

Figure 2. Thermogram of 0.1 gram of H_2O at 50 p.s.i.g. of N_2

1. H_2O boiling point ($145^\circ C.$)
2. Peak of H_2O boiling. All H_2O has been vaporized at this point

(Figure 3). The thermogram of water alone showed a clean endotherm with no side band, whereas the endotherm in Figure 3, B, has a side band. The presence of this side band is probably due to the initiation of hydrogen evolution which may be only slightly endothermic at the beginning of the reaction. The evolution of hydrogen, after initiation, is exothermic. This interpretation of the thermogram is in accordance with the results obtained by

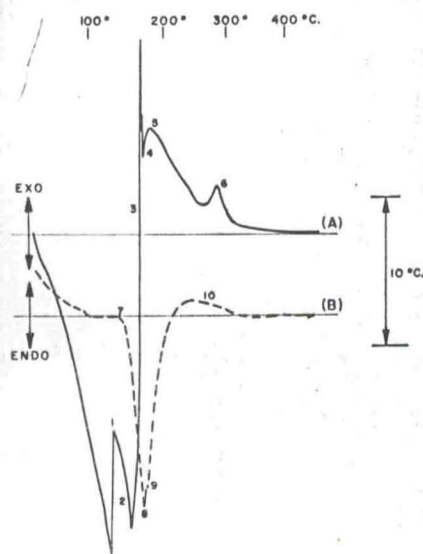


Figure 3. Thermograms of Raney nickel and water

- 0.32 gram in air at atmospheric pressure
 - 0.17 gram at 50 p.s.i.g. N_2
- $\times 0.5$ mv.
 - Boiling endotherm
 - Ignition exotherm
 - $\times 2.0$ mv.
 - High exotherm due to presence of air
 - Secondary oxidation effects
 - H_2O boiling point
 - Peak of H_2O boiling
 - Start of H_2 evolution
 - Exotherm due to H_2 evolution

previous investigators using methods other than DTA (11, 17).

Figure 3, A, is a thermogram of a similar sample run in an air atmosphere. The presence of air caused the catalyst to ignite spontaneously after water had been lost, as evidenced by the large exotherm. Dry Raney nickel when exposed to air is known to be pyrophoric (8).

Dinitrotoluene. The thermal stability of dinitrotoluene (80% 2,4 and 20% 2,6 isomers) was investigated because the inherent stability of this compound is important in itself and may add another hazard to the reduction reaction.

The thermogram of Figure 4, A shows that dinitrotoluene did not decompose below $300^\circ C.$ at 100 p.s.i.g. but began to decompose violently slightly above $300^\circ C.$ To determine the pressure sensitivity of this compound, the previous run was repeated at 1000 p.s.i.g. Again, a reaction did not occur below $300^\circ C.$ (see Figure 4, B). However, at $320^\circ C.$, violent decomposition occurred, as evidenced by both the instantaneous exotherm and pressure surge. These thermograms show that a higher pressure did not appreciably affect the temperature at which the reaction was initiated and therefore had no effect on the decomposition temperature.

Reduction of Dinitrotoluene. Dinitrotoluene and Raney nickel were mixed and loaded into the sample container, to determine if reductions could be observed using the present technique.

The thermogram in Figure 5, at 400 p.s.i.g. of nitrogen, shows that hydrogenation began at approximately $85^\circ C.$ accompanied by a large exotherm due to the heat of reaction. No abnormal effects such as a sharp exotherm or pressure surge were observed. Higher pressures up to 1500 p.s.i.g. of nitrogen and hydrogen were utilized. The higher pressures did not appear to affect the smooth hydrogenation, except possibly to provide a more quantitative yield.

The products from the run shown in Figure 5 were analyzed by gas liquid chromatography. The results of this analysis confirmed the interpretation of the thermogram in that mostly tolylene diamine was present, showing that the yield was nearly quantitative.

Dinitrotoluene and Tolylendiamine. The possibility of the reaction of dinitrotoluene with tolylendiamine (80% 2,4 and 20% 2,6 isomers) was explored. Previous DTA thermograms of tolylendiamine revealed no decomposition at pressures up to 1500 p.s.i.g.

Tolylendiamine and dinitrotoluene were dissolved in methanol and mixed in order to circumvent any possible phase separation effects and were run under

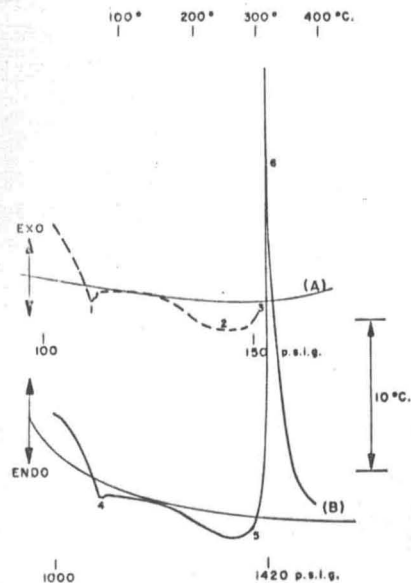


Figure 4. Thermograms of dinitrotoluene

- 0.1603 gram at 100 p.s.i.g. N_2
 - 0.1709 gram at 1000 p.s.i.g. N_2
- 1, 4. Dinitrotoluene melting
 5. Initiation of reaction
 3. Start of decomposition
 6. High exotherm due to violent decomposition

50 p.s.i.g. of nitrogen. The thermogram of this sample (Figure 6) shows that a large exotherm with two distinct peaks was produced, which indicates that a relatively nonviolent, two-step decomposition had occurred.

The endotherm observed is probably methanol boiling and/or the initial reaction required to produce the thermal decomposition. The exotherm began at $200^\circ C.$ and showed cessation at $255^\circ C.$, followed by a second exotherm which was complete at $270^\circ C.$ This may be

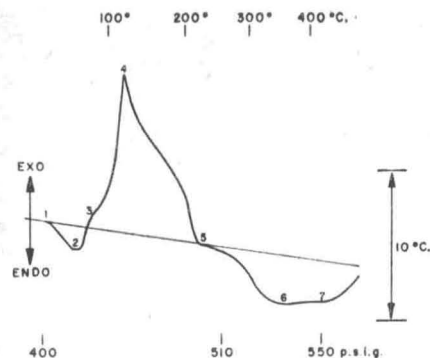


Figure 5. Thermogram of reduction of 0.7530 gram of dinitrotoluene with 0.2333 gram of Raney nickel and water at 400 p.s.i.g. N_2

- Start of dinitrotoluene melting
- Peak melting endotherm
- Hydrogenation starting
- Peak exotherm
- H_2O boiling ($244^\circ C.$, b.p. of H_2O at 510 p.s.i.g.)
- Peak of H_2O boiling
- Probable tolylendiamine sublimation