



Figure 1. High pressure sample container

EXPERIMENTAL

Apparatus. The apparatus consists of a differential thermal analyzer Model 12BC2, recorder-controller assembly Model JAC, and furnace platform assembly Model GS-2, manufactured by the Robert L. Stone Co. A separate recorder, which records furnace temperature, in conjunction with an L and N Series 60 linear temperature programmer is an integral part of the instrument.

The apparatus is equipped with an L and N Speedomax G, dual-pen recorder and two ARA Model 4A-DC amplifiers which are necessary because the system contains dual differential thermocouples. A sensitivity of 300 μv . (37.5° C.) full scale was utilized for all experiments unless specifically marked on the thermograms.

The sample holder assembly, Model SH-M4BL, consists of a hollow Inconel block containing ceramic cores in which two separate Pt/Pt-10% Rh differential thermocouples have been placed. A Chromel-Alumel furnace couple is used for programming as well as recording the temperature of the furnace. Only one of the two differential thermocouples was utilized in the following experiments. A quick-cool furnace, Model F-1-F, positioned over the sample holder by two guide pins, was utilized throughout. This instrumentation, including amplifiers, furnaces, sample holders, etc., has been fully described (21).

The small Inconel cups in which the sample is placed contain a recess which fits over the thermocouple so that the thermocouple is not in actual contact with the sample. The sample containers are normally prepared from two sections which are subsequently pressed

into a single container. This type of sample container would not allow pressure studies.

Since it was impossible to study systems of interest requiring high pressures, suitable modification of the sample containers was necessary and a closed system was needed to prevent sublimation before temperatures of interest could be achieved.

A sample container was designed to be formed from Inconel 702, for maximum heat transfer, and to withstand pressures up to 3000 p.s.i.g. Every effort was made to keep the total mass to a minimum in order to ensure maximum heat transfer. The sample cup portion of the high pressure container itself is very similar in design to the original, except for wall dimensions. The thicknesses required, together with other details of the single machined container to withstand pressures up to 3000 p.s.i.g. at 500° C., are shown in Figure 1.

A $1/16$ - to $1/8$ -inch 316 stainless steel Swagelok union, which had the threads of the $1/8$ -inch end removed, was pre-drilled to pass $1/16$ -inch tubing completely through the center. This part was silver-soldered to the sample cup which had been machined from bar stock.

An 18-inch piece of $1/16$ -inch 316 stainless steel tubing was attached to the sample container with a standard Swagelok fitting. Attached to the other end was a stainless steel Tee fitting. A high pressure stainless steel micro ball valve was connected to one end of the Tee and a 0- to 3000-p.s.i.g. pressure transducer (Model 70-M2244S) manufactured by the International Resistance Co. was connected to the other end.

This configuration allowed the system to be easily pressurized at known values after sample loading, and vapors to be removed after a run into a chromatographic column for subsequent analysis.

The tubing connecting the sample container with the valve and pressure transducer was maintained at approximately 150° C. to prevent condensation of any liquid components that volatilized during the analysis. The total volume of the closed system was 5.67 cc. Care was taken to maintain a reasonable volume that would allow for expansion of any gases formed during the analysis without creating a system approaching the parameters of a bomb, since the rate of energy release must be considered.

The sample containers were balanced by weight and symmetry, so that inert reference material was not required for the sensitivities employed. This procedure provided an acceptable base line. The "blank" base line produced on a thermogram with both reference and sample containers in place, but without sample, was evaluated after every two to three runs to aid in correct interpretation of subsequent thermograms.

The samples were introduced into the containers by means of a glass capillary or as a fine powder with a small spatula. Both techniques were employed in this study. Any residue remaining after the run was removed by taking the sample container to red heat and subsequently treating with acid.

RESULTS AND DISCUSSION

All samples were programmed at a linear rate of 10° C. per minute from ambient temperatures. The transition temperature in this type of system—e.g., boiling, sublimation, etc.—is the temperature at which deviation from the base line is observed and not the peak endothermic temperature, because the block (furnace) temperature is being plotted against ΔT , and DTA is a dynamic method. Therefore, the transition temperature (T_T), occurs at a definite value, but a finite time is required for the entire sample to undergo the transition, and the sample in the center of the holder will be below T_T by a slight amount (20, 24).

To determine whether or not the system was operating properly, water was run at 50 p.s.i.g. to serve as a system check. The determined boiling point of water, shown in Figure 2, is in excellent agreement with the literature value.

Catalyst. Since it was desired to utilize the previously described system to study the reduction of dinitrotoluene as well as decomposition, Raney nickel was selected as a typical, commercially available catalyst.

Thermograms of Raney nickel were obtained in air at atmospheric pressure and under nitrogen at 50 p.s.i.g.