with chemical reversibility. The peak separations for the second oxidation is slightly higher (70–100 mV) but similar to the separation observed with FeCp$_2$ (E_{pa} = 0.59 V, ΔE = 70 mV). The i_{pa} values scale linearly with the square root of the sweep rate as expected for a diffusion-limited reaction. Chronocoulometry for the first reaction showed a linear q vs $t^{1/2}$ dependence. For VII, D is 1.2 × 10^{-5} cm^2/s, and n is 1.04 for the first oxidation, where n is obtained from a comparison of $nD^{1/2}$ from the slope in the q vs $t^{1/2}$ plot with $n^{3/2}D^{1/2}$ from the slope in the i_{pa} vs $v^{1/2}$ plot. With this same procedure, n equal to 0.99 was obtained with ferrocene. For the second oxidation, n equal to ca. 1 was obtained from the relative slopes in the q vs $t^{1/2}$ plots for steps anodic of the first and the second wave, respectively. Similar values were obtained for V. The ca. 0.2-V separation between the two waves parallels the separation observed with unsubstituted polythiophene films[4] and those containing alkoxy[5,6] and methyl[8-10] groups. The second oxidation is irreversible with the timer III and not visible with the dimer II. Thus four or more thiophene units are required to stabilize the dication at room temperature.

The E_{pa} values for the five oligomers in Table I plot linearly with both 1/(the number of rings) with slope 1.7 and with the band edge in the visible spectrum of the neutral oligomer with slope 0.57. The corresponding slopes for the unsubstituted series are 1.5 and 0.52, respectively.[28] Thus in solution, the methyl groups do not affect the π-conjugation in the monotonically increasing segments as is observed with other substituents,[29] and the α-TMS group is known to have a small effect on the redox potential.[30]   The VII and V dications support 0.3–0.4 charges/ring, which compares well with the stable oxidation level (average) of 0.06–0.35 charges/ring for polythiophene films.[1,2,8,31-36]

Chemical oxidation[13,17,18] of V and VII with 2 mol of FeCl$_3$ yields the radical cation as evident by the strong signal in the ESR spectrum with g = 2.004 which almost vanishes upon further oxidation with an additional 2 mol of FeCl$_3$. Therefore, the two oxidation waves observed electrochemically correspond to the successive formation of the radical cation and dication. Concurrent with the evolution of the ESR signal is a dramatic change in the vis/near-IR spectra. The absorption at 447 nm for the neutral VII disappears upon oxidation to the radical cation and double peaks appear at 745 and 829 nm and at 1427 and 1785 nm (blue) in line with previous reports.[13,17,18] The radical cation is stable at room temperature for at least several hours. Further oxidation to the dication changes the absorption spectrum, and only peaks at 1064 and 1230 nm are observed. Similar changes are observed in the spectra for the pentamer except that the absorptions are blue shifted. Finally, III can be oxidized to the radical cation which has a strong ESR signal (g = 2.004) and shows two major peaks at 557 and 878 nm in the vis/near-IR spectrum.

In summary, the stepwise oxidation to form the stable radical cation and dication can be accomplished at room temperature with thiophene oligomers containing four or more units. The ca. 0.2-V separation between the first and second oxidation suggests that two separate oxidation waves should be visible in the room-temperature voltammogram for the next higher oligomers and for the π-conjugated segments of polythiophene. This is in marked contrast with the conclusion that conducting polymers are expected to be oxidized in one broad single step.[11,37-39] The broad, featureless voltammograms observed with the polythiophene films may not be an inherent property of the polymer segments but instead may reflect the complications caused by irregular couplings,[21] molecular weight distributions,[22] lattice interactions,[23] film capacitance,[24,25] and resistance.[26]

(37) Heinze, J. Mortensen, J.; Mullen, K.; Schenk, R. *J. Chem. Soc., Chem. Commun.*, 1987, 701.

(38) Meerholz, K.; Heinze, J. *Angew. Chem., Int. Ed. Engl.* 1990, 29, 692.

(39) Gale, D. C.; Gaudiello, J. G. *J. Am. Chem. Soc.* 1991, 113, 1610.

Condensed Aryl-Bridged Siliconates. New Ladder and Network Ionomers

K. J. Shea,* D. A. Loy, and J. H. Small

*Department of Chemistry
University of California, Irvine
Irvine, California 92717*

Siliconates have been implicated as intermediates in many nucleophilic substitution reactions at silicon.[1-8] Coordination to silicon by electron-withdrawing (fluoride) and chelating (catechol) groups can result in the formation of *stable* five- and six-coordinate siliconates. Structural data for these complexes have been reviewed.[9] It is in-

(28) Diaz, A. F.; Crowley, J.; Bargon, J.; Gardini, G. P.; Torrance, J. B. *J. Electroanal. Chem.* 1981, 121, 355.

(29) Leclerc, M.; Daoust, G. *J. Chem. Soc., Chem. Commun.* 1990, 273.

(30) Lemaire, M.; Buchner, W.; Garreau, R.; Hoa, H. A.; Guy, A.; Roncali, J. *J. Electroanal. Chem.* 1990, 281, 293.

(31) Tourillon, G.; Garnier, F. *J. Electroanal. Chem.* 1982, 135, 173.

(32) Colaneri, N.; Nowak, M.; Spiegel, D.; Hotta, S.; Heeger, A. J. *Phys. Rev. B* 1987, 36, 7964.

(33) Chung, T.-C.; Kaufman, J. H.; Heeger, A. J.; Wudl, F. *Phys. Rev. B* 1984, 30, 702.

(34) Nagatomo, T.; Omoto, O. *J. Electrochem. Soc.* 1988, 135, 2124.

(35) Tourillon, G.; Garnier, F. *J. Phys. Chem.* 1983, 87, 2289.

(36) Jugnet, U.; Tourillon, G.; Duc, T. M. *Phys. Rev. Lett.* 1986, 56, 1862.

(1) Holmes, R. R. *Chem. Rev.* 1990, 90, 17.

(2) Corriu, R. J. P.; Guerin, C. *Adv. Organomet. Chem.* 1982, 20, 265.

(3) (a) Corriu, R. J. P.; Guerin, C.; Moreau, J. J. E. *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley, New York, 1989; Part 1, pp 305–307. (b) Corriu, R. J. P.; Young, *Ibid.*; Part 2, pp 1241–1288.

(4) Fleming, I. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, D. W., Eds.; Pergamon Press: Oxford, 1979; *Vol. 3*, p 555.

(5) (a) Corriu, R. J. P.; Guerin, C.; Moreau, J. J. E. *Top. Stereochem.* 1984, 15, 43. (b) Johnson, S. E.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* 1989, 28, 3182. (c) Johnson, S. E.; Payne, J. S.; Day, R. O.; Holmes, J. M.; Holmes, R. R. *Inorg. Chem.* 1989, 28, 3190. (d) Damraver, R.; O'-Connell, B.; Denahey, S. E.; Simon, R. *Organometallics* 1989, 8, 1167.

(6) Shklover, V. E.; Struchkov, Yu, T.; Voronkov, M. G. *Russ. Chem. Rev.* 1989, 58, 211.

(7) Johnson, S. E.; Deiters, J. A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* 1989, 111, 3250.

(8) Sakurai, H. *Selectivities in Lewis Acid Promoted Reactions*; Schinzer, D., Ed.; Kluwer: Dordrecht, Holland, 1989; p 203.

(9) For a review of the electronic and molecular structure of penta- and hexacoordinate silicon compounds, see: Tandura, S. N.; Voronkov, M. G.; Alekseev, N. V. *Top. Stereochem.* 1986, 131, 99.

teresting that the occurrence of siliconates in nature is rare and confined to minerals created under extreme conditions. Stishovite, a polymorph of quartz thought to be formed during meteoric impacts, is one such example.[10]

Synthetic materials that embody hypervalent silicon are limited to siloxane–phthalocyanines,[11] a remarkable family of linear polymers with unique optical and electrical properties. The stability of five- and six-coordinate silicon catecholates[9] make them potential building blocks for *ionomeric materials*. In this communication, we report the synthesis of aryl-bridged siliconates, the first representatives of novel ionomeric materials that contain five- and six-coordinate silicon.[12]

Model compounds for these new materials were prepared by the condensation of catechol with (triethoxysilyl)benzene and tetraethoxysilane (TEOS) in the presence of triethylamine affording penta- and hexacoordinate siliconates 1[13] and 2.[14] Similarly, the first aryl-bridged

1

2

3

bis-siliconate 3 was obtained from the reaction of 1,4-bis(triethoxysilyl)benzene[15] with catechol. An X-ray crystal structure of 3[16] reveals two pentacoordinate silicons, each chelated by two catecholate groups. The silicons

occupy a distorted trigonal-bipyramidal geometry[17] with the phenyl group occupying an equatorial position.

These procedures have been adapted for the preparation of linear oligomeric/polymeric and network materials incorporating five- and six-coordinate anionic silicon as part of the backbone. The first representative, a linear ladder structure (5, Scheme I) was prepared by condensation of (triethoxysilyl)benzene with 1,2,4,5-tetrahydroxybenzene (THB), 4,[18] and triethylamine in THF. A precipitate (73%) formed within several hours. The material 5, which darkened upon standing in air, was soluble in DMSO, solutions of which were used for subsequent characterization.

The ^{1}H NMR of 5 revealed phenyl-1,2,4,5-tetraoxobenzene and triethylammonium resonances in a ratio consistent with the assigned structure.[19,20] The ^{29}Si NMR spectra of 5 revealed at least four resonances clustered between −85.1 and −87.2 ppm. The model for this material, siliconate 1, exhibits [29]Si absorption at −87.5 ppm. The ^{13}C NMR spectra exhibited absorptions in the positions expected for the siliconate structure 5 including the triethylammonium ion. The IR spectrum of 5 (solution and solid) revealed strong absorptions at 1489 and 881 cm^{-1}, analogous to those found in model siliconate 1. Absorptions for EtO–Si or Si–O–Si bonds between 1000 and 1100 cm^{-1} are negligible.

The condensation of THB (4) with 1,4-bis(triethoxysilyl)benzene (6) and with TEOS results in five- and six-coordinate extended networks 7 and 8 (Scheme II). In the reaction of 6 with THB (4) and triethylamine in diglime at 100 °C, a slightly orange precipitate was found within 30 min (93%).[21] A portion of the material was soluble in DMSO, indicating a fraction contained oligomeric or only partially condensed ionomers. The DMSO soluble fraction was characterized by a combination of ^{1}H, ^{13}C, and ^{29}Si NMR techniques. The ^{29}Si NMR spectra of the phenyl-bridged polysiliconate 7 included resonances between −85.3 and −87.2 ppm[22] characteristic of five-coordinate silicon, along with minor resonances at −59.9 ppm attributed to unreacted ethoxysilyl groups. Most importantly, the ^{29}Si CP/MAS NMR of the solid sample 7 (3 ms contact time, 2500 Hz) revealed the major silicon resonance at −85.9 ppm with a shoulder at −77.5 ppm. No signals above the baseline corresponding to tetracoordinate Si were observed. ^{1}H NMR of the DMSO soluble fraction reveals the expected absorption from the triethylammonium ion (2.96, 1.06 ppm) and an aromatic region comprised of broad resonances from the THB residue (6.03 ppm) and the bridging phenyl group (7.30 ppm). (These values are shifted from those of the starting materials.) Also found are resonances between 3.4 and 3.8 ppm due to residual ethoxysilyl groups. The NMR results coupled with the fact that the ratio of integrals of the phenyl-bridge hydrogens to the THB residue was greater than 1:1 (1.5:1) suggest that the DMSO soluble fraction has undergone only incomplete condensation. The IR spectra of the solid,

(10) (a) Thomas, J. M.; Gonzales-Calbert, J. M.; Fyfe, C. A.; Gobbi, G. C.; Nicol, M. *Geophys. Res. Lett.* 1983, *10*, 91. (b) Edge, R. A.; Taylor, H. F. W. *Nature* 1969, *224*, 363.

(11) Marks, T. J. *Angew. Chem., Int. Ed. Engl.* 1990, *29*, 857 and references therein.

(12) After submission of this paper, related reports of five-coordinate siliconate building blocks appeared. (a) Laine, R. M.; Blohowiak, K. Y.; Robinson, T. R.; Hoppe, M. L.; Nardi, P.; Kampf, J.; Uhm, J. *Nature* 1991, *353*, 642. (b) Youngdahl, K. A.; Nardi, P.; Robinson, T.; Laine, R. M. *NATO ASI Ser. E: Appl. Sci.*; Laine, R. M., Ed.; Kluwer: Dordrecht, Holland, 1991; Vol. 206, pp 99–114.

(13) Rosenheim, A.; Baibmann, B.; Schendel, G. *Z. Anorg. All. Chem.* 1931, *196*, 160.

(14) Frye, C. L. *J. Am. Chem. Soc.* 1964, *86*, 3170.

(15) (a) Shea, K. J.; Loy, D. A.; Webster, O. W. *Chem. Mater.* 1989, 512. (b) Shea, K. J.; Loy, D. A.; Webster, O. W. *J. Am. Chem. Soc.*, in preparation.

(16) X-ray diffraction data for $C_{42}H_{52}N_2O_8Si_2$: The crystals belong to the monoclinic system with unit cell parameters at 183 K: a = 8.1952 (14) Å, b = 16.135 (4) Å, c = 15.308 (3) Å, β = 105.152 (15)°, and V = 1953.9 (7) Å^3. The space group is $P2_1/c$ with Z = 2 formula units/unit cell and D_{calcd} = 1.31 Mg/m^3. Intensity data (2899 total) were collected on a Siemens R3m/V diffractometer system using monochromatized Mo Kα radiation (λ = 0.710730 Å) via a θ–2θ scan technique.[15a] Those 2107 reflections with $|F_o| > 2.0\sigma(|F_o|)$ were considered observed. The structure was solved by direct methods and refined by full-matrix least-squares techniques.[15b] Hydrogen atoms were included using a riding model with fixed isotropic U values. At convergence, R_F = 6.9%, R_{wF} = 6.9%, and GOF = 1.41 for 245 variables. A final difference-Fourier map was featureless. See also the supplementary material for a description of the X-ray diffraction experiment, tables of experimental data, atomic coordinates, thermal parameters, distances and angles, and structure factor amplitudes. (a) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* 1977, *16*, 265–271. (b) UCLA Crystallographic Computing Package, University of California, Los Angeles, 1981, C. Strouse, personal communication. (c) SHELXTL PLUS Program Set; Siemens Analytical X-ray Instruments, Inc.; Madison, WI, 1989.

(17) Boer, F. P.; Flynn, J. J.; Turley, J. W. *J. Am. Chem. Soc.* 1968, *90*, 6973.

(18) Prepared by reduction of 2,5-dihydroxybenzoquinone with Sn in concentrated HCl. (a) Weider, P. R.; Hegedus, L. S.; Asada, H.; D'Andreq, S. V. *J. Org. Chem.* 1985, *50*, 4276. (b) Jackson, C. L.; Beggs, S. A. *J. Am. Chem. Soc.* 1914, *36*, 1210.

(19) Experimental details for the synthesis and characterization of the siliconates is included in the supplementary material.

(20) A preliminary viscosity measurement of 5 in DMSO as determined by dilution viscometry; [N] = 0.045 dL/g,[18] suggests that the material may be oligomeric (or cyclic).
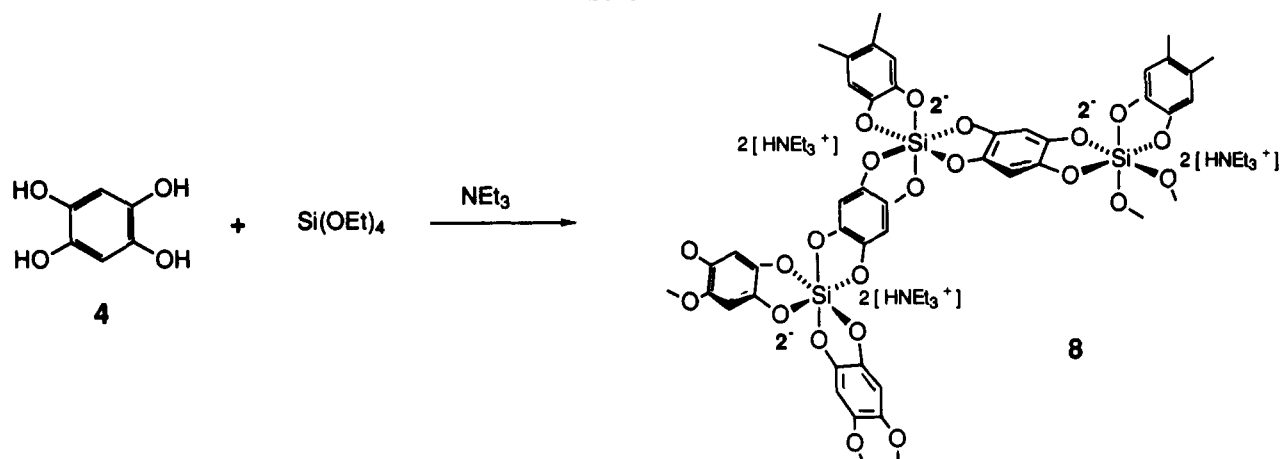
(21) The orange and red hues presumably arise from air oxidation of residual dihydroxyaryl moieties in the material to benzoquinone species.

(22) Cella, J. A.; Cargioli, J. D.; Williams, E. A. *J. Organomet. Chem.* 1980, *186*, 13.

Communications

Chem. Mater., Vol. 4, No. 2, 1992 257

Scheme I

5

7

Scheme II

8
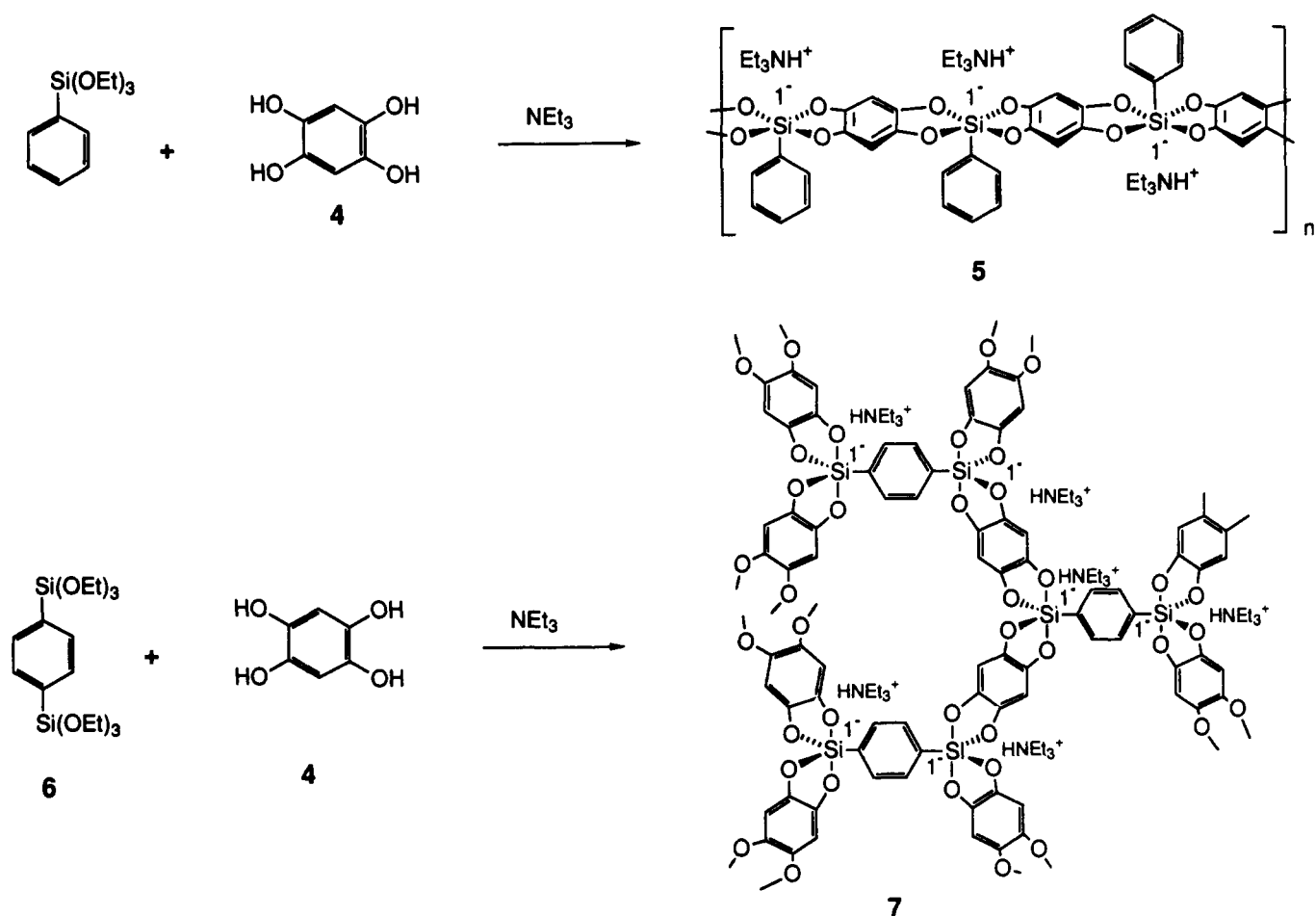
however, exhibits major absorptions similar to the model bis-siliconate **3**.

Hexacoordinate siliconates were prepared from TEOS and THB (**4**) with triethylamine in EtOH (73%). The material was quite air-sensitive. Key diagnostics included the hexacoordinate siliconate at –135 ppm in addition to minor absorptions due to tetrahedral species at –92 to –98 ppm. On the basis of the solubility behavior (partially soluble in DMSO) and NMR data, the condensation process was prematurely halted before complete formation of a network material due to lack of solubility or formation of cyclic oligomers.

These materials represent some of the first examples of synthetic ionic penta- and hexacoordinate siliconates. The

penta- and hexacoordinate states of silicon are characterized by an extremely low barrier to pseudorotation.[5,23] In addition, siliconates may dissociate to the neutral tetracoordinate state. The consequences of these characteristics as they relate to the properties of the bulk material make these compounds particularly interesting candidates for study. Furthermore, the new class of aryl-bridged polysiliconates possesses the capacity for systematic modification by varying the length and nature of the aryl spacer.[15] We are currently synthesizing these derivatives and investigating the morphology of these materials.

(23) Carre, F.; Cerveau, G.; Chuit, C.; Corriu, J. P.; Reye, C. *Angew. Chem., Int. Ed. Engl.* 1989, *28*, 489.

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

Li Di and Bruce M. Foxman*

Department of Chemistry, Brandeis University
P.O. Box 9110, Waltham, Massachusetts 02254-9110
Received January 8, 1992
Revised Manuscript Received February 10, 1992

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.
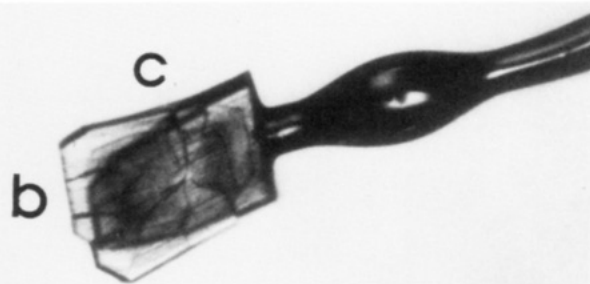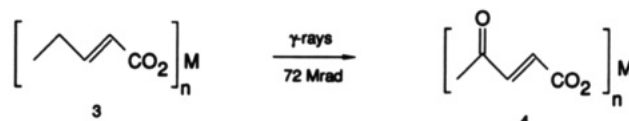

Figure 1. Crystal of 5, mounted on a Pyrex fiber. Upon irradiation with Mo Kα X-rays, the crystal cleaved (along bc planes) into two pieces, as shown (magnification 65×).

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.

$$\left[\diagdown\diagup\diagdown CO_2 \right]_n M \xrightarrow[\text{72 Mrad}]{\gamma\text{-rays}} \left[\diagup\!\!\!\!\overset{O}{\diagdown}\!\!\diagdown CO_2 \right]_n M$$

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

(1) Davydov, B. E.; Krentsel, B. A. *Adv. Polym. Sci.* **1977**, *25*, 1.
(2) Foxman, B. M.; Jaufmann, J. D. *Mol. Cryst. Liq. Cryst.* **1984**, *106*, 187.
(3) Booth, C. A.; Foxman, B. M.; Jaufmann, J. D. In *Crystallographically Ordered Polymers*; Sandman, D. J., Ed.; ACS Symposium Series 337; American Chemical Society: Washington, DC, 1987; pp 95–105.
(4) Brodkin, J. S.; Foxman, B. M. *J. Chem. Soc., Chem. Commun.* **1991**, 1073.
(5) Sandman, D. J.; Hamill, G. P.; Samuelson, L. A.; Foxman, B. M. *Mol. Cryst. Liq. Cryst.* **1984**, *106*, 199.
(6) Sandman, D. J.; Velazquez, C. S.; Hamill, G. P.; Preses, J. M.; Weston, Jr., R. E.; Foxman, B. M. *Mol. Cryst. Liq. Cryst.* **1988**, *156*, 103.
(7) Wheeler, K. A.; Foxman, B. M. *Mol. Cryst. Liq. Cryst.* **1992**, *211*, 347.
(8) Morawetz, H.; Rubin, I. D. *J. Polymer Sci.* **1962**, *57*, 669.
(9) Delgado, G. C. D.; Wheeler, K. A.; Snider, B. B.; Foxman, B. M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 420.
(10) Naruchi, K.; Tanaka, S.; Yamamoto, M.; Yamada, K. *Nippon Kagaku Kaishi* **1983**, 1291; *Chem. Abstr.* **1983**, *99*, 195488q. Naruchi, K.; Miura, M. *J. Chem. Soc., Perkin Trans. 2* **1987**, 113.

(11) A Gammacell 220 irradiation chamber (Atomic Energy of Canada, Ltd.) equipped with a ^{60}Co source was used for all γ-irradiation experiments. The nominal activity of the source as of Dec 1, 1991 was 0.0403 Mrad/h. All experiments were carried out under constant-irradiation conditions.
(12) (a) Foxman, B. M.; Delgado, G. C. D., unpublished observations. (b) Clegg, W.; Little, I. R.; Straughan, B. P. *J. Chem. Soc., Chem. Commun.* **1985**, *73*; *J. Chem. Soc., Dalton Trans.* **1986**, 1283; *Acta Crystallogr., Sect C: Cryst. Struct. Commun.* **1986**, *42*, 919, 1319; *Inorg. Chem.* **1988**, *27*, 1916. Clegg, W.; Harbron, D. R.; Homan, C. D.; Hunt, P. A.; Little, I. R.; Straughan, B. P. *Inorg. Chim. Acta* **1991**, *186*, 51.