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[Letter]

Formation Pathway of By-products in Methacrolein Oxidation over $H_3PMo_{12}O_{40}$ Investigated by Using ^{13}C-Labeled Methacrolein

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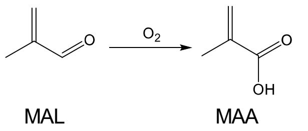
Understanding the mechanism for the formations of by-products as well as a main product can give us useful information for improvement in the catalytic performances. In the present study, formation pathway of by-products in oxidation of methacrolein (MAL) was investigated by using MAL with ^{13}C-labeled methyl group as a reactant. The reaction pathway for the formation of the by-products was proposed based on GC-MS analysis as follows: The first step is oxidative cleavage of C=C double bond in MAL, giving pyruvaldehyde, and pyruvaldehyde is subsequently hydrolyzed to acetic acid.

Keywords: Methacrolein oxidation, Heteropoly acid, Isotopic labeling method, Reaction mechanism, Acetic acid

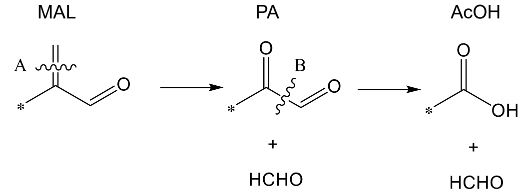
Methacrylic acid (MAA) is an important basic chemical to produce methyl methacrylate (MMA) polymers. C_4 direct oxidation process, which is one of the MMA production processes, has been commercialized by Mitsubishi Rayon Co., Ltd. and Nihon Methacryl Monomer Co., Ltd.1), 2). The process consists of sequential two-stage oxidation of isobutylene or *t*-butyl alcohol to MAA via methacrolein (MAL) followed by esterification of MAA to MMA. MAL is an intermediate in the two-stage oxidation and is selectively oxidized to MAA over P-Mo based-heteropoly acid catalyst in gas-phase shown in Eq. (1).



(1)

A problem on MAL oxidation is formation of by-products including acetic acid (AcOH) and CO_x, leading to unsatisfactory productivity of MAA in a commercial process. Elucidation of the reaction mechanism can give us knowledge useful for improvement of the catalytic performance for MAL oxidation. While several reports on the reaction mechanism of MAL oxidation have been published, those focus on the formation of MAA3)～7). To the best of our knowledge, there are only a few reports focusing on the side reactions3) and the detailed formation mechanism of by-products in MAL oxidation has not been clarified. Thus, we investigated the formation mechanism of by-products in MAL oxidation in the present study.

Because AcOH has a methyl group, a plausible pathway for the formation of AcOH from MAL is a successive reaction that is oxidative cleavage of C=C bond of MAL followed by hydrolysis of the formed pyruvaldehyde (PA) as shown in **Scheme 1**.



Scheme 1 Plausible Formation Pathway of AcOH from MAL

According to this pathway, $^{13}CH_3$-MAL, in which the carbon of methyl group is labeled with ^{13}C, yields AcOH with labeled methyl group as a by-product (**Scheme 1**). Formaldehyde (HCHO) formed along with AcOH is highly reactive and would be immediately oxidized to CO_x. In this study, $^{13}CH_3$-MAL was utilized as reaction substrate for MAL oxidation in the presence of a typical P-Mo based-heteropoly acid, $H_3PMo_{12}O_{40}$, which is a basic component of industrial catalysts1). The fractional abundance of labeled products (MAA and AcOH) and the labeled position in AcOH were investigated in detail and a mechanism for the formation of by-products, especially AcOH, was proposed.

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”^{13}C 標識メタクロレインを用いた $H_3PMo_{12}O_{40}$ 上でのメタクロレイン酸化反応における副反応経路の解析” 菅野 充†1)*, 平田 純†1), 梅澤 大樹†2), 二宮 航†1), 神谷 裕一†2), †1)三菱ケミカル（株）広島研究所，739-0693 広島県大竹市御幸町 20-1, †2) 北海道大学大学院地球環境科学研究院，060-0810 札幌市北区北 10 条西 5 丁目

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$^{13}CH_3$-MAL was synthesized from 2-chloroacetyl chloride, ^{13}C-labeled iodomethane and formaldehyde in 5 steps with about 11 % yield (see Supporting information). Because only a small amount of $^{13}CH_3$-MAL was synthesized, the synthesized $^{13}CH_3$-MAL was mixed with a commercial non-labeled MAL ($^{12}CH_3$-MAL). The formulated mixture is named **Mixed-MAL**. ^{13}C purity of **Mixed-MAL** was determined as follows.

Molecular weights of MAL without any ^{13}C and that containing one ^{13}C are 70 and 71, respectively. Existing probabilities of them in **Mixed-MAL** are represented as $P(70)$ and $P(71)$, respectively. Considering the natural fractional abundance of ^{13}C ($\alpha = 0.01108$), $P(70)$ and $P(71)$ can be expressed probabilistically in the following equations (see Supporting information),

$$P(70) = (1-\alpha)^{n-1}(1-x) \tag{2}$$

$$P(71) = (n-1)\alpha(1-\alpha)^{n-2}(1-x) + (1-\alpha)^{n-1}x \tag{3}$$

where n is the number of carbons in MAL ($n = 4$) and x is fractional abundance that methyl group in **Mixed-MAL** is labeled with ^{13}C ($0 < x < 1$). Since abundance of MAL with two or more ^{13}C in **Mixed-MAL** was negligibly small, those MAL were not considered in the analysis. Fractional abundance of MAL with molecular weight of 71 in **Mixed-MAL**, which is represented as P_{MAL^*}, is expressed by Eq. (4).

$$P_{\mathrm{MAL}^*} = \frac{P(71)}{P(70)+P(71)} \tag{4}$$

Substituting Eqs. (2) and (3) into Eq. (4) and solving the resulting equation for x gives Eq. (5).

$$x = \frac{\{(n-2)\alpha+1\}P_{\mathrm{MAL}^*}-(n-1)\alpha}{(1-n)\alpha P_{\mathrm{MAL}^*}-n\alpha+1} \tag{5}$$

On the other hand, actual P_{MAL^*} for **Mixed-MAL** was able to be experimentally determined from the peak intensities at m/z = 70 and 71 on the mass spectrum of MAL for **Mixed-MAL** (denoted as $I(70)$ and $I(71)$, respectively) and is expressed by Eq. (6).

$$P_{\mathrm{MAL}^*} = \frac{I(71)}{I(70)+I(71)} \tag{6}$$

To determine actual P_{MAL^*}, we analyzed **Mixed-MAL** with GC-MS, and $I(70)$ and $I(71)$ were 65.0 and 15.7, respectively (Fig. S-1 in Supporting information). We carried out GC-MS analysis at least three times and found that the reproducibility of the fractional abundance for each compound was good. Thus, the fractional abundance was the average of the values obtained from multiple GC-MS analyses. Thus, P_{MAL^*} was estimated at 0.194. Substituting $P_{\mathrm{MAL}^*} = 0.194$, $n = 4$ and $\alpha = 0.01108$ into Eq. (5) gave $x = 0.173$, namely ^{13}C purity of MAL in **Mixed-MAL** was calculated to be 17.3 %.

Catalytic reaction was carried out in a fixed-bed continuous flow reactor at 593 K under atmospheric pressure using **Mixed-MAL**. After the pretreatment of the catalyst ($H_3PMo_{12}O_{40}$, Nippon Inorganic Colour and Chemical Co., Ltd.) under a flow of a mixture of O_2 (10.7 vol%), H_2O (17.9 vol%) and N_2 (balance) at 593 K for 1 h, the reactant gas mixture consisted of **Mixed-MAL** (3 vol%), O_2 (6 vol%), H_2O (15 vol%) and N_2 (balance) was fed to the reactor. Reaction products were analyzed by on-line GC-FID and GC-TCD to estimate the conversion of MAL and yield of each product. The products and unreacted MAL were also collected using a cold trap cooled at 194 K for 200 min and the collected sample was analyzed by GC-MS to obtain mass spectra of the products and unreacted MAL. The reaction was also performed with non-labeled MAL, $^{12}CH_3$-MAL, instead of **Mixed-MAL**. For the reaction with **Mixed-MAL**, the reaction result was as follows: MAL conversion 48.9 %, and selectivity to MAA 38.7 %, AcOH 27.5 %, CO 21.4 %, and CO_2 11.3 %, which were almost the same as those for the reaction with $^{12}CH_3$-MAL (MAL conversion 55.2 %, and selectivity to MAA 32.7 %, AcOH 28.6 %, CO 23.8 %, and CO_2 13.1 %).

Structural formula, molecular weights (m/z) of the compounds and a main fragment of AcOH ($-CO_2H$) focused on the GC-MS analysis are shown in Table S-1 in Supporting information. The products collected in a cold trap for the oxidation of **Mixed-MAL** were analyzed by GC-MS. The peak intensities at m/z = 86 and 87 on a mass spectrum for MAA are represented as $I(86)$ and $I(87)$, respectively, and fractional abundance of labeled MAA with m/z = 87 (P_{MAA^*}) is expressed by Eq. (7).

$$P_{\mathrm{MAA}^*} = \frac{I(87)}{I(86)+I(87)} \tag{7}$$

The fractional abundance (x) that methyl group in MAA is labeled with ^{13}C is also expressed by Eq. (8) in the same manner of Eq. (5) for labeled MAL.

$$x = \frac{\{(n-2)\alpha+1\}P_{\mathrm{MAA}^*}-(n-1)\alpha}{(1-n)\alpha P_{\mathrm{MAA}^*}-n\alpha+1} \tag{8}$$

x for MAA was determined to be 0.174 from actual P_{MAA^*} calculated using $I(86)$ and $I(87)$ on the mass spectrum of MAA (Fig. S-2 in Supporting information). This value was almost the same as that of **Mixed-MAL** (x = 0.173). The match between the two values within experimental error allowed us to conclude that scrambling of ^{13}C in MAL by dimerization did not occur in the oxidation of MAL.

Next, the mass spectrum of AcOH formed by the oxidation of **Mixed-MAL** was analyzed. **Table 1** shows fractional abundance of labeled AcOH (P_{AcOH^*}) calculated from the peak intensities of molecular ions of AcOH with m/z=60 and 61 (represented as $I(60)$ and $I(61)$, respectively) on the mass spectrum of AcOH (Fig. S-3 in Supporting information). **Table 1** also shows the expected P_{AcOH^*}, which is denoted as P_{AcOH^*}(expected), obtained by assuming that AcOH is formed only by the reaction pathway shown in **Scheme 1**. P_{AcOH^*}(expected) was calculated with the procedure same as that from Eqs. (2) to (4) for MAL except that n was 2 and x was fractional abundance of ^{13}C-labeled methyl group in AcOH. As shown in **Table 1**, actual P_{AcOH^*} was 0.143. However, this value was smaller than P_{AcOH^*}(expected) = 0.180. This difference indicated that there was a formation pathway for AcOH other than that in **Scheme 1**. The contribution of that formation pathway to all the formation of AcOH can be calculated from actual x_{AcOH^*} and x_{AcOH^*}(expected) by Eq. (9) and it was 22.0 %, where x_{AcOH^*} was fractional abundance that methyl group in AcOH is labeled with ^{13}C and was the same as x of MAL and x_{AcOH^*}(expected) was obtained by substituting P_{AcOH^*} and n = 2 into Eq. (5).

$$\frac{x_{\mathrm{AcOH}^*}(\mathrm{expected})-x_{\mathrm{AcOH}^*}}{x_{\mathrm{AcOH}^*}(\mathrm{expected})}\times 100$$

$$=\frac{0.173-0.135}{0.173}\times 100 = 22.0\% \qquad (9)$$

To know the position of ^{13}C in the structure of AcOH formed from **Mixed-MAL**, *i.e.* whether methyl or carbonyl group was labeled, we focused on the fragment of AcOH (-CO_2H, m/z = 45, 46). This fragment is formed by the elimination of methyl group from AcOH. If the carbonyl group was labeled with ^{13}C, fractional abundance of the labeled fragment (P_{fragment^*}) must be the same as P_{AcOH^*}. P_{fragment^*} was only 0.014 and was much smaller than P_{AcOH^*} (= 0.143), meaning rather comparable to the value calculated on the assumption that the fragment contained only ^{13}C with natural fractional abundance was 0.011. In other words, almost all ^{13}C in AcOH formed from **Mixed-MAL** was present in methyl group, but 22.0 % of ^{13}C in **Mixed-MAL** did not transfer to AcOH as discussed above.

Table 1 Fractional Abundance of Labeled AcOH and Fragment of AcOH (-CO_2H)

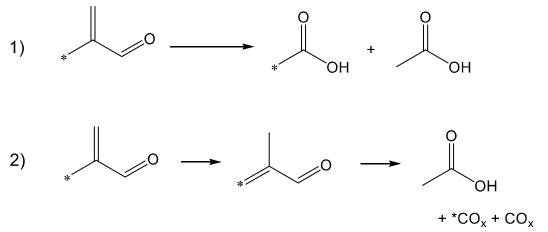
	Fractional abundance		
	$\frac{I(46)}{I(45)+I(46)}$	$\frac{I(61)}{I(60)+I(61)}$	x[c]
Expected[a]	0.011	0.180	0.173
Actual[b]	0.014	0.143	0.135

[a] Assuming that AcOH is only formed via Scheme 1.

[b] Estimated from mass spectrum for AcOH taken on GC-MS.

[c] Expected x is x_{AcOH^*}(expected) and actual x is x_{AcOH^*}.

Now, we consider a formation pathway of AcOH other than that shown in **Scheme 1**. There are two possible pathways to explain the difference between P_{AcOH^*} and P_{AcOH^*}(expected) (**Scheme 2**); 1) two AcOH are formed from MAL, and 2) C=C double bond in MAL is isomerized, changing the labeled position from methyl (-$^{13}CH_3$) to methylene group (=$^{13}CH_2$), and the formed MAL is oxidized to AcOH as the pathway in **Scheme 1**.



Scheme 2 Possible Formation Pathways from MAL to AcOH Other than That in Scheme 1

If AcOH is produced from MAL only by 1) in **Scheme 2**, P_{AcOH^*} must be half of P_{AcOH^*}(expected) because ^{13}C-labeled and unlabeled AcOH are produced in a ratio of 1 to 1. However, the actual P_{AcOH^*} (= 0.143) was greater than the half of P_{AcOH^*}(expected), 0.180. Thus, 1) in **Scheme 2** as the formation pathway for AcOH was unlikely. However, the possibility of the formation of AcOH by pathways of both 1) in **Scheme 2** and **Scheme 1** is still not excluded.

As for 2) in **Scheme 2**, since $H_3PMo_{12}O_{40}$ is superacid[8], recombination of C=C double bond in MAL is readily proceeded by acid catalysis. Therefore, this formation pathway giving unlabeled AcOH was quite possible. If 2) is only the formation pathway to AcOH other than that in **Scheme 1**, the contribution of 2) to form AcOH was 22.0 % and the formed CO_x must contain comparable amount of ^{13}C to this contribution.

To check it, mass balance of ^{13}C for the oxidation of **Mixed-MAL** was calculated on the assumption that the formed CO_x contained ^{13}C with the amount equivalent to 22.0 % of the predicted value of labeled AcOH (**Table 2**). The amount of ^{13}C in **Mixed-MAL** reacted during 200 min, which was the period of time for collecting the products in a cold trap, was calculated from the MAL conversion and ^{13}C purity of **Mixed-MAL** (=17.3 %) as 0.83 mmol-^{13}C. On the other hand, the amounts of ^{13}C in the formed MAA, AcOH, and CO_x were estimated to be 0.28, 0.41, and 0.12 mmol-^{13}C, respectively, from those yields and ^{13}C content for each product. In this estimation, it was assumed that surplus CO_x expected from 2) in **Scheme 2** was formed by complete oxidation of MAL, *i.e.* four molecules of CO_x were formed from one MAL. The estimation clearly demonstrated that the sum of the amounts of ^{13}C in the formed products (= 0.80 mmol) was in good agreement with the amount of ^{13}C in **Mixed-MAL** reacted (= 0.83 mmol), supporting that 2) in **Scheme 2** was plausible as the formation pathway other than that in **Scheme 1**. The first-order rate constant for AcOH combustion reaction over $H_3PMo_{12}O_{40}$ measured using AcOH as a reactant under the same conditions as those for MAL oxidation reaction was $k = 2.8 \times 10^{-4}$ mol h^{-1} $g_{catalyst}^{-1}$. This was an order of magnitude smaller than the rate constant ($k = 1.6 \times 10^{-3}$ mol h^{-1} $g_{catalyst}^{-1}$) for MAL oxidation reaction (Table S-2 in Supporting information). Furthermore, the concentration of formed AcOH in the MAL oxidation reaction was low. Thus, it is reasonable to think that the contribution of CO_x formation from AcOH to the product selectivity during the MAL oxidation reaction was negligibly small.

Based on the above discussion, we propose a reaction pathway for the formation of by-products mainly AcOH from MAL as shown in **Scheme 3**. The first step is oxidative cleavage of C=C double bond in MAL, giving pyruvaldehyde (**1**) and HCHO (**2**). **1** is subsequently hydrolyzed to AcOH (**3**) and HCHO (**4**). Since HCHO is highly reactive, it is immediately oxidized to CO_x. A part of MAL undergoes recombination of C=C double bond on Brønsted acid sites of $H_3PMo_{12}O_{40}$ and then the formed MAL with labeled methylene group (**5**) is oxidized to AcOH via pyruvaldehyde. The presence of a trace amount of pyruvaldehyde in the collected products supported this reaction pathway.

Table 2 Mass Balance of ^{13}C for the Oxidation of **Mixed-MAL**

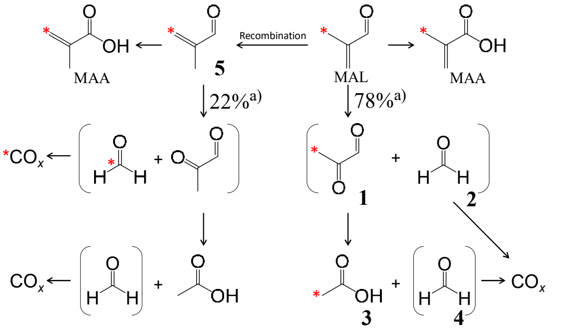
	[mmol-$^{13}C^{a)}$]				
	MAL	MAA	AcOH	CO_x	Total
Converted MAL$^{b)}$	0.83	-	-	-	0.83
Products$^{c)}$	-	0.28	0.41	0.12$^{d)}$	0.80

a) Integrated value for 200 min.

b) The amount of ^{13}C in **Mixed-MAL** reacted.

c) The amount of ^{13}C in the formed products.

d) Assuming that formed CO_x contained ^{13}C with the amount equivalent to 22.0 % of the predicted value of labeled AcOH.



Scheme 3 Proposed Reaction Pathway for the Formation of By-products from MAL in MAL Oxidation over $H_3PMo_{12}O_{40}$

a) "22 %" and "78 %" indicate abundance ratios of the methyl group-labeled MAL and the methylene group-labeled MAL that is formed by the recombination of C=C double bond, respectively.

Supporting information

Supplementary data associated with this article can be found in the online version at https://jstage.jst.go.jp/browse/jpi/-char/en (DOI: doi.org/10.1627/jpi.66.128)

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