

# Effect of Water on the Oxo Synthesis

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Hydroformylation of unsaturated esters or olefins in the presence of esters is retarded or may even be untimely discontinued in the presence of water. Esters are hydrolyzed and the acid, thus liberated, decomposes the catalyst. On the other hand, hydroformylation of olefins is not affected. A small decrease in reaction rate in the case of higher concentration of water, is a result of extraction of cobalt tetracarbonyl hydride from the organic phase in which, essentially, the oxo synthesis takes place.

Water has been used as a solvent in the case of hydroformylation of lower olefins [1–8]. We found previously [9] that controlled addition of water into reaction medium had practically no effect on the rate of oxo synthesis in the case of hydroformylation of propylene. Iwanaga [10, 11] investigated the effect of water on the reaction rate of hydroformylation of methyl acrylate and learnt, that when more than 15% of water was present in the methanol, used as a solvent, the reaction was untimely discontinued. He accounted this phenomenon for dissociation of cobalt tetracarbonyl hydride with water [10]. Although we trust Iwanaga's carefulness with which he obtained his results we consider his explanations not quite correct or at least not adequate.

## Experimental

### *Substances*

A mixture of higher olefins in petroleum was obtained by thermal cracking of *n*-alkanes. The fraction having b.p. 70–150°C/752 Torr,  $d_4^{20}$  0.7448 g cm<sup>-3</sup>, bromine number 157.7 g Br<sub>2</sub>/100 g, maleic anhydride number 0.3, was used.

Allyl acetate — b.p. 102–103°C/754 Torr,  $n_D^{20}$  1.4059, bromine number 186.8 g Br<sub>2</sub>/100 g, acidity number 0.8 mg KOH/g, 0.09 weight % of water.

Vinyl acetate — b.p. 71.8–72°C/754 Torr,  $n_D^{20}$  1.3951, bromine number 186.1 g Br<sub>2</sub>/100 g, acidity number 0.0 mg KOH/g, 0.09 weight % of water.

Methyl acrylate — b.p. 79–81°C/754 Torr,  $n_D^{20}$  1.403, bromine number 180 g Br<sub>2</sub>/100 g, saponification number 638 mg KOH/g, acidity number 0.0 mg KOH/g, 0.08 weight % of water.

Anal. grade methanol and toluene having water content 0.24 and 0.038%, respectively, were used.

Specifications of octacarbonyldicobalt and those of the equimolar mixture of carbon monoxide–hydrogen (synthesis gas) were published previously [9, 12].

### Procedure

Procedure similar to the one applied when investigating the effect of acids on the oxo synthesis [12] was used. Hydroformylation of unsaturated esters and higher olefins as well as the investigation of the effect of water on the oxo synthesis was carried out at  $140 \pm 2^\circ\text{C}$  at the pressure ( $\text{CO} : \text{H}_2 = 1 : 1$ )  $240\text{--}250 \text{ kp cm}^{-2}$ . The rate constants  $k$  were calculated from the decrease of pressure using the known kinetic equation [13] for the first order

$$k = \frac{2.303}{t} \log \frac{p_0 - p_k}{p_t - p_k}$$

where  $t$  is time in minutes,

$p_0$  is the initial pressure [ $\text{kp cm}^{-2}$ ],

$p_k$  is the terminal pressure,

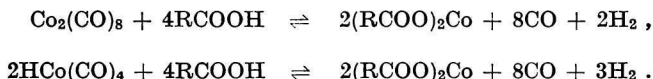
$p_t$  is the pressure at time  $t$ .

The degree of conversion at the end of experiment was tested by determination of the unconverted olefinic compounds and by weighing the reaction products. The content of aldehydes in the products was determined by oximation method.

### Results and Discussion

Despite a considerable amount of information collected in previous works concerned with hydroformylation olefinically unsaturated esters, mainly esters of  $\alpha, \beta$ -unsaturated acids [11, 14–20], we were surprised to learn that at lower concentration of octacarbonyldicobalt (about 0.2 weight % of Co/unsaturated ester) and at discontinuous experiments the hydroformylation ceased to proceed before the conversion has been complete (Table 1). In the previous paper [21] we described preparation of  $\gamma$ -butyrolactone from allyl acetate by oxo synthesis and subsequent oxidation and hydrolysis of the product. This work [21] as well as the results of hydroformylation of vinyl acetate and methyl acrylate (Table 1) are good examples of the fact that in order to achieve complete conversion at least 0.4 weight % of cobalt (based on the amount of unsaturated ester) in the form of octacarbonyldicobalt has to be used. Alternatively, a solvent *e.g.* methanol which, under the conditions of oxo synthesis diminishes the rate of hydrolysis of the ester, can be used. The ester is hydrolyzed, as it was mentioned above, by the presence of water which may be present in the reaction medium either as an admixture in the raw material or as a product of side reactions.

The wanted reaction is, before the complete conversion is reached, discontinued as a result of decomposition of the catalyst with the liberated carboxylic acid



These facts were proved previously [12] when the effect of acids on the hydroformylation of olefins was investigated. The results showed that the effect of acid depends both upon its strength and concentration in the reaction medium.

Table 1

## Hydroformylation of some unsaturated esters

Unsaturated ester		Solvent		Cobalt content (%/ester) [w/w]	Initial water content (%/ester) [w/w] in reaction medium	Duration [min]		Conversion of the unsaturated ester [%]
Kind	Amount [g]	Kind	Amount (%/ester) [w/w]			of hydroformylation	of the whole experiment	
allyl acetate	50	toluene	20	0.31	0.1	80	300	77
allyl acetate	50	toluene	20	0.62	0.1	40	180	99
vinyl acetate	86	toluene	16	0.19	0.1	40	240	45
vinyl acetate	86	methanol	46	0.19	0.3	50	180	84
vinyl acetate	86	toluene	16	0.38	0.1	50	210	88
methyl acrylate	86	toluene	46	0.19	0.1	90	180	74
methyl acrylate	86	methanol	46	0.19	0.2	30	70	99
methyl acrylate	86	methanol	41	0.19	5.2	35	150	83
methyl acrylate	86	methanol	35	0.19	11.8	35	180	62
methyl acrylate	86	methanol	28	0.19	18.1	45	180	36
methyl acrylate	86	methanol	23	0.19	23.3	60	180	18
methyl acrylate	86	methanol	22	0.19	24.1	60	180	16

The course of the hydroformylation complied with first-order kinetics and the rate constant  $k = 0.145 \text{ min}^{-1}$ ; the products contained 75-95% of corresponding aldehydes.

The unwanted effects of acids are clear also from the results of effects of water on the hydroformylation of methyl acrylate (Table 1). The decrease of conversion of methyl acrylate, even in case the methanol was used as a solvent, was quite pronounced when larger amount of water was added. The addition of 24.1 weight % of water (based on methyl acrylate) stopped the hydroformylation spontaneously after 60 minutes, the conversion being 16% only. For the conversion  $P$  (in per cent) of methyl acrylate as a function of concentration of water  $c$  (in weight % based on methyl acrylate) an equation was found

$$P = 99 - (3.3 \pm 0.2) c.$$

In the case of hydroformylation of mixture of higher olefins in petroleum (Table 2) even additions of as much as 50 weight % of water did not stop the process of oxo

Table 2

Effect of water on the hydroformylation of higher olefins in petroleum (cobalt content 0.2%/petroleum (w/w); duration max. 200 minutes)

Water added (%/petroleum) [w/w]	Conversion of olefins [%]	Rate constant $k \times 10^2$ [min <sup>-1</sup> ]
0.0	99	5.6 ± 0.5
0.0	99.5	5.3 ± 0.5
2.0	99	5.2 ± 0.5
3.0	99	5.3 ± 0.5
5.0	98.5	5.4 ± 0.5
7.0	99	5.1 ± 0.5
10.0	99	4.4 ± 0.5
20.0	99	3.8 ± 0.5
50.0	99	3.5 ± 0.5

synthesis; the conversion was complete and the reactions in individual experiments followed the first-order kinetics. With the additions of water, however, the rate constant  $k$  only a little decreases. This is obviously connected with the decrease of concentration of cobalt tetracarbonyl hydride in the organic phase in which, essentially, the oxo synthesis takes place. As higher olefins are practically water insoluble the fraction of cobalt tetracarbonyl hydride dissolved and dissociated in water remains unutilized. The interface is probably the site of the catalyst's greatest effectiveness.

The obtained results explain also why a satisfactory hydroformylation of unsaturated esters cannot be accomplished with the amounts of catalyst (0.2% of Co based on unsaturated compound) usual for hydroformylation of olefins.

It follows from the foregoing that, under usual conditions, the water alone does not poison the hydroformylation catalyst. On the other hand, when esters are hydroformylated or when these are used as solvents for hydroformylation of olefins, water is an unwanted component in the reaction medium because it hydrolyzes the esters, and the acid, thus liberated, decomposes the catalyst. In order to suppress the hydrolysis, which saves the hydroformylation catalyst, the use of alcohols as solvents is recommended.

## References

1. Wennerber A. N., Alm R. M., Peter H. H., *U.S. Patent 2 894 990* (1959).
2. Ruhrchemie A. G., *Austral. Patent 158 973* (1954).
3. Standard Oil Development, *Brit. Patent 703 491* (1954).
4. Nienburg H., *Ger. Fed. Rep. Patent 948 150* (1956).
5. Smith W. M., *U.S. Patent 2 754 331* (1956).
6. Fritzsche H., *Ger. Fed. Rep. Patent 888 097* (1953).
7. Owen J. J., Buchmann F. J., *U.S. Patent 2 706 206* (1955).
8. Nieder H. J., Kölsch W., Eckert E., *Ger. Fed. Rep. Patent 946 621* (1956).
9. Macho V., Mistrík E. J., Střešinka J., *Chem. Prům. 13, 343* (1963).
10. Iwanaga R., *Bull. Chem. Soc. Jap. 35, 869* (1962).
11. Iwanaga R., *Bull. Chem. Soc. Jap. 35, 778, 865* (1962).
12. Macho V., Komora L., *Chem. Zvesti 21, 164* (1967).
13. Natta G., Ercoli R., *Chim. Ind. (Milan) 34, 503* (1952).
14. Wender I., Sternberg H. W., Orchin M., *Catalysis V*, p. 86. Reinhold, New York, 1957.
15. Adkins H., Krsek G., *J. Amer. Chem. Soc. 71, 3051* (1949).
16. Hagemayer H. J., Hull D. C., *U.S. Patent 2 610 203* (1952).
17. Ohasi K., Suzuki S., *J. Chem. Soc. Jap. 56, 792* (1953).
18. Uchida H., Bando K., *Bull. Chem. Soc. Jap. 29, 953* (1956).
19. Takegami Y., Yokokawa Ch., Watanabe Y., Masada H., Okuda Y., *Bull. Chem. Soc. Jap. 37, 1190* (1964).
20. Falbe J., Huppel N., Korte F., *Chem. Ber. 97, 863* (1964).
21. Marko M., Macho V., unpublished results.

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