The Effect of Thiols on the Oxo Reaction

By Masanobu MORIKAWA

(Received October 15, 1963)

The reaction of olefins with carbon monoxide and hydrogen to form saturated aldehydes is well known as the oxo reaction or hydroformylation.[1] In general, this reaction is carried out at an elevated temperature and under a high pressure in the presence of the salts or oxides of cobalt. In this case the reaction products are composed of a mixture of isomeric aldehydes, accompanied by other by-products formed by the secondary reaction of the aldehydes.

In this sense, a high selectivity of the reaction is very desirable. For this purpose, the reaction is carried out at a relatively low temperature. In addition, aliphatic acids,[2] organic bases[3] or noble metals[4] have been proposed as promoters of the lower temperature reaction.

In the course of our studies of the effect of organic ligands co-ordinating with cobalt on the oxo reaction products and conditions, we have found that the reaction is most accelerated by the addition of a small amount of an organic sulfur-compound such as thiol, because of the weak ability of such compounds to co-ordinate.

This accelerating effect of thiols has been investigated; the results of the experiments with cyclohexene are shown in Table I. The results clearly indicate that the reaction can proceed at a lower temperature with a short induction period and with a rapid reaction rate in the presence of a limited amount of thiol. The activation energy of the reaction of cyclohexene was found to be reduced, by the addition of thiophenol, to 13 kcal./mol. from the about 30 kcal./mol. reported without the addition.[5]

The lower temperature-reaction of propylene upon the addition of thiophenol resulted in the selective formation of a straight chain aldehyde. Thus, *n*-butyraldehyde was obtained in a 83% yield at 120°C, as compared to 57% at 160°C without the addition.

It seems likely that thiol has an accelerating effect not only on the reaction catalyzed by the salts or oxides of cobalt, but also on the reaction catalyzed by cobalt calbonyl. Although the raction usually takes place at a lower temperature in the presence of cobalt carbonyl, it has a lengthy induction period under a pressure lower than 110 kg./cm². Upon the additon of thiol, the reaction proceeds with a short induction period, as is shown in Table II.

Experimental[6]

The experimental results listed in the tables were obtained in the following way.

In a 100 ml. stainless steel perssure reactor, 0.05 mol. of olefin and 20 ml. of toluene were charged with a cobalt catalyst and additives in the amounts specified in the tables. The air was purged, and a carbon monoxide-hydrogen mixture (1:1) was

TABLE I. EFFCT OF THIOLS ON OXO REACTION WITH CYCLOHEXENE*

Additive	10^3 mol.	Temp. °C	Ind. period min.	Sp. rate 10^2k, min^{-1}	Yield %
None	0	120	85	0.9	80
EtSH	3	120	22	1.9	81
EtSH	2	100	100	0.3	72
EtSH	2	160	0	7.3	87
PhSH	3	80	17	3.3	70
PhSH	2	150	0	4.5	81
EtSH	20	120	3	2.2	74

* Cyclohexene = 0.05 mol., toluene = 20 ml., cobalt oxide = 0.02 mol., initial pressure of 200 kg./cm² of hydrogen and carbon monoxide mixture (1:1).

---

[1] I. Wender and H. W. Sternberg, "Catalysis," Vol. V, Ed. by P. H. Emmett, Reinhold, New York (1957), p. 73.

[2] Japanese Pat. 6319 (1958).

[3] R. Iwanaga, This Bulletin, 35, 865 (1962).

[4] Japanese Pat. 14608 (1961).

[5] G. Natta and R. Ercoli, *Chim., ind.* (*Milano*), **34**, 503 (1952).

[6] Materials were obtained from commercial sources.

TABLE II. EFFECT OF THIOPHENOL ON OXO REACTION WITH PROPYLENE CATALYZED BY COBALT CARBONYL*

10^3 mol. of thiophenol	Max. press. kg./cm^2	Ind. period min.	Sp. rate $10^2 k$, min^{-1}	Yield** %	Selec.*** %
0	185	3	3	81	78
1	195	0	6	70	79
0	104	160	0.5	85	68
1	103	5	1.3	81	72
10	108	3	1.0	66	65
0	70	⩾7400	—	—	—
2	75	35	0.4	66	55

* Propylene=0.05 mol., toluene containing cobalt carbonyl (10 g./l.)=20 ml., at 120°C.

** Total yield of aldehyde.

*** % of selective formation of *n*-butyraldehyde.

introduced up to the pressure of 200 kg./cm^2. As soon as the reactor was heated to a specified reaction temperature, agitation was started.

The induction period of the reaction was defined as the time taken for the reaction to start after the beginning of agitation.

The reaction rate deteremined by the rate of gas absorption, while the rate constant was calculated on the basis of the linear relationship between the rate and the olefin concentration.[5)]

The reaction was continued until no further pressure drop was observed. The yield of aldehydes and the ratio of the straight chain aldehyde to the branched aldehyde were determined by gas chromatography using an internal standard carried out with a 2 m. "Silicone DC-550" column operated at 120°C or 180°C and with the flow rate of 50 ml./min. of helium gas.

The products was identified by comparing the retention time of the gas chromatograph, the infrared spectra and the melting points of the 2, 4-dinitrophenylhydrazones of the aldehydes with those of authentic samples.

The author would like to thank Dr. Toshio Hoshino, the director of the Laboratories, for his guidance throughout this work.

Basic Research Laboratories
Toyo Rayon Co., Ltd.
Kamakura, Kanagawa