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Supplementary Material Available: Description of the X-ray diffraction experiment, tables of experimental data, atomic coordinates, thermal parameters, and bond distances and angles (24 pages); table of structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

Solid State Reactivity of Metal *trans*-2-Pentenoates

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Metals play an especial role in activating α,β-unsaturated carboxylic acids toward solid-state reactivity. Thus, irradiation (^{60}Co γ-rays) of solid metal propynoates leads readily to the corresponding polypropynoates;[1] factors such as the relative distance between the reactive centers, crystal lattice energy, and the absorption cross section of the materials for X- or γ-rays influence the reactivity of these materials.[2-4] Crystalline metal propynoates exhibit much higher reactivity than other solid organic acetylenes, even in cases where the alignment and proximity of the groups in the "all-organic" crystal are nearly ideal.[5-7] We know considerably less about the radiation-induced reactions of metal alkenoates, from both the points of view of the nature of the products and the criteria governing the reactivity of alkenoate salts. Thus, while γ-irradiation of potassium acrylate produces sodium corresponding polyacrylate,[8] γ-irradiation of sodium *trans*-2-butenoate (**1**) leads stereospecifically to *one of eight* possible diastereoisomers of trisodium 2,4-dimethyl-6-heptene-1,3,5-tricarboxylate.[9] Heating solid **1** converts it, by a unique ene reaction, to one of two possible diastereoisomers of disodium 1-hexene-3,4-dicarboxylate.[10] The unusual behavior of **1** suggested that a complete study of the reaction chemistry of other α,β-unsaturated alkenoates was in order. Accordingly, as part of a program to investigate the physical, chemical, and structural factors which influence the reactivity of solids, we synthesized a number of salts of *trans*-2-pentenoic acid (**2**). This communication reports our findings, viz., a new, well-defined, *general* solid-state oxidation reaction for metal *trans*-2-pentenoates.

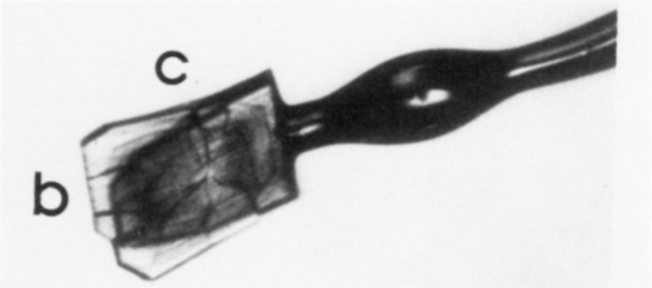

Figure 1. Crystal of **5**, mounted on a Pyrex fiber. Upon irradiation with Mo Kα X-rays, the crystal cleaved (along *bc* planes) into two pieces, as shown (magnification 65×).

Metal pentenoates (**3**; M = Li, Na, K, Mg, Ca, Sr, Ba, Zn, Cd, Pb) were synthesized by reaction of metal hydroxides and oxides with **2**, or by metathesis of the corresponding metal chlorides with sodium *trans*-2-pentenoate; single crystals of most materials were grown by slow evaporation of aqueous or MeOH–H$_2$O solutions. Samples of the metal pentenoates were placed in loosely capped vials and exposed to ^{60}Co γ-rays (72 Mrad) at room temperature.[11] A preliminary examination of the samples at this point revealed that reactions had occurred to a significant degree (17–84% conversion) in *all* of the materials. We did not anticipate this result, since the corresponding metal *trans*-2-butenoates do not show widespread sensitivity to ionizing radiation.[12] Inspection of the ^{1}H NMR spectra of solutions of the samples revealed another surprise: all spectra were qualitatively very similar. An analysis of the spectra showed that the major soluble product of the irradiation was a metal acetylacrylate (**4**); smaller amounts of acetate and formate were also observed. In some of the reactions, insoluble oligomers also appeared as products.

When metal alkynoates and other metal alkenoates are exposed to γ-rays in the presence of oxygen, detectable quantities of oxidation product are not observed.[2-4,8,9] When the metal pentenoates described here were irradiated in vacuo (72 Mrad), two patterns of behavior emerged: either (i) no reaction was detected [Li, Mg, Zn, Cd, Pb] or (ii) C–C bond formation occurred, leading to dimers [K] or complex mixtures of oligomers [Na, Ca, Sr, Ba]. All spectral evidence indicates that the acetylacrylate moiety does not form in the absence of air; this eliminates the carboxylate group and/or coordinated or hydrated water as possible oxygen sources.

To explore this process in greater detail, we investigated the behavior of single crystals of triaquabis(*trans*-2-pentenoato)calcium (**5**). The initial experiments, as described above, showed that the calcium salt produced both an acetylacrylate and an insoluble oligomer upon irradiation in air. In the absence of air, only the insoluble oligomer

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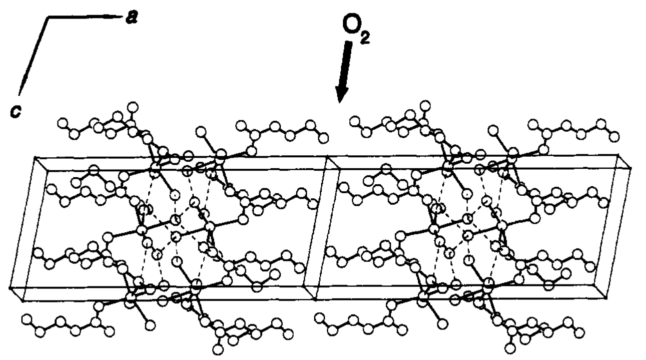

Figure 2. View of the crystal structure of **5**, showing hydrogen bonds between facially coordinated water molecules, facile cleavage direction, and likely pathway for the observed oxidation reaction.

is formed. Single crystals of **5** were grown from aqueous solution; two pristine crystals were mounted on glass fibers and were subjected to X-ray structural investigations. Since prior experience indicated that similar transformations are effected by X- and γ-rays, attempts were made to collect data as rapidly as possible, at a speed consistent with at least a reasonable level of precision. However, both crystals decomposed very rapidly in the X-ray beam (Mo Kα radiation, 45 kV, 17.5 ma), as determined by monitoring the intensities of three standard reflections. After 24–48 h, the crystals did not diffract X-rays. Inspection of each crystal under the microscope showed that it had split into two "halves" (Figure 1). As determined by diffractometric analysis, the radiation-induced cleavage and reaction had split the crystal along *bc* planes. The final X-ray structure determination reported here was carried out[13] on a third crystal which was mounted in a glass capillary; no degradation in standard intensities and no cracking or splitting of the crystal were observed throughout the data collection.

The contents of two unit cells of **5** are shown in Figure 2. The calcium ion has a distorted octahedral geometry, with *facial* coordination of the three water molecules. The remaining three oxygen atoms are derived from the two independent pentenoates. One pentenoate coordinates to the calcium ion in a monodentate fashion, while the other pentenoate bridges two calcium ions in an anti, syn fashion.[15] This bridging leads to a one-dimensional coordination polymer, along the crystal *c* axis (Figure 2). Given the highly anisotropic nature of the observed gas–solid reaction, we now turn our attention to the crystal *bc* planes. Inspection of Figure 2 reveals that, for pairs of coordination polymers packed along the *a* axis, the octahedral faces containing the three water molecules are directed toward one another. Thus, strong hydrogen bonds connect individual molecules along the coordination polymer and connect pairs of coordination polymers along *a*. The facially coordinated pentenoate moieties are thereby disposed on the opposite side; the hydrophobic tails of the pentenoates meet in crystal *bc* planes. Thus the geometrical propagation of this single-crystal reaction is the result of both the weak packing forces in *bc* planes, and the location of the methylene groups prior to oxidation. The other reaction which occurs in solid **5**—oligomer formation—is expected to occur, since there are short —C=C—···—C=C— contacts in the crystal structure (T–T′ interorbital distance = 1.58 Å).[16]

In conclusion, a set of new solid-state reactions has been discovered. One of the reactions, air oxidation of the pentenoate moiety to acetylacrylate, is a *general* reaction for all metal pentenoates. Pentenoate salts incorporating heavy metals show the greatest sensitivity to ionizing radiation; this pattern is similar to that seen for the polymerization of metal propynoates. The production of acetylacrylate may occur by a mechanism similar to those proposed for the oxidation of polymers;[17] this interesting possibility merits further study. Important experiments by Schmidt and Cohen[18] demonstrated how the solid state can control product stereochemistry and/or distribution, while the work of Curtin, Paul, and others[19] showed how the fixed environment of the solid state could be used to advantage in gas–solid reactions. The introduction of a metal, with its influence on the structure and reactivity of solids, provides an opportunity to exploit both phenomena in a *single* class of materials. As an example, the most efficient production of acetylacrylate, in the absence of oligomeric products, would follow from irradiation of a finely divided, heavy metal pentenoate (e.g., Pb), with no short —C=C—···—C=C— contacts in its crystal structure. On the other hand, oligomeric products would be prepared readily by irradiation of appropriate phases (e.g., Ca, K) in vacuo. Further details of the relationship between structure, products, and physical changes in solid metal pentenoates will be probed in future studies.

Acknowledgment. We are grateful to Professor B. B. Snider for helpful discussions and to the National Science Foundation (DMR-8812427) for the support of this research.

Supplementary Material Available: Detailed experimental procedure for preparation of compounds **2–5**, tables I through IV, listing experimental detail for the X-ray structure determination, all coordinates, bond lengths and angles (9 pages); tables of observed and calculated structure amplitudes for **5** (9 pages). Ordering information is given on any current masthead page.

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[13] Crystals of **5** are monoclinic, space group $P2_1/c$, $a = 19.973$ (6), $b = 8.547$ (3), $c = 9.004$ (3) Å; $\beta = 100.30$ (3)°; $Z = 4$. Data were collected to a maximum $2\theta(\lambda_{\mathrm{MoK}\alpha}) = 45°$. Operations were carried out as described previously;[14] a complete experimental report is available as supplementary material. Methyl carbon atoms on each of the two independent pentenoate moieties were disordered in a 7:3 ratio; the disorder was successfully resolved in the refinement of the structure. Full-matrix least-squares refinement of positional and anisotropic displacement parameters for all atoms (isotropic displacement parameters for methyl C atoms and H atoms, total parameters = 185) led to $R = 0.064$ and $R_w = 0.056$, using 1130 data for which $I > 1.96\sigma(I)$.

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