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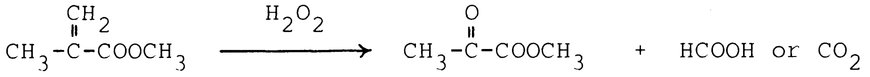
The Oxidation of Methacrylic Acid Esters with H_2O_2 in the Presence of Chromium Catalysts. A Novel Route to Pyruvic Acid Esters

Masami INOUE,* Toshitaka URAGAKI, Hiroshi KASHIWAGI, and Saburo ENOMOTO
Faculty of Pharmaceutical Sciences, Toyama Medical and
Pharmaceutical University, Sugitani, Toyama 930-01

The oxidation of methacrylic acid esters to pyruvic acid esters was carried out with aqueous H_2O_2 in CH_3CN in the presence of a catalytic amount of chromium compounds such as Cr(III)(acac)$_3$, chromium salts, and chromic acid. The oxidation of methyl methacrylate in the presence of chromic acid and triethylamine (1:1) gave an 82% conversion with a 72% selectivity to methyl pyruvate at 40 °C for 20 h.

Pyruvic acid, an important metabolite of lactic acid, is widely found in muscle. Synthetically ethyl pyruvate has been obtained by the oxidation of ethyl lactate with $KMnO_4$.[1)] Also, hydroxyacetone has been oxidized with molecular oxygen in the presence of Pt catalysts to give pyruvic acid.[2)] Although oxidation from methacrylic acid esters to pyruvic acid esters is an attractive pathway, such strong peracid as trifluoroperacetic acid has afforded epoxides exclusively.[3)] During the course of study on the oxidation of methyl methacrylate by using aqueous H_2O_2, authors found that the presence of a catalytic amount of chromium compounds gave methyl pyruvate as a major product accompanied with formic acid and carbon dioxide.



$$CH_3\text{-}\overset{\overset{CH_2}{\|}}{C}\text{-}COOCH_3 \xrightarrow{H_2O_2} CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}COOCH_3 + HCOOH \text{ or } CO_2$$

Results are shown in Table 1. The activity of various metal acetylacetonates were examined and among them Cr(III)(acac)$_3$ gave methyl pyruvate in a 70% yield at 50 °C for 8 h. Chromium salts also catalyzed the oxidation and the activity decreased in the order: $Cr(AcO)_3 > Cr(NO_3)_3 > CrPO_4 > CrCl_3 \sim Cr_2(SO_4)_3$. In the case of Cr(III)(acac)$_3$, $Cr(AcO)_3$, and CrO_3 catalysts, a long term of induction period(2 h) and elevation of temperature(5 - 10 °C) were observed. However, the copresence of triethylamine or pyridine accerelated the oxidation without an induction period under a slight elevation of temperature(2 °C). These amines seems to work for the stability of active species formed during the reaction. Unknown by-products (ca. 25%) obtained at the initial stage of the oxidation limited the selectivity to pyruvic acid esters at most 74%.

In a typical example (Entry 14), CrO_3(0.3 mmol), triethylamine(0.3 mmol), and 60% H_2O_2(0.4 mol), methyl methacrylate(10 g, 0.1 mol) were added in acetonitrile(150 ml), and heated at 40 °C. After one hour the reaction temperature reached 42 °C. The reaction was continued for 20 h. The products were analyzed by GLC using an OV-17(3 mm x 2 m) column under the programmed oven temperature from 50 to 150 °C(3 °C/min). The conversion of methyl methacrylate reached 82% with a 72% selectivity to methyl pyruvate. After unreacted H_2O_2 was decomposed with a VO^{3-}-anion-exchanged resin(Amberlite IRA-93, 1 g), the solution was dried over anhydrous $MgSO_4$. The fractional distillation gave 3.4 g (a 41% yield) of methyl pyruvate based on methyl methacrylate consumed. The ester isolated as colorless oil was stable at room temperature.

Table 1. Oxidation of methacrylic acid esters to pyruvic acid esters with aqueous H_2O_2 in the presence of chromium compounds

Entry	Catalyst	Substrate[a)]	Temp/°C	Time/h	Conv./%	Selectivity/%[b)]
1	none	MMA	50	8	0	0
2	Cr(III)(acac)$_3$	MMA	50	8	96	74
3	Cr(III)(acac)$_3$	EMA	50	8	79	64
4	$Cr(AcO)_3 \cdot H_2O$	MMA	50	8	96	74
5	$Cr(NO_3)_3 \cdot 9H_2O$	MMA	50	8	73	70
6	$CrCl_3 \cdot 6H_2O$	MMA	50	8	23	0
7	$CrPO_4$	MMA	50	24	42	39
8	$Cr_2(SO_4)_3 \cdot 5H_2O$	MMA	50	20	23	0
9	CrO_3	MMA	40	9	53	30
10	CrO_3 + Et_3N (1:1)	MMA	30	8	71	58
11	CrO_3 + Pyridine (1:1)	MMA	30	8	57	37
12	CrO_3 + Et_3N (1:1)	EMA	40	20	77	64
13	CrO_3 + Et_3N (1:1)	PMA	40	20	98	64
14	CrO_3 + Et_3N (1:1)	MMA	40	20	82	72

a) MMA ; methyl methacrylate, EMA ; ethyl methacrylate, PMA ; isopropyl methacrylate. Pyruvic acid esters were identified by comparison with authentic materials (IR and ^1H-NMR spectra, and GLC). b) Selectivity to pyruvic acid esters. Entries 1-8; Methacrylic acid esters (5 mmol), 60% H_2O_2 (Tokai Electro-Chemical Co.) (15 mmol), catalyst (3.0×10^{-2} mmol) and CH_3CN (10 ml) were used. Entries 9-11; Methacrylic acid esters (15 mmol), 60% H_2O_2 (60 mmol), CrO_3 (0.1 mmol) and CH_3CN (30 ml) were used. Entries 12 and 13; EMA or PMA (0.1 mol), 60% H_2O_2 (0.4 mol), CrO_3 (0.3 mmol), triethylamine (0.3 mmol) and CH_3CN (150 ml) were used.

References

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