt hydrocarbonyl from the complex and hydrogen as follows:



$$\mathrm{Co_2(CO)_8} + 2\mathrm{B} \rightarrow \underset{\text{Complex}}{\mathrm{(CO)_4}\underset{\vdots \atop \mathrm{B}}{\mathrm{Co}}\cdots\underset{\vdots \atop \mathrm{B}}{\mathrm{Co}}\mathrm{(CO)_4}} \quad (5)$$

$$\text{Complex} + \mathrm{H_2} \rightarrow 2\mathrm{HCo(CO)_4} + 2\mathrm{B} \quad (6)$$

$$\mathrm{HCo(CO)_4} + \mathrm{B} \rightleftarrows [\mathrm{BH}]^+[\mathrm{Co(CO)_4}]^- \quad (7)$$

However, the amount of free cobalt hydrocarbonyl decreases while the hydrocarbonyl combined with amine, as shown in Eq. 7, increases in amount as the basicity of amine becomes stronger. Therefore, in the oxo reaction the effects of amines must appear in different manners from that in the formation of the anion as shown in Table III.

Plots of $\log\{(P_0-P_f)/(P_t-P_f)\}$ against time in the oxo reaction of methylacrylate in benzene under a 1:1 synthesis gas yielded approximate straight lines (P_0=initial pressure at reaction temperature, P_f=pressure at the end of reaction, P_t=pressure at time t), indicating that the rate of decrease of the pressure was linear with the total pressure drop. Several such plots are given in Fig. 2. The relative rate listed in Tables I and II gives the ratio between the slope of a straight line for the reaction with the amine and that for the reaction without the amine.

As illustrated in Table I, the rate of the oxo reaction of methylacrylate in benzene about doubles in the presence of an amount of pyridine equi-molar to the cobalt of the dicobalt octacarbonyl added as a catalyst, and the rate increases with the increasing amount of pyridine, although the effect becomes smaller, the larger the amount of pyridine is. Although the author did not measure such an amount of pyridine by which the maximum effect could be obtained, the oxo reaction may be rather suppressed or inhibited completely when a large amount of it is present.

The effects of other amines on the rate of the oxo reaction are listed in Table II. The amines listed in Table II are conveniently divided into three structural classifications for the purpose of comparison.

Aromatic Tertiary Amines.—This type of amine shows a completely positive effect on increasing the rate. Like pyridine, pyridine homologues, except 2,6-lutidine, show the effect to a remarkable extent, but there are small differences in effects. The effect decreases

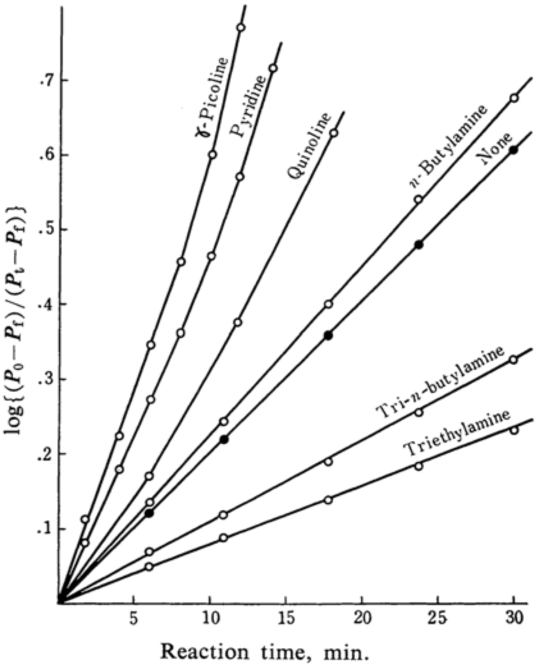


Fig. 2. Effects of amines on the rate of oxo reaction of methylacrylate in toluene at 120°C.

TABLE I. RATE OF OXO REACTION OF METHYLACRYLATE IN THE PRESENCE OF PYRIDINE

Methylacrylate: 232 mmol./dl.; $\mathrm{Co_2(CO)_8}$: 1.16 mmol./dl. as Co, in benzene.

Pyridine mmol./dl.	Reaction temp. °C	Reaction time min.	Relative rate
0	100	305	1.00
0.58	100	175	1.82
1.16	100	130	2.13
11.6	100	120	3.14
0	120	55	1.00
1.16	120	22	2.46
11.6	120	18	4.28

TABLE II. RATE OF OXO REACTION OF METHYLACRYLATE IN THE PRESENCE OF AMINES

Methylacrylate : 232 mmol./dl.; $Co_2(CO)_8$: 1.16 mmol./dl. as Co; Amine : 1.16 mmol./dl., at 120°C, in benzene.

Amine	Reaction time, min.	Relative Rate
None	55	1.00
Pyridine	18	2.46
α-Picoline	24	2.16
β-Picoline	22	2.84
γ-Picoline	20	3.52
2,4-Lutidine	24	2.68
2,6-Lutidine	45	1.11
Quinoline	35	1.58
N,N-Diethylaniline	40	1.37
Aniline	47	1.03
Cyclohexylamine	50	1.07
n-Butylamine	70	1.13
N-Methylaniline	57	1.10
N-Ethylaniline	57	1.20
Diethylamine	70	1.03
Di-*n*-butylamine	68	0.95
Triethylamine	>125	0.44
Tri-*n*-butylamine	>120	0.62

TABLE III. INITIAL RATE OF FORMATION OF $[Co(CO)_4]^-$ FROM $Co_2(CO)_8$ IN TOLUENE IN THE PRESENCE OF PYRIDINE OR TRIETHYLAMINE

$Co_2(CO)_8$: 0.87 g./dl.; Pyridine or Triethylamine : 2.5 mmol./dl. at 100°C and at 100 kg./cm^2 of synthesis gas.

Amine	Initial rate of formation of $[Co(CO)_4]^-$ mol. % as Co per min.
None	1.7
Pyridine	10.0
Triethylamine	21.2

in the order of the decreasing strength of base, as γ-picoline> β-picoline> pyidine. 2,4-Lutidine and α-picoline are stronger than γ- and β-picoline in basicity, but show smaller effects. This may be due to weak steric factors. The far smaller effect of 2,6-lutidine and *N,N*-diethylaniline may be explainable in terms of great steric hindrance, probably in complex formation. Quinoline shows a small effect, and this may be due to its weak basicity.

Primary and Secondary Amines.—This type of amine shows little or no effect on increasing or decreasing the rate. The reason may be that these compounds with an NH-group are readily carbonylated with carbon monoxide to the corresponding formamide in the presence of dicobalt octacarbonyl[5], and consequently are weak in basicity.

Aliphatic Tertiary Amines.—Since all aliphatic tertiary amines have a very strong base and can not be carbonylated, they may form stable salts with cobalt hydrocarbonyl. Therefore, the major part of the cobalt added into the system converts to unreactive cobalt carbonyl anions, and the rate of the oxo reaction may be rather decreased as compared with the rate in their absence. The results obtained for them indeed show great negative effects.

Finally, the effect of pyridine and its homologues on increasing the rate of the oxo reaction may be accounted for by comparing the above results for the three types of amines. Namely, pyridine and its homologues have no NH-group to be carbonylated with carbon monoxide and consequently can be kept active for the formation of an intermediate complex with a cobalt carbonyl formed in the course of the oxo reaction and the rapid formation of that cobalt hydrocarbonyl presumed to be the catalyst of the oxo reaction from the complex. This concept may be supported by the small effect of 2,6-lutidine, which is likely hindered from forming the complex by a steric factor. On the other hand, pyridine and its homologues are far weaker in basicity than aliphatic tertiary amines such as triethylamine, and it may be considered that when the amount of pyridine is small in the solution, the free hydrocarbonyl formed reacts as the catalyst of the oxo reaction without forming a salt with pyridine.

Summary

It has been found that the rate of the formation of cobalt carbonyl from cobaltic oxide in benzene with the high pressure of 1 : 1 synthesis gas at 110°C is remarkably accelerated by the presence of a small amount of pyridine.

When the oxo reaction of methylacrylate in benzene is carried out in the presence of an amount of pyridine equi-molar to the cobalt of dicobalt octacarbonyl added as a catalyst, the rate is about doubled. By examining the oxo reaction in the presence of other organic bases, the following results were obtained : the rates are decreased by aliphatic tertiarx amines such as triethylamine and tributylamine, and are scarcely affected by primary and secondary amines such as aniline and dibutylamine. Pyridine homologues except 2,6-lutidine, are as

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5) It was reported by Sternberg et al.[6] that dimethylformamide is produced from dimethylamine and dicobalt octacarbonyl at 0°C and atmospheric pressure, and that at 220°C and at carbon monoxide pressure of 200 atm. dimethylamine and piperidine are readily carbonylated to the corresponding formamide in the presence of catalytic amounts of dicobalt octacarbonyl.

6) H. W. Sternberg, I. Wender, R. A. Friedel and M. Orchin, *J. Am. Chem. Soc.*, **75**, 3148 (1953).

effective as pyridine. On the basis of these results, the mechanism of the effects of organic bases on the rate of oxo reaction has been discussed.

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Central Research Laboratory
Ajinomoto Co., Inc.
Suzuki-cho, Kawasaki