Thermal Cross-coupled Dimerization of Sodium Acrylate/Crotonate and Methacrylate/Crotonate Binary Systems in the Solid State

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The solid state thermal reactions of binary crystals obtained from an equimolar mixture solution of either sodium acrylate/crotonate Na(AA/CA) or sodium methacrylate/crotonate Na(MA/CA) give cross-coupled dimers. The main product obtained in a 51.4% yield from Na(AA/CA) on heating at 250 °C for 2 h is, after conversion to a methyl ester, dimethyl pent-1-ene-3,4-dicarboxylate, and that from Na(MA/CA) obtained in a 41.7% yield on heating at 230 °C for 2 h was dimethyl hex-1-ene-2,4-dicarboxylate. In either case, X-ray diffraction analysis of the mixed sodium salts shows a new phase different from that of the individual salt. As dimerization proceeds, a solid solution is formed, resulting in a high selectivity of dimer formation.

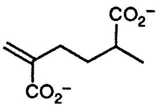
Schmidt *et al.* studied the topochemical effect in solid state reactions of organic compounds and reported that one of the controlling factors in such reactions is the geometry of crystal structure of the reactant species.[1] Morawetz *et al.*[2,3] reported that irradiation of crystalline metal salts of acrylic and methacrylic acids gives high polymers. They suggest that the bulk of the polymer lies in an amorphous phase, but the reactive end of the growing chains is effectively anchored in the lattice of the monomer crystal. In their study, dimers and trimers were not reported to be formed.

In previous papers, we reported the thermal oligomerization of alkali and alkaline earth metal salts of methacrylic and crotonic acids in the solid state.[4–10] The alkaline earth metal salts of methacrylic acid predominantly afforded dimer and trimer products. The magnesium, calcium and strontium salts, while undergoing crystal lattice destruction, gave a dimer product, hex-1-ene-2,5-dicarboxylate **1**, and a trimer product, non-1-ene-2,5,8-tricarboxylate.[5,7] The barium salt, on the other hand, maintained the crystal lattice, and yielded 4-methylpent-1-ene-2,4-dicarboxylate **2** and 4-methyloct-1-ene-2,4,7-tricarboxylate.[6,7] The thermal reaction of sodium crotonate at 230 °C in the solid state gave a dimer product, hex-1-ene-3,4-dicarboxylate **3** in a virtually quantitative yield.[9,10] In the latter case, the monomer and the dimer product **3** formed a solid solution crystal and thus the crystal lattice was maintained during dimerization. This fact might lend a high selectivity to dimer formation. On the other hand, the reaction of potassium salt under the same conditions gives three dimers, including **3**, without formation of a solid solution.[10] Recently, Snider and Foxman[11] reported that γ-ray irradiation of crystalline sodium crotonate gave a stereospecific trimer.

Similarly, we have attempted the thermal reaction of salts of binary acid systems. For calcium and barium salts of binary acrylic acid/methacrylic acid, the solid state thermal reaction showed little selectivity and afforded, in additions of **1** and **2**, cross-coupled dimers, pent-1-ene-2,5-dicarboxylate and pent-1-ene-2,4-dicarboxylate.[12,13]

In the preceding paper, we have reported thermal reactions of seven alkali and alkaline earth metal salts of the methacrylic acid/crotonic acid (MA/CA) system in the solid state, and that only Na, K and Ba salts afford the cross-coupled dimer, hex-1-ene-2,4-dicarboxylate **4**.[14]

We have further investigated the reaction of Na(MA/CA) and similar reactions in the sodium salt of the acrylic acid/crotonic acid (AA/CA) system.



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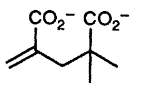

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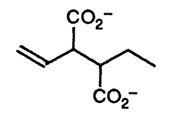

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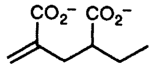

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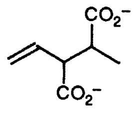

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Results and Discussion

Thermal Analysis.—Thermogravimetry of NaCA, NaAA and NaMA showed weight loss at 450, 447 and 460 °C, respectively. Differential thermal analysis exhibited exothermic peaks at 320, 284 and 342 °C. These exotherms might be due to addition of the monomer. Binary salts, Na(MA/CA) and Na(AA/CA), prepared from an equimolar mixture of the two acids, revealed decomposition at 454 and 460 °C, respectively, and exothermic peaks appeared at 246 and 316 °C, respectively.

Structures of Cross-coupled Dimers Obtained from Na(AA/CA).—Binary crystals derived from an equimolar mixture of AA and CA were heated at 250 °C for 2 h under reduced pressure. Reaction products were esterified with diazomethane. Gas chromatography of the product showed two peaks due to dimers. Conversions to these products were determined to be 51.4 and 9.0%, respectively. The major product was isolated by two-step distillation, and the minor product was collected by preparative gas chromatography. The main product was identified, by ^1H and ^{13}C NMR spectroscopy and mass spectrometry, as dimethyl pent-1-ene-3,4-dicarboxylate **5a**, a cross-coupled dimer, and the minor product as the dimethyl ester of **3**.

Dimer Formation from Binary Salts Na(AA/CA) and Na(MA/CA).—Thermal reaction of Na(AA/CA) crystal derived

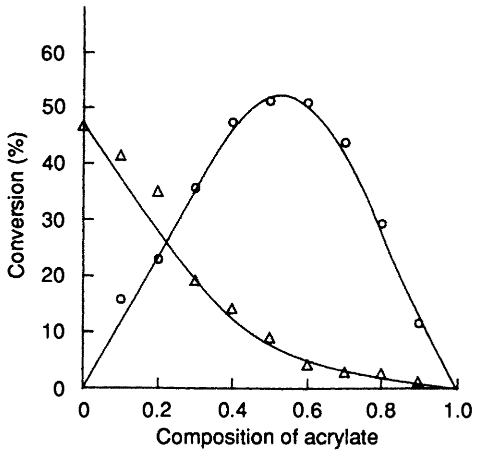


Fig. 1 Thermal dimerization of sodium acrylate/crotonate at 250 °C for 2 h: △, dimethyl hex-1-ene-3,4-dicarboxylate **3**; ○, dimethyl pent-1-ene-3,4-dicarboxylate **5**

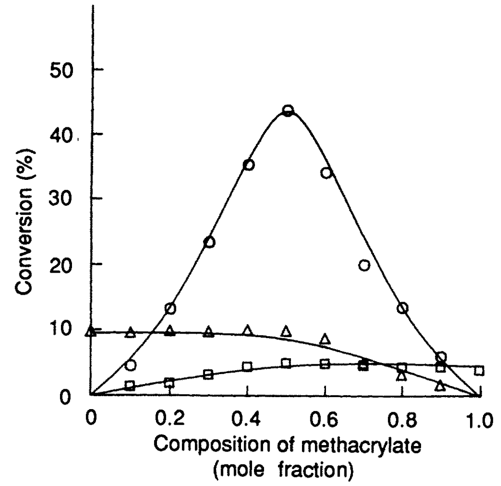


Fig. 2 Thermal dimerization of sodium methacrylate/crotonate at 230 °C for 2 h: □, dimethyl 4-methylpent-1-ene-2,4-dicarboxylate **2**; △, dimethyl hex-1-ene-3,4-dicarboxylate **3**; ○, dimethyl hex-1-ene-2,4-dicarboxylate **4**

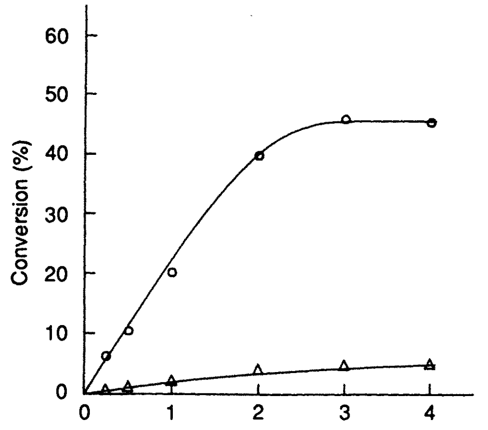


Fig. 3 Thermal dimerization of sodium acrylate/crotonate (equimolar mixture) at 230 °C: △, dimethyl hex-1-ene-3,4-dicarboxylate **3**; ○, dimethyl pent-1-ene-3,4-dicarboxylate **5**

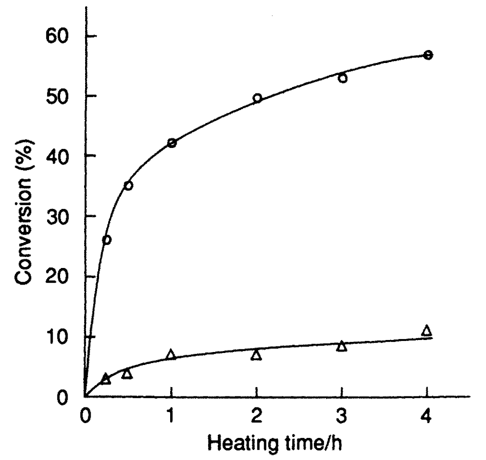


Fig. 4 Thermal dimerization of sodium acrylate/crotonate (equimolar mixture) at 250 °C: △, dimethyl hex-1-ene-3,4-dicarboxylate **3**; ○, dimethyl pent-1-ene-3,4-dicarboxylate **5**

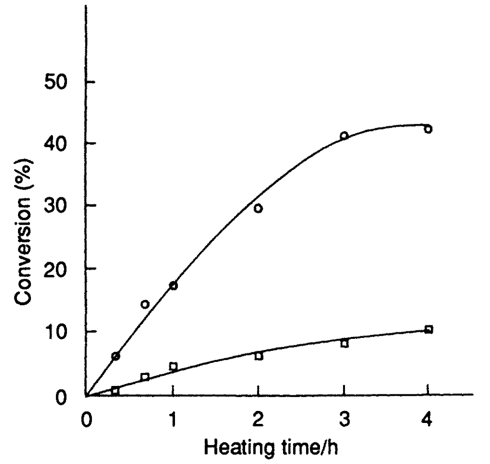


Fig. 5 Thermal dimerization of sodium methacrylate/crotonate (equimolar mixture) at 215 °C: □, dimethyl 4-methylpent-1-ene-2,4-dicarboxylate **2**; ○, dimethyl hex-1-ene-2,4-dicarboxylate **4**

from an equimolar mixture of two acids yields the cross-coupled dimer, pent-1-ene-3,4-dicarboxylate **5**, and CA dimer **3**. In the preceding paper, we have reported that Na(MA/CA) gave **4** as the major product, and **2** and **3** as minor products.[14] Here, we attempted the thermal reaction of binary salts in various compositions. The binary salts were heated and the products were converted to dimethyl esters. Conversions were determined by gas chromatography. Na(AA/CA) was heated at 250 °C for 2 h. As shown in Fig. 1, NaCA gave exclusively **3** in a 47.2% yield. The formation of **3** decreased with increasing AA content. Conversion to cross-coupled dimer **5** was the highest, *i.e.*, 51.4%, with the equimolar mixture. NaAA gave a small amount of polymer without dimers or trimers. Na(MA/CA) was heated at 230 °C for 2 h (Fig. 2). In this case, NaCA gave **3** in a 9.5% yield. A lower yield of **3** compared with those in Fig. 1 is attributed to the lower heating temperature. NaMA at 230 °C afforded predominantly polymers, with **2** in a 5.0% yield. As with Na(MA/CA), conversion to cross-coupled dimer **4** was highest with an equimolar mixture of MA and CA, *i.e.*, 48.1%.

Conversion of sodium salts derived from an equimolar mixture of AA/CA or of MA/CA was examined in relation to heating time. The results are shown in Figs. 3–6. In the case of Na(AA/CA) heated at 250 °C, conversion to **5** showed a rapid increase, reaching 35.2% in 0.5 h and 56.8% in 4 h. At 225 °C, however, the conversion to **5** increased linearly through 2 h and reached a plateau, *i.e.* 45.8%, in 3 h. This may be attributed to the lower thermal activation of the molecules in crystals at 225 °C. The formation of minor product **3** at 225 °C increased steadily with heating time, reaching 2.8% conversion after 4 h. At 250 °C, an 11% conversion was attained after 4 h.

In the case of Na(MA/CA) at 260 °C, the yield of **4** was as high as that of **5**, reaching 56.0% after 2 h, but then it decreased

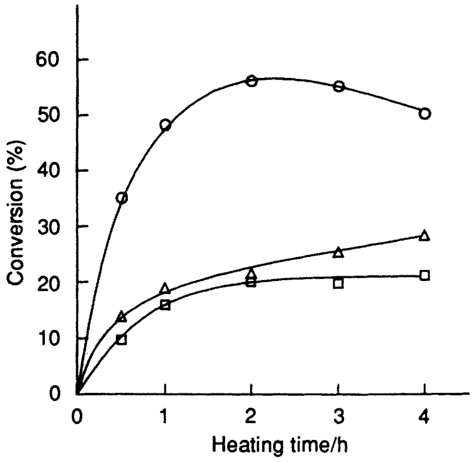


Fig. 6 Thermal dimerization of sodium methacrylate/crotonate (equimolar mixture) at 260 °C: □, dimethyl 4-methylpent-1-ene-2,4-dicarboxylate **2**; △, dimethyl hex-1-ene-3,4-dicarboxylate **3**; ○, dimethyl hex-1-ene-2,4-dicarboxylate **4**

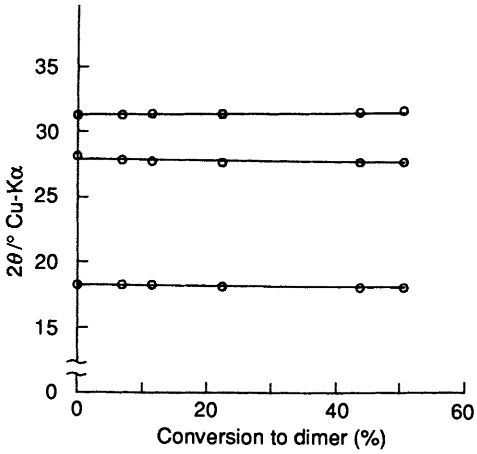


Fig. 7 Relationship between the conversion of acrylate/crotonate dimer and the peak (2θ) shift on X-ray diffraction. Dimerization at 225 °C.

gradually. The gradual decrease is due to polymerization of **4**; **5** having an allylic double bond is considered to possess less tendency to polymerize.

Heating of Na(MA/CA) gave at 215 °C a 41.2% yield for **4** after 3 h. Na(MA/CA) gave **2** and **3** as minor products. At 260 °C, heating for 2 h gave 21.2 and 20.1% conversions for **2** and **3**, respectively. Lowering of heating temperature to 230 and 215 °C increased the yield of **4** with total suppression of formation of **3**.

X-Ray Diffraction of Na(AA/CA) and Na(MA/CA).—The X-ray diffraction patterns of the 1 : 1 binary sodium salts of AA/CA and MA/CA were quite different from those of sodium salts of individual acids, suggesting that new phases are formed. When one of the acids was in excess, the diffraction pattern of its sodium salt overlapped the new pattern, indicating the crystals of the salt of the excess acid and those of 1 : 1 binary salts are present. Recently, Straughan *et al.*[15] reported that the crystals obtained from an initial equimolar mixture of zinc tiglate and benzoate had a 1 : 3 ratio of carboxylates. In the case of Na(AA/CA) or Na(MA/CA), their carboxylates in the crystal obtained by the recrystallization of the 1 : 1 binary salt were analysed to be of 1 : 1 composition.

The diffraction peaks of the binary salts gave slight shifts in the course of dimer formation. As shown in Figs. 7 and 8, the initial peaks at 2θ = 18.2, 28.0 and 31.2° for Na(AA/CA) shifted to 17.9, 27.7 and 31.4°, respectively, at 50.2% dimer formation.

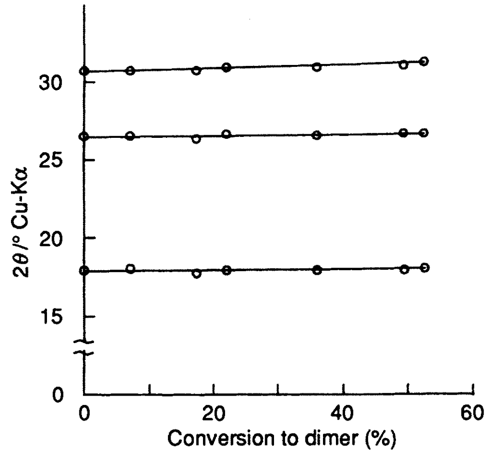
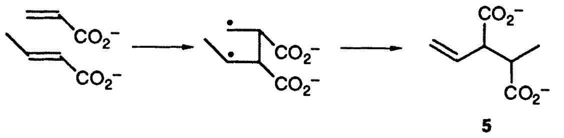


Fig. 8 Relationship between the conversion of methacrylate/crotonate dimer and the peak (2θ) shift on X-ray diffraction. Dimerization at 215 °C.

In the case of Na(MA/CA), peaks at 2θ = 17.9, 26.5 and 30.7° shifted to 18.0, 26.6 and 31.2°, respectively. These observations suggest formation of solid solution crystals between the unreacted starting material and the resulting dimers.

Formation of Cross-coupled Dimers **4** *and* **5**.—Each of the binary salts Na(AA/CA) and Na(MA/CA) consists of a new crystal form different from the salts of the individual acids. In the course of dimerization, the monomer salt forms a solid solution with the resulting dimer salts. Consequently, the crystal lattice is maintained throughout the dimer formation, leading to the high selectivity of **5** or **4** formation. The type of metal salts is a crucial factor in the formation of solid solution crystals. As reported in the preceding paper, among alkali and alkaline earth metal salts of MA/CA, only Na, K and Ba afforded **4**, and Na salt gave the highest selectivity. For the AA/CA binary system, these salts exhibited almost no selectivity toward the formation of **5**, except for the Na salt. Based on these results, the size of both the acid anion and the metal cation in the binary system crystal are of great importance in determining the selectivity toward the formation of cross-coupled dimers. The mechanism of cross dimerization through a biradical intermediate is proposed to be as shown in Scheme 1.



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Scheme 1

Experimental

Materials.—Na(AA/CA) and Na(MA/CA) were obtained by neutralizing a binary acid solution of a predetermined molar ratio with aqueous sodium hydroxide using phenolphthalein as an indicator. After distilling off the water completely, the obtained crystals were vacuum-dried at 50–60 °C over P_2O_5.

Thermal Reaction and Analysis of Products.—About 1 g of Na salt was loaded into a Pyrex tube (10 mm i.d. x 200 mm) and heated under reduced pressure in an oil bath. The heat-treated salt was weighed and dissolved in aqueous hydrochloric acid. The solution was extracted with diethyl ether, and the extracts were treated with diazomethane. The methyl ester products were analysed by gas chromatography with dimethyl malonate as an internal standard. Gas chromatography analysis of the crude esters (*e.g.* AA:CA = 1 : 1, 250 °C, 2 h; silicone SE-30 packing, 2 m × 3 mm i.d., 50→250 °C, 10° min^{-1}, N_2, 30 cm^3 min^{-1}) indicated the presence of two unreacted starting materials, two dimers and some inseparable oligomers in the ratio 1 : 10 : 40 : 7 : 12. The elution times of the two dimer products were 7.2 and 8.2 min. The minor dimer product was the methyl ester of **3**.

Isolation and Identification of Cross-coupled Dimers.—Na(AA/CA) derived from an equimolar mixture of acids (28 g) was heated at 250 °C for 2 h. The products were treated as described above. Crude methyl esters (20 g) were separated into four fractions by distillation. A fraction, b.p. 101–112/20 mmHg (9.9 g), was distilled again to afford dimethyl pent-1-ene-3,4-dicarboxylate (**5a**): m/z 186 ($M^{\bullet+}$), 155 ($M^{\bullet+}$ –OCH_3); δ_H(400 MHz; $CDCl_3$) 1.18 (3 H, d), 2.94 (1 H, m), 3.26 (1 H, t), 3.66 (3 H, s), 3.72 (3 H, s), 5.18 (2 H, d), 5.84 (1 H, dt); δ_C(67.8 MHz; $CDCl_3$) 15.19 (CH_2), 42.17 (CH), 51.69 (–OCH_3), 52.04 (–OCH_3), 53.51 (CH), 119.19 (=CH_2), 133.37 (=CH), 172.56 (C=O) and 174.44 (C=O).

Analysis of the Crystals Obtained from 1 : 1 *Binary Salts.*—The binary salts prepared from an equimolar mixture of two acids were recrystallized three times from methanol. The crystals obtained were converted by the above method to methyl esters which were analysed by gas chromatography and shown to consist of equimolar mixtures of two esters.

X-Ray Data.—X-Ray measurements were conducted on a powder X-ray diffractometer (Rigaku; horizontal-type goniometer). Conditions were as follows: target Cu-Kα, voltage 25 kV, current 10 mA, time constant 0.5 s, scanning speed 4° min^{-1}, slit SS 1°, RS 0.3 mm, DS 1°. Although the accuracy of 2θ was not checked as to its absolute value using an internal standard, errors due to sample setting were considered to be within ± 0.05°.

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