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Thermal Dimerization of Alkali Acrylate/3-Methyl-3-butenoate and Alkali Methacrylate/3-Methyl-3-butenoate Binary Systems in the Solid State

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The thermal reaction in the solid state of binary salts, obtained from an equimolar mixture solution, of lithium 3-methyl-3-butenoate/methacrylate (3-MBA/MA) or potassium 3-MBA/MA, after esterification, produced mainly dimethyl (*Z*)-3,6-dimethyl-2-heptenedioate as a novel cross-coupled dimer. The cross-coupled dimer was obtained from the potassium salts in 35.5% yield upon heating at 230 °C for 2 h. Similary, a methyl ester of the cross-coupled dimer, dimethyl (*Z*)-3-methyl-2-heptenedioate, was given from sodium 3-methyl-3-butenoate/acrylate (3-MBA/AA) or potassium 3-MBA/AA after esterification. The cross-coupled dimer was obtained from potassium 3-MBA/AA in 57.5% yield upon heating at 230 °C for 2 h. The X-ray diffraction pattern of potassium 3-MBA/MA or potassium 3-MBA/AA indicates the formation of a new phase, that is different from that of the individual salts. The crystal system of K–(3-MBA/AA) was transformed to a more stable state by initial heating for 20 min. The selective cross-coupled dimerization was caused by the new phase of binary salts and maintaining the crystal state of the reaction system by the formation of solid-solution crystals.

We previously studied the thermal reaction of salts of several unsaturated carboxylic acids, e.g., methacrylic acid (MA),[1—7] crotonic acid,[8,9] and 3-butenoic acid,[10,11] in the solid state, and reported that these reactions produce oligomers, and that the productions are controlled by the crystal state of the reaction system. In addition, we investigated the thermal reaction of salts of binary acid systems. From sodium acrylate/crotonate or from sodium methacrylate/crotonate, cross-coupled dimers were obtained, respectively.[12,13] The solid-state thermal reaction of binary potassium salts of methacrylic acid/3-butenoic acid, or that of acrylic acid/3-butenoic acid, produced the cross-coupled dimers almost selectively.[14] It was found that these thermal reactions are led to selective cross-coupled dimerization by the formation of new crystals of equimolar binary salts that are different from those of the individual salts, as well as by maintaining the crystallinity of the reaction system by the formation of solid solution crystals.

Different from salts of acrylic acid (AA), methacrylic acid, crotonic acid, and 3-butenoic acid, those of 3-methyl-3-butenoic acid (3-MBA) were found not to react in the solid state upon heating at 200 °C in this study. Thus, the thermal reactions of the binary systems of alkali 3-methyl-3-butenoates, which do not react thermally individually, and alkali methacrylates or alkali acrylates, were investigated.

Experimental

Materials. 3-Methyl-3-butenoic acid was prepared from 3-chloro-2-methyl-1-propene, obtained from Tokyo Kasei Chem. Co., by the Grignard reaction according to a method reported by Wagner.[15] Bp 80—81 °C/14 mmHg (lit,[15] 68—70 °C/5 mmHg) (1 mmHg=133.322 Pa). Anhydrous lithium (Li), sodium (Na), and potassium (K) salts were used as monomers. The monomeric salts were prepared by neutralizing a binary acid solution of a prescribed molar ratio with aqueous metal hydroxide using phenolphthalein as an indicator. After removing water completely by means of distillation under reduced pressure, the obtained salt was dried under reduced pressure at 60 °C over phosphorus pentoxide.

Thermal Reaction. The monomeric salt (1.5 g) was put into a Pyrex tube, and heated in an oil bath under reduced pressure at 175—230 °C for 2 h. The reaction mixture was dissolved in water, acidified with hydrochloric acid, and then extracted with ether. The extracts were treated with diazomethane in ether. The methyl ester derivatives of the products were subjected to analysis by gas chromatography (GC) using dimethyl succinate as an internal standard.

The obtained ester from equimolar K–(3-MBA/MA) was purified by column chromatography (200 mesh silica gel; hexane : ethyl acetate=7 : 3), which gave dimethyl (*Z*)-3,6-dimethyl-2-heptenedioate (dimethyl ester of **2**): ^{1}H NMR (400 MHz; CDCl$_3$) $\delta = 1.19$ (d, $J = 6.96$ Hz, 3H), 1.57 (m, 1H), 1.84 (m, 1H), 1.89 (d, $J = 1.29$ Hz, 3H), 2.53 (m, 2H), 2.71 (m, 1H), 3.67 (s, 3H), 3.69 (s, 3H), 5.67 (s, 1H); ^{13}C NMR (100 MHz; CDCl$_3$) $\delta = 17.1$ (CH$_3$), 25.1 (CH$_3$), 31.0 (CH$_2$), 31.8 (CH$_2$), 39.4 (CH), 51.5 (OCH$_3$), 51.6 (OCH$_3$), 116.2 (=CH), 159.9 (=C), 166.6 (C=O), 176.9 (C=O); IR (KBr, neat) 1648 (C=C), 1722 (C=O), 1738 cm^{-1} (C=O). MS (FAB) $m/z = 215$ [M+H]$^+$.

The obtained ester from equimolar K–(3-MBA/AA) was purified by means of column chromatography (200 mesh silica gel; hexane : ethyl acetate=8 : 2), which gave dimethyl (*Z*)-3-methyl-2-heptenedioate (dimethyl ester of **3**): ^{1}H NMR (500 MHz; CDCl$_3$) $\delta = 1.82$ (tt, $J,J' = 7.70$ Hz, 2H), 1.90 (d, $J = 1.10$ Hz, 3H), 2.37 (t, $J = 7.56$ Hz, 2H), 2.67 (t, $J = 7.70$ Hz, 2H), 3.68 (s, 3H), 3.69 (s, 3H), 5.69 (s, 1H); ^{13}C NMR (125 MHz; CDCl$_3$) $\delta = 23.2$ (CH$_2$), 25.0 (CH$_3$), 32.4 (CH$_2$), 33.6 (CH$_2$), 50.8 (OCH$_3$), 51.5 (OCH$_3$), 116.5 (=CH), 159.5 (=C), 166.6 (C=O), 173.9 (C=O); IR (KBr, neat) 1648 (C=C), 1722 (C=O), 1736 cm^{-1} (C=O). MS (FAB) $m/z=201$ $[M+H]^+$.

Measurement. IR spectra were recorded on a Hitachi 270-30 spectrophotometer. ^{1}H NMR spectra were obtained with a 400 MHz FT-NMR spectrometer (JEOL JNM-GSX400) or a 500 MHz one (JEOL JNM-GSX500). ^{13}C NMR spectra were obtained with a 100 MHz FT-NMR spectrometer (JEOL JNM-GSX400) or a 125 MHz one (JEOL JNM-GSX500). Wide-angle X-ray diffraction patterns were obtained for specimens on a Rigaku Denki XG X-ray diffraction apparatus with Cu $K\alpha$ radiation (35 kV, 20 mA). For gas chromatography (GC) measurements, a Hitachi 263-50 apparatus was used under the following conditions: column packing, Silicone SE-30 (3 mm×2 m); column temperature, range of 50—250 °C; heating rate, 10 K min^{-1}; carrier gas, nitrogen; gas flow, 30 ml min^{-1}. The mass spectra were recorded on a JEOL JMS-HX110 mass spectrometer.

Results and Discussion

Thermal Reactions of Salts of 3-MBA. Thermal reactions of the salts of 3-MBA, such as Li–3-MBA, Na–3-MBA, and K–3-MBA, were conducted at 200 °C for 2 h. The products were acidified and subsequently converted to methyl esters using diazomethane. The gas chromatograms of all the esters obtained from Li–3-MBA, Na–3-MBA, and K–3-MBA showed the only single peak. The esterified product was identified by spectroscopic data as the monomeric ester, methyl 3-methyl-3-butenoate. These results suggested that alkali salts of 3-MBA do not react at 200 °C in the solid state.

Thermal Reactions of Salts of 3-MBA/MA. Thermal reactions of the binary alkali salts of equimolar 3-MBA/MA were performed at 200 °C for 2 h. The gas chromatograms of the esterified products obtained from K–(3-MBA/MA) showed three peaks. The product corresponding to the first peak was methyl methacrylate, and that corresponding to the second, was methyl 3-methyl-3-butenoate. The product corresponding to the third peak was isolated by column chromatography and identified by ^{1}H NMR, ^{13}C NMR, mass, and IR spectroscopy as dimethyl (*Z*)-3,6-dimethyl-2-heptenedioate (dimethyl ester of **2**), which is a methyl ester of the novel cross-coupled dimer of 3-MBA and MA. The yield of the dimer was determined by GC using dimethyl succinate as an internal standard after esterification. The formation of a polymer or an oligomer was not found. The results are summarized in Table 1.

Table 1. Dimerization of Binary Salts of 3-MBA/MA

Salts	Condition		Yield[a]/%	
	Temp/°C	Time/h	**1**	**2**
Li	200	2	—	5.5
Na	200	2	N.r.[b]	
K	190	2	T[c]	22.2
K	190	4	T[c]	26.3
K	200	2	T[c]	28.1
K	230	2	1.3	35.5

a) Determined by GC after esterification. b) No reaction. c) Trace.

The sodium salts did not react under this condition. The low reactivity of Na–(3-MBA/MA) may be due to the unfavorable molecular arrangements of monomeric salts in the crystal lattice, which make it difficult for Na–(3-MBA/MA) to produce dimers. From Li–(3-MBA/MA), although the cross-coupled dimer **2** was obtained, the yield was low (5.5%). From K–(3-MBA/MA), the cross-coupled dimer **2** was obtained in the 28.1% yield. The thermal reaction of the potassium salts, which indicated the highest yield of the cross-coupled dimer **2** in the alkali binary equimolar salts used, was further investigated.

When the reaction temperature was changed to 230 °C, although the yield of **2** increased to 35.5%, a dimer of methacrylic acid, 2,2-dimethyl-4-methylenepentanedioic acid (**1**),[1,2] was also slightly produced in the 1.3% yield. The yields of the cross-coupled dimer **2** at 200 °C are shown as functions of the composition of K–(3-MBA/MA) in Fig. 1. The yield of **4** was highest in equimolar composition. Even in the 1/9 molar ratio of 3-MBA/MA, the formation of the MA dimer **1** did not appear. This was attributed to the unsuitable molecular arrangements for the production of the MA dimer due to the formation of mixed crystals. The yield at 190 °C in relation to time are shown in Fig. 2. The yield increased with time, and reached 26.3% after 4 h. The formation of a trimer and an oligomer was not found even after 4 h. The X-ray diffraction pattern of the equimolar K–(3-MBA/MA) indicated crystalline salt, which was different from an individual pattern of K–3-MBA or that of K–MA. This suggested a new crystal phase of equimolar K–(3-MBA/MA) that is different from that of a mixture of K–3-MBA and K–MA. Moreover, the diffraction peaks gave slight shifts while maintaining the crystal state as the cross-coupled dimerization proceeded. The initial peaks of the monomeric salts at $2\theta=27.20°$, 30.10°, 37.90°, slightly shifted to 27.05°, 30.16°, 37.96°,

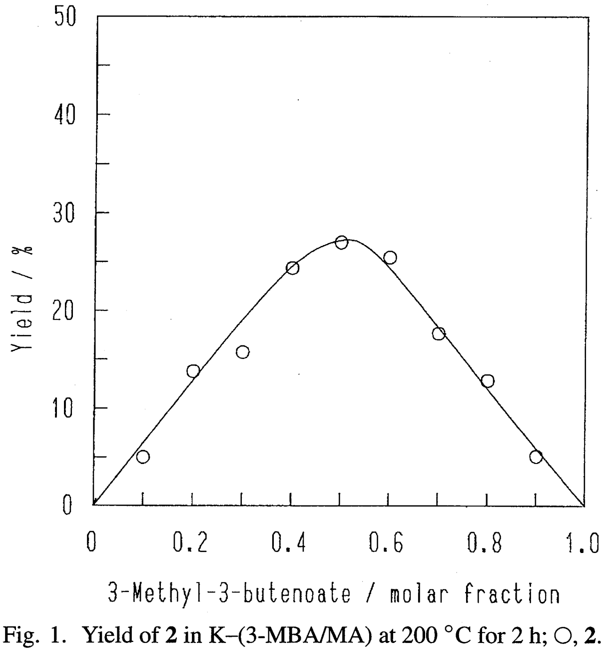


Fig. 1. Yield of **2** in K–(3-MBA/MA) at 200 °C for 2 h; ○, **2**.

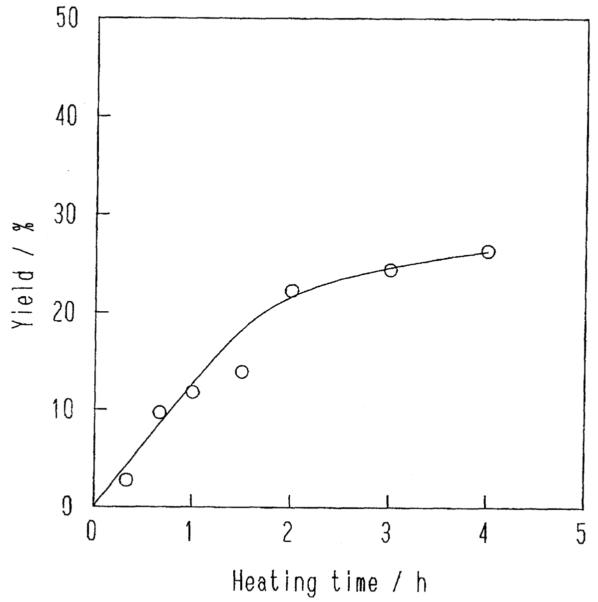
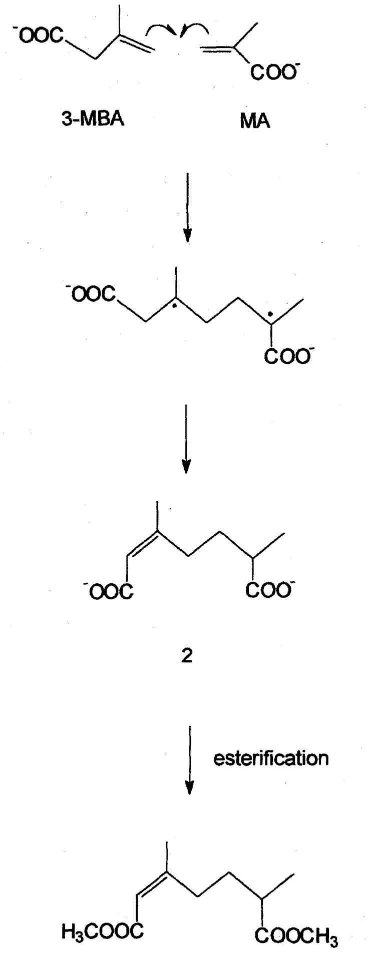


Fig. 2. Yield of **2** in K–(3-MBA/MA) at 190 °C; ○, **2**.

respectively, at 26.3% cross-coupled dimer formation after heating at 190 °C for 4 h. This indicates the formation of solid solution crystals between the monomeric salts and the cross-coupled dimer salt.

It was considered that the cross-coupled dimer **2** was formed by a disproportionation reaction, as shown in Scheme 1; that is to say, the biradical was produced as an intermediate by bonding between the terminal double bonds, followed by a hydrogen transfer. We previously reported a similar mechanism in the thermal dimerization of salts of other unsaturated carboxylic acids.[9,11,13,14] It is known that a compound having a cyclobutane ring forms in the thermal reaction of methyl methacrylate.[16—18] However, in this reaction, the formation of no compound containing a cyclobutane ring was found.

It was previously reported that the solid-state thermal reactions of alkali methacrylates, e.g., Li–MA, Na–MA, and K–MA, at 200 °C produce polymers having high molecular weight (number average molecular weight, 388000–475000).[7] As described above, the solid-state thermal reaction of alkali 3-methyl-3-butenoates at 200 °C did not occur. However, from binary equimolar K–(3-MBA/MA), the cross-coupled dimer **2** was obtained almost selectively. It is concluded that the selective production of **2** is due to the formation of new crystals of the binary salts that are different from that of the individual salts, and to keeping the crystal state of the reaction system by the formation of solid solution crystals between the monomeric salts and the dimer salt.



Scheme 1.

Thermal Reactions of Salts of (3-MBA/AA). Thermal reactions of the binary alkali salts of equimolar 3-MBA/AA were carried out at 200 °C for 2 h. All of the gas chromatograms of the esterified products showed three peaks. The product corresponding to the first peak was methyl acrylate, and the second, methyl 3-methyl-3-butenoate. The product corresponding to the third peak was purified by column chromatography, and was identified by spectroscopic data as dimethyl (*Z*)-3-methyl-2-heptenedioate (dimethyl ester of **3**), which is a methyl ester of the novel cross-coupled dimer of 3-MBA and AA. The yield was determined by GC, as described above. The formation of a polymer or an oligomer was not found. The results are summarized in Table 2.

Using the equimolar salts, these thermal reactions caused selective cross-coupled dimerization without any dimerization of the salts of AA. In lithium salts, the yield of **3** was low (2.6%). Na–(3-MBA/AA) showed a higher reactivity than Na–(3-MBA/MA), and the yield of **3** was 29.4%. In the

Table 2. Dimerization of Binary Salts of 3-MBA/AA

Salts	Condition		Yield[a)]/%
	Temp/°C	Time/h	**3**
Li	200	2	2.6
Na	200	2	29.4
K	175	2	21.8
K	175	4	28.3
K	200	2	46.1
K	230	2	57.5

a) Determined by GC after esterification.

potassium salts, the yield of **3** was the highest in those of the salts used; the value was 46.1%. The yield of the cross-coupled dimer in K–(3-MBA/AA) was higher than that in K–(3-MBA/MA). The thermal reaction of the potassium salts was further investigated.

When the reaction temperature was changed to 230 °C, the yield increased to 57.5% without producing the AA dimer. The yields of **3** at 230 °C are shown as functions of the composition of K–(3-MBA/AA) in Fig. 3. The yield was highest in the equimolar composition. In the 1/9 or 2/8 molar ratio of 3-MBA/AA, products regarded as the AA dimer was produced in 4.4% or 4.8% yield, respectively. In equimolar K–(3-MBA/AA), the yields of **3** in relation to time at 175 °C are shown in Fig. 4. The formation of a trimer or an oligomer was not found, even after 4 h. The yield increased with time, and reached 28.3% after 4 h. The X-ray diffraction pattern of equimolar K–(3-MBA/AA) indicated crystalline salts, and suggested the formation of a new crystal system of equimolar K–(3-MBA/AA) that is different from the individual salts. The initial peaks of monomeric salts at $2\theta=21.55°$, 22.65°, 26.86°, 27.45°, 30.33°, and 30.33°, disappeared completely after heating at 175 °C for 20 min (dimer conversion, 5.2%); different peaks at $2\theta=21.32°$, 27.10°, and 29.42°, appeared simultaneously. The newly appearing peaks gradually gave slight shifts, reaching 21.01°, 27.20°, and 28.73°, after 3 h, respectively, at 25.7% cross-coupled dimer formation. These data suggested that the crystals of the monomeric salts transformed to more stable crystals during the initial heating; then, the formation of solid-solution crystals between the monomeric salts and the dimer salt occurred as dimerization proceeded. The higher yield in K–(3-MBA/AA) than that in K–(3-MBA/MA) was attributed to the more favorable arrangements of K–(3-MBA/AA) in the crystal lattice due to the transformation, and to the higher reactivity of K–AA than that of K–MA.

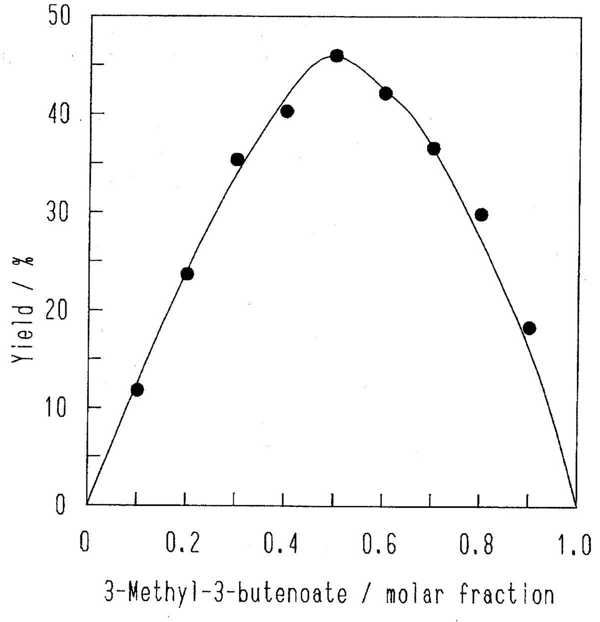


Fig. 3. Yield of **3** in K–(3-MBA/AA) at 200 °C for 2 h; ●, **3**.

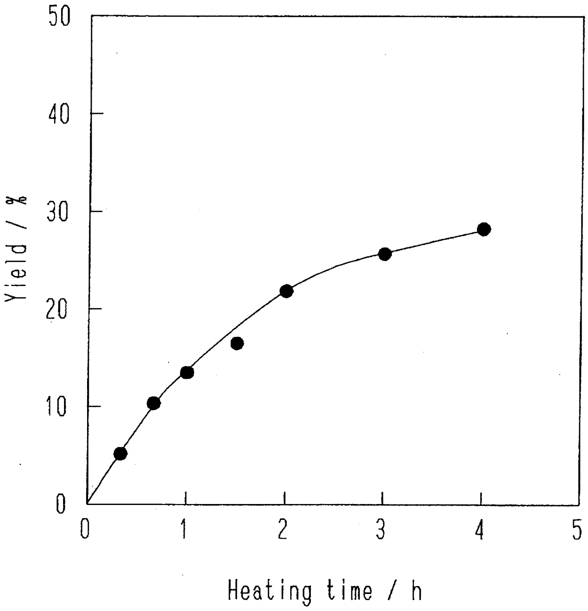
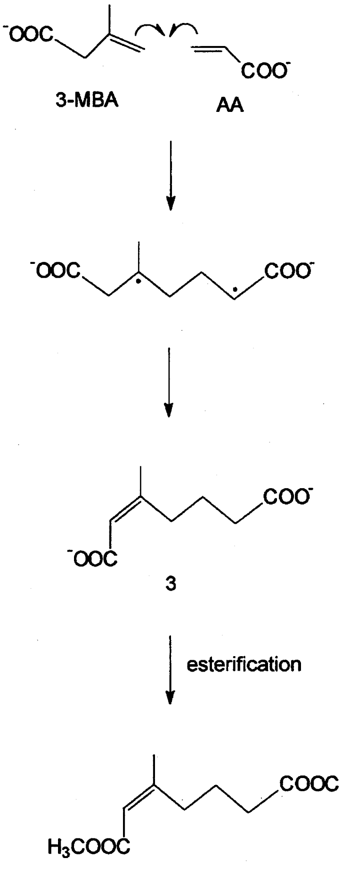


Fig. 4. Yield of **3** in K–(3-MBA/AA) at 175 °C; ●, **3**.



Scheme 2.

It was considered that, similar to the formation of **2**, the cross-coupled dimer **3** was formed by a disproportionation reaction through a diradical, as shown in Scheme 2. We previously reported that, in the solid-state reaction system maintaining the crystallinity by the formation of solid-solution crystals, although the reaction proceeds selectively, the yield of the product is low due to the remaining monomers.[12,13] This was attributed to controlling the reaction by the crystal structure. However, the yield of the cross-coupled dimer **3** (57.5%) was highest in those of the solid-state cross-coupled thermal dimerizations, which we have never reported.

We previously found that the solid-state thermal reactions of alkali acrylates, (Li–AA, Na–AA, and K–AA) at 200 °C produce cross-linked polymers.[19] However, from binary equimolar K–(3-MBA/AA) and Na–(3-MBA/AA), cross-coupled dimer **3** was obtained almost selectively. It is concluded that these results are due to the formation of new crystals of the binary salts that are different from that of the individual salts, due to the transformation of the crystal system to a more stable state, and due to maintaining the crystallinity of the reaction system by the formation of solid-solution crystals during dimerization.

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