BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 571—572 (1969)

The Cobalt Carbonyl-catalyzed Hydroesterification of Methyl Acrylate with Carbon Monoxide and Methanol

Akio MATSUDA

Government Chemical Industrial Research Institute, Tokyo, Mita, Meguro-ku, Tokyo

(Received July 2, 1968)

In a previous paper it was reported that the cobalt carbonyl-catalyzed hydroesterification of acrylonitrile with carbon monoxide and methanol occurred in the presence of a small amount of hydrogen and a limited amount of pyridine, and that the amount of methyl α-cyanopropionate produced was larger than that of methyl β-cyanopropionate.[1] The present report is concerned with the results obtained when methyl acrylate was used in this reaction instead of acrylonitrile. The reaction procedure and the method of analyses were essentially the same as have been described in the previous report.[1]

Standard samples for the gas chromatographic analyses were obtained as follows. Dimethyl succinate was obtained commercially. Dimethyl methylmalonate was synthesized by the action of methanol and 86% sulfuric acid on methyl α-cyanopropionate, which was the main product of the hydroesterification of acrylonitrile and which had already been identified.[1] Dimethyl γ-ketopimelate was separated by distillation from the reaction product and was purified by recrystallization from cyclohexane.

Identification of Dimethyl γ-Ketopimelate. Mp 53°C. IR spectrum: C=O (ester) 1748 cm^{-1}, C=O (ketone) 1725 cm^{-1}. NMR spectrum at 60 Mc (in carbon tetrachloride, with tetramethyl-

---

[1] A. Matsuda, This Bulletin, **40**, 135 (1967).

silane as the internal standard): α-CH_2 τ 7.42 (triplet), β-CH_2 τ 7.35 (triplet), OCH_3 τ 6.39 (singlet).

Found: C, 53.50; H, 6.96%. Calcd for $C_9H_{14}O_5$: C, 53.46; H, 6.98%.

Results

The hydroesterification of methyl acrylate occurred in the presence of a small amount of hydrogen and pyridine, resulting in a high yield of dimethyl succinate and a very small yield of dimethyl methylmalonate. This exclusive formation of β-methoxycarbonylated product is in contrast to the case of the hydroesterification of acrylonitrile, where α-methoxycarbonylation predominates.[1] Dimethyl γ-ketopimelate was found as a by-product.

The effect of the reaction temperature is shown in Table 1.[2] The reaction rate is almost independent of the temperature in the 120—160°C range. The yield of dimethyl succinate decreases as the temperature increases, whereas the yield of dimethyl γ-ketopimelate increases with the temperature. The α/β ratio, contrary to the case of acrylonitrile,[1] increases along with the temperature.

TABLE 1. THE EFFECT OF REACTION TEMPERATURE

1/2 mol methyl acrylate, 2 mol methanol, 4 mmol $Co_2(CO)_8$, 30 mmol pyridine; total pressure 200 kg/cm^2; reaction time 1 hr; hydrogen content of the gas used, 5%.

Reaction temp. °C	Rate const. k min^{-1}	Conversion mol %	Products yields (mol %) DM	DS	DK[a]	α/β[b]
120	10×10^{-2}	100	1.9	82	2.3	0.023
140	13×10^{-2}	100	2.0	78	5.5	0.026
160	12×10^{-2}	100	1.9	67	7.8	0.029

a) Abbreviations DM, DS, and DK stand for dimethyl esters of methylmalonic acid, succinic acid, and γ-ketopimelic acid.

b) α/β stands for the mole ratio DM/DS.

The effect of the amount of pyridine is shown in Table 2; the rate constant and the selectivity toward each product are plotted against the amount of pyridine in Fig. 1.[3] The rate constant, k, increases almost in proportion to the amount of pyridine; this indicates that the reaction rate is first order with respect to the pyridine concentration. The selectivity toward dimethyl succinate increases with the amount of pyridine, whereas the selectivity toward dimethyl methylmalonate decreases slightly. The α/β ratio remarkably decreases as the amount of pyridine increases; this trend is again opposite to the case of acrylonitrile, where the methyl α-cyanopropionate/methyl β-cyanopropionate mole ratio increases along with the amount of pyridine.[1] The selectivity toward methyl γ-ketopimelate becomes larger as the amount of pyridine is reduced.

TABLE 2. THE EFFECT OF THE AMOUNT PYRIDINE

1/2 mol methyl acrylate, 1/2 mol methanol, 4 mmol $Co_2(CO)_8$; reaction temperature 110°C, total pressure 160 kg/cm^2; hydrogen content of the gas used, 7%.

Pyridine mmol	Rate const. k min^{-1}	Reaction time min	Conversion mol %	Products yields (mol %) DM	DS	DK	α/β
1	1.2×10^{-2}	120	60	2.6	29	15	0.090
3	2.3×10^{-2}	120	100	3.2	75	13	0.043
10	8.8×10^{-2}	25	90	2.0	73	7.0	0.027

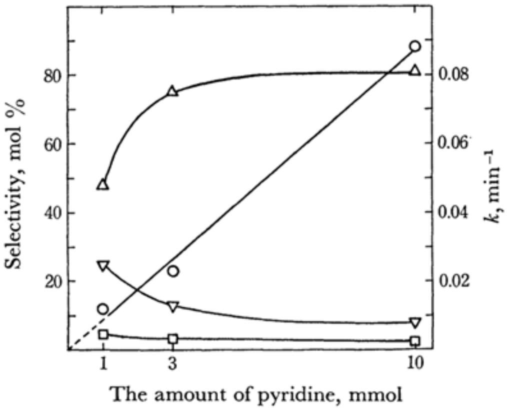

Fig. 1. The plot of k and the selectivity against the amount of pyridine.

-○- : k (min^{-1}).

-△- : Dimethyl succinate (mol %).

-▽- : Dimethyl γ-ketopimelate (mol %).

-□- : Dimethyl methylmalonate (mol %).

A more detailed study aimed at obtaining enough information to explain the above differences between the results of the hydroesterification of methyl acrylate and that of acrylonitrile will be reported in the future.

---

[2] The overall first-order rate constant, k, was roughly estimated from the amount of gas supplied during the early stages of the reaction. The conversion was also roughly estimated from the total amount of gas supplied during the reaction. Although the product contained small amounts of acetal and methyl propionate resulting from the hydroformylation and hydrogenation of methyl acrylate, their yields are not listed in the table because of the lack of data.

[3] The selectivity was calculated from Table 2 by dividing the yield by the conversion.