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Thermal Decomposition of Cholesteryl Oleyl Carbonate

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Abstract—Cholesteryl oleyl carbonate decomposes spontaneously, above its melting point, to liberate CO_2 independently of the atmosphere. In the presence of O_2, CO is evolved in appreciable quantities due to oxidative attack which probably occurs at the olefinic bonds.

The stability of cholesteric liquid crystals has been the object of little investigation.(1,2) O'Connor and Nace(1) pyrolyzed cholesteryl ester carbonates and xanthates above 150 °C, and showed that decomposition occurred by a first order reaction, possibly via a concerted 6-membered ring intermediate.

Most of the other work has been directed towards examining the effects of various environments upon the performance of liquid crystals as sensors in electro-optical devices. These sensors contained cholesteryl oleyl carbonate (OCC) and preliminary experiments indicated that this material decomposes to liberate CO_2 even at room temperature. However, it is necessary to include OCC in the materials used in these sensors in order to have a sensor which can be used at room temperature. The field-sensitive component of these sensors, cholesteryl chloride (CC), has a crystal-liquid crystal transition at 96°. Above this temperature, CC decomposes to liberate an acidic vapor, presumably HCl. Hence, the lowering of the liquid crystal range by OCC is also presumed to reduce or prevent the CC decomposition.

The effect of prolonged use of this material at 39 °C has now been investigated *in vacuo*, in oxygen (a radical source), and in nitric oxide (a radical inhibitor). This temperature was chosen as being close to that to which the sensor would be exposed in use.

The OCC (obtained from Eastman Chemicals) was recrystallized from methanol until differential thermal analysis (DTA) showed only two transition points above − 10 °C. Before recrystallization, endothermic peaks were obtained at 2.5°, 7.5°, and 17° on heating. After recrystallization, only two endotherms were obtained at 17.5° and 33°. The material was then stored in a refrigerator until used.

Samples of the material (*ca.* 0.1 g) were weighed into glass boats which were placed in glass tubes (12.0 cm × 1.0 cm I.D.) having a break seal at one end and a sealing constriction at the other. Each tube was attached to a vacuum line and degassed at *ca.* 10^{-4} torr (measured with a McLeod gauge) for approximately 1 hour. Some tubes were then sealed under vacuum, others filled with oxygen or nitric oxide to about 17 mm Hg and then sealed. The tubes were aged in the dark at 39° ± 1 °C. Duplicate samples were removed every 3 weeks and sealed to a manifold inlet attached to a mass spectrometer (CEC 21–103C). The break seal was opened and the gases evolved during the heating period were analyzed. The partial pressures of CO and CO_2 liberated were calculated from the peak intensities of m/e 28 and 44. From the perfect gas law, the numbers of moles of CO and CO_2 evolved from each sample were determined. The amount of CO_2 liberated in the various atmospheres was plotted, as a percentage of the sample weight, against time of aging. Least squares analysis of the data gave a straight line, as shown in Fig. 1.

This graph indicates that the rate of thermal decomposition of OCC is independent of the environment, agreeing with O'Connor's(1) findings. Obviously, decomposition must be occurring at the carbonate linkage for CO_2 to be produced in the presence of NO or in a vacuum.

In the presence of O_2, oxidative decomposition occurs at other sites liberating CO, this being the predominant reaction. Figure 2 shows the evolution of CO, as a percentage of the sample weight, plotted against aging time. The results of duplicate tests for CO evolution (circles) and oxygen consumption (squares) are shown with the evolution of CO_2 (dotted line) for comparison. The behavior of the graph can be explained by considering an initial induction period followed by rapid evolution of CO. Termination of this evolution coincides with total consumption of the O_2.

The most likely points of oxidation to produce CO are the olefinic bonds (one each in the cholesteryl and oleyl moieties). Significantly, no CO was produced in the presence of NO. Analysis of N_2/Ar ratios

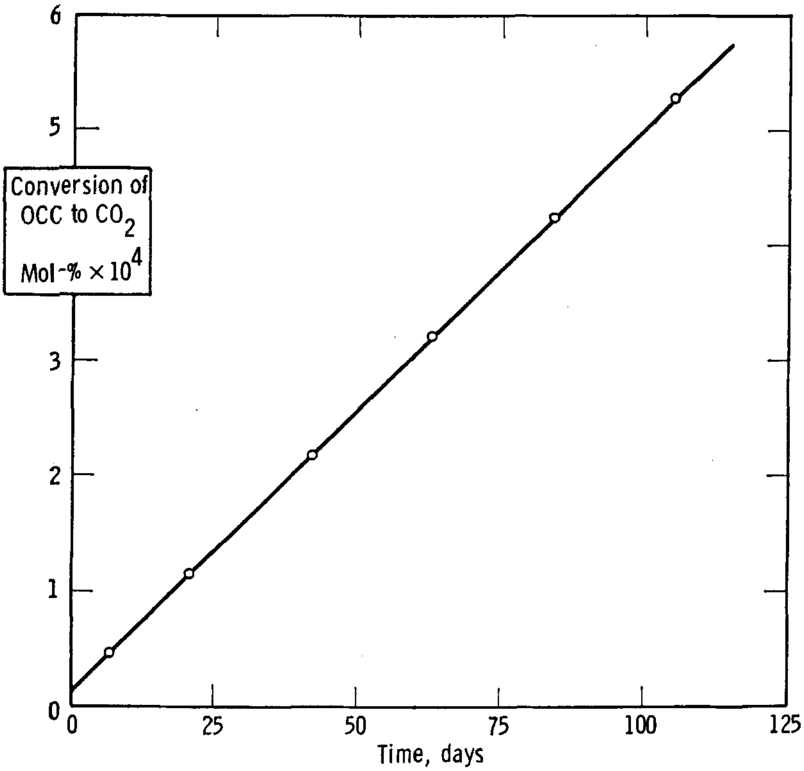

Figure 1. Evolution of carbon dioxide on aging cholesteryl oleyl carbonate.

show that traces of air had been retained in the OCC samples aged *in vacuo*; this accounted for small amounts of CO among the volatile products.

The most important conclusion to be obtained from this work is that OCC, in the liquid crystal or liquid states, will decompose spontaneously whatever its environment. This rate of decomposition is small; *in vacuo* it is of the order of 1×10^{-5} mol% OCC per day, to give a variety of volatile products. Even so, this rate is still too large to allow this material to be used as the principal sensor in an evacuated chamber such as an electron beam device, where the upper pressure limit is about 10^{-6} torr, unless the device is continuously evacuated.

On the other hand, decomposition in an O_2 atmosphere can be considerable. Appreciable quantities of this gas are retained by the

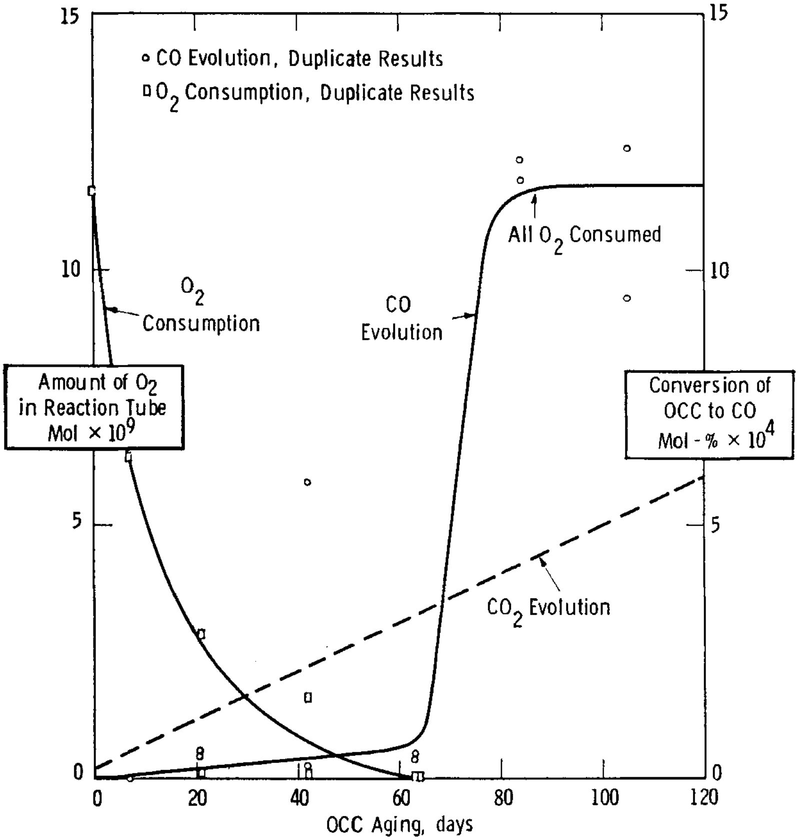

Figure 2. Evolution of carbon monoxide from cholesteryl oleyl carbonate aged in oxygen.

substrate at 39 °C as non-volatile oxidation products and relatively large volumes of CO are evolved as a consequence of this process.

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