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Supporting Information

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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Derivation of the equations (2) and (3)

For MAL with ^{13}C-labeled methyl groups, the ratio of ^{13}C labeled methyl group carbons is x. Thus, the probabilities that methyl group carbon is ^{12}C and that methyl group carbon is ^{13}C are 1-x and x, respectively.

For the other skeletal carbons, the natural abundance ratio of ^{13}C is α. Thus, the probabilities that the carbon is ^{12}C and that the skeletal carbon is ^{13}C are 1-α and α, respectively.

For **Mixed-MAL** used in this study, the existence probability P(70) of MAL consisting of only ^{12}C skeletal carbons is expressed as the product of the ^{12}C abundance ratios of each skeleton carbon. Thus, when the number of MAL carbons is n (n = 4 for MAL, but we left n to generalize the formula to other products so that the same calculation can be performed), it is expressed as follows

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

On the other hand, the existence probability P(71) of MAL consisting of ^{13}C for one of the skeletal carbons and ^{12}C for the others are expressed as the product of the ratio of ^{13}C for one skeletal carbon and ^{12}C for the other skeletal carbons,

$$\begin{aligned} P(71) &= (1-\alpha)^{n-1}x + \alpha(1-\alpha)^{n-2}(1-x) + \cdots + (1-\alpha)^{n-2}\alpha(1-x) \\ &= (n-1)\alpha(1-\alpha)^{n-2}(1-x) + (1-\alpha)^{n-1}x \qquad (3) \end{aligned}$$

Note that ^{14}C, ^{2}H, ^{3}H, ^{17}O, and ^{18}O, which change the molecular weight of MAL, were not considered in the calculations because of their small natural abundances.

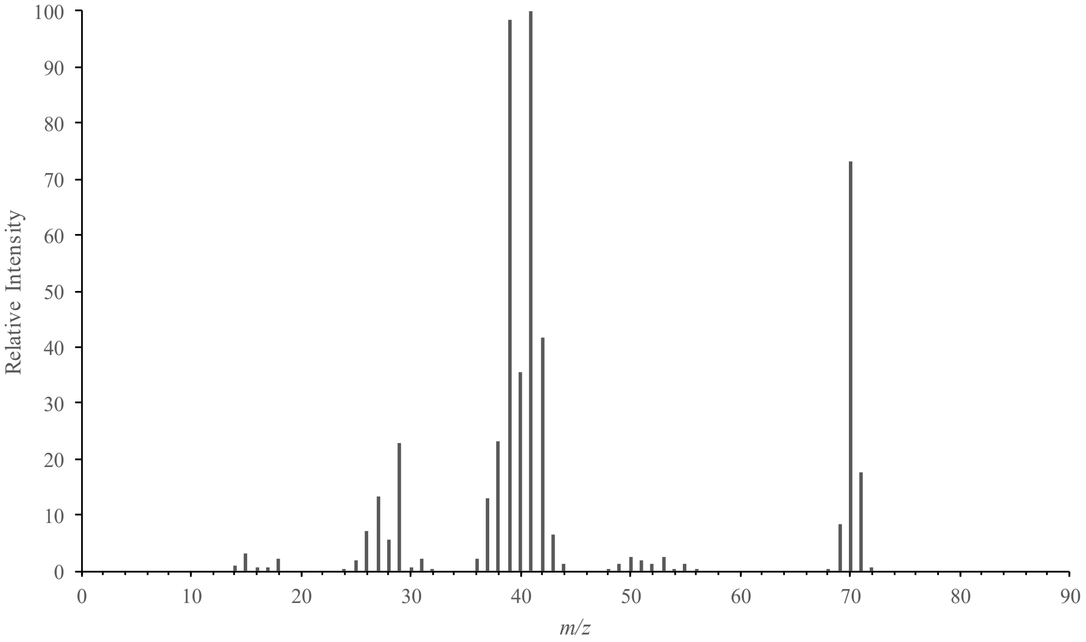


Figure S-1 Mass spectrum of MAL obtained by GC-MS analysis for **Mixed-MAL**.

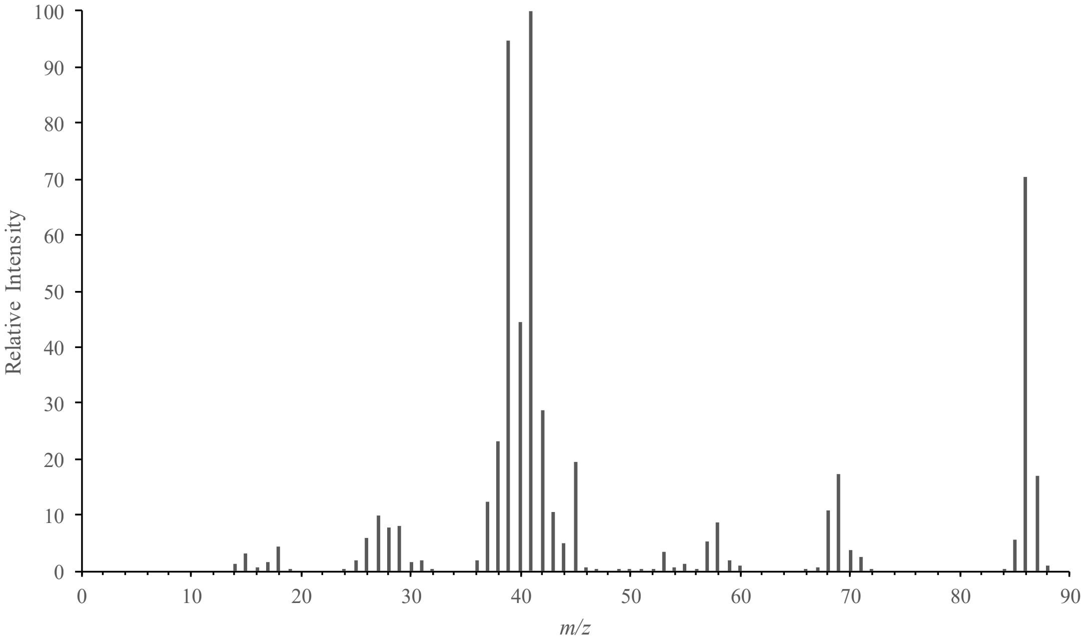


Figure S-2 Mass spectrum of MAA obtained by GC-MS analysis for the products collected in a cold trap for the oxidation of **Mixed-MAL**.

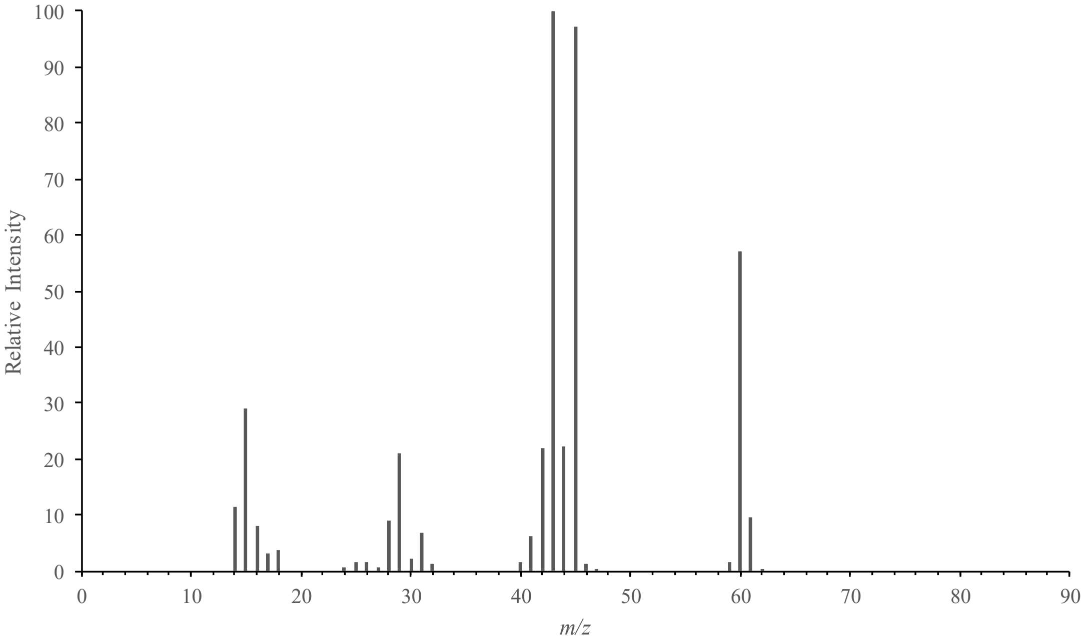
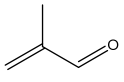
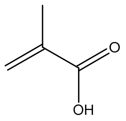
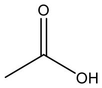
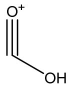


Figure S-3 Mass spectrum of AcOH obtained by GC-MS analysis for the products collected in a cold trap for the oxidation of **Mixed-MAL**.

Table S-1 Mass numbers and carbon numbers of non-labeled and ^{13}C-labeled compounds.

Compound	*m*/*z*		Carbon number
	Non-labeled	^{13}C-labeled	n
 (MAL)	70	71	4
 (MAA)	86	87	4
 (AcOH)	60	61	2
 (Fragment of AcOH)	45	46	1

Reaction results with acetic acid as substrate

Catalytic reaction with acetic acid (AcOH) as substrate was carried out in a manner similar to the catalytic reaction using MAL. The reactant gas mixture consisted of AcOH (4.6 vol%), O_2 (9.8 vol%), H2O (9.8 vol%) and N2 (balance) was fed to the reactor. Other conditions and procedures were the same as for the catalytic reaction using MAL. The reaction result was as follows: AcOH conversion 1.4%, and selectivity to CO 45.2%, and CO_2 54.8%.

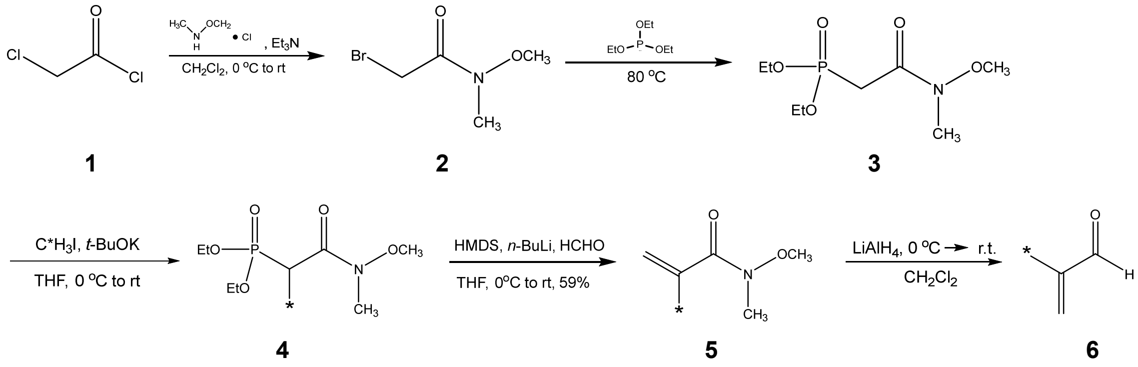
We assumed that the MAL or AcOH conversion reactions had a first–order dependence on the partial pressure of the substrate. And the first–order reaction rate constants for the conversion of MAL and AcOH were estimated in Table S-2. The reaction rate constant for the conversion of MAL was estimated from results for the reaction with $^{12}CH_3$-MAL.

Table S-2 The first–order reaction rate constants for the conversion of MAL and AcOH.

	k / mol (h g-catalyst)$^{-1}$
MAL	1.6×10^{-3}
AcOH	2.8×10^{-4}

Synthesis of MAL labeled with ^{13}C-methyl group ($^{13}CH_3$-MAL)

The synthetic route of $^{13}CH_3$-MAL is shown in Scheme S-1.



Scheme S-1 Synthetic route of $^{13}CH_3$-MAL.

Triethylamine (Kanto Chemical, 28.6 mL, 205 mmol) was added to CH_2Cl_2 (256 mL) and N,O-dimethylhydroxylamine hydrochloride (Kanto Chemical, 10.0 g, 103 mmol) and 2-chloroacetyl chloride **1** (Tokyo Chemical Industry Co., Ltd., 8.15 mL, 103 mmol) were added. The mixture was then stirred at room temperature for 20 h.

Product **2** was extracted with 1 M HCl and ethyl acetate. Triethoxyphosphine (Tokyo Chemical Industry Co., Ltd., 11.4 mL, 71.8 mmol) was added to the unpurified **2** and stirred at 80°C for 15 hours. After concentrating the reaction solution at 100°C, **3** was separated on a silica gel column. (Hexane:EtOAc=7:3 then 0:10).

3 (7.37 g, 30.8 mmol) was dissolved in tetrahydrofuran (THF, 102 mL), t-BuOK (Kanto Chemical, 4.14 g, 36.9 mmol) was added at 0°C under Ar atmosphere, and after 10 minutes $^{13}CH_3I$ (Kanto Chemical, 2.49 mL, 40.1 mmol) was added and the mixture stirred at room temperature for 15 hours. The mixture was extracted with saturated ammonium chloride and ethyl acetate.

Hexamethyldisilazane (ALDRICH, 4.94 mL, 23.7 mmol) was dissolved in THF (99 mL) and n-BuLi (Kanto Chemical, 1.64 mol/L in hexane, 14.5 mL, 23.7 mmol) was added at 0°C under Ar atmosphere and stirred for 30 min. Then unpurified **4** (5.00 g, 19.8 mmol) was dissolved in THF (30 mL) and added to the mixture with a cannula and stirred for 20 min. HCHO (Kanto Chemical, 0.710 g, 23.7 mmol) was then added and stirred at room temperature for 1 h. The mixture was extracted with 0.5 M NaOH and ethyl acetate. The column was Hexane:EtOAc=9:1 then 7:3.

5 (2.00 g, 15.5 mmol) was dissolved in CH_2Cl_2 (52.0 mL), shaded with aluminum foil, and $LiAlH_4$ (LAH) (Kanto Chemical, 294 mg, 7.74 mmol) was added at 0°C under Ar atmosphere, and the reaction was stirred at room temperature for 2 hours at room temperature.Saturated Na_2SO_4 solution was added until no bubbles appeared, then a catalytic amount of MeHQ was added. The mixture was filtered through Celite and extracted with CH_2Cl_2 and 0.1M HCl. The product was shaded and concentrated at 300~400 mmHg to give methacrolein **6** with the methyl group of the target product labeled with ^{13}C.