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Technique and Applications of High Pressure Differential Thermal Analysis

Study of Reactions of Dinitrotoluene and Tolylenediamine

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► A technique of high pressure-high temperature differential thermal analysis has been developed. By utilizing a suitably designed sample container, temperature and pressure changes can be measured up to 3000 p.s.i.g. at 500° C. This procedure can be adapted to commercially available instrumentation and allows the safe study of dangerous reactions that present safety hazards on a macro scale. The application of this technique to the study of dinitrotoluene reactions has permitted the determination of the thermal stability of dinitrotoluene, reduction temperature of dinitrotoluene with Raney nickel, decomposition reactions of dinitrotoluene with tolylenediamine, and parameters affecting the violent decomposition of reduction mixtures.

DIFFERENTIAL thermal analysis has been utilized in many applications to study inorganic (4, 7, 22) and organic reactions (5, 15). This is in addition to the extensive use for characterization (14) and identification of many substances (1, 10).

In spite of the usefulness of the DTA

technique, relatively few applications have utilized high pressures. The types of apparatus that have appeared are limited in the usable pressure range (13, 23, 25). This sparsity of reporting could be due in part to limited applications and the highly specialized and limited equipment.

Bohon has described an apparatus specifically built for work with rocket propellants and capable of operating at several hundred pounds per square inch gauge (2). The main application of this apparatus has been for the study of heats of explosion of propellants (3).

Lodding and Hammell have utilized their apparatus to study reactions and phase changes of iron hydroxide and oxides up to 400 p.s.i.g. Provision has also been made to analyze the effluent vapors (12).

The present technique utilizes a suitably designed sample container, to achieve pressures up to 3000 p.s.i.g. at 500° C. This sample container is readily adaptable to many commercially available instruments and this technique can be applied to the study of organic reactions and transitions such as decomposition, melting, sublimation,

coupling, and reduction. Provision has also been made to measure any sudden pressure surges up to 3000 p.s.i.g. as well as to transfer effluent vapors into a gas chromatograph.

We wished to show the utility of this technique for the safe study of the hazards of high pressure-high rate reactions under strenuous conditions of temperature and pressure that would be cumbersome, impractical, and dangerous to perform by methods other than DTA.

Since nitro compounds are of practical interest to the urethane industry (18), and they represent a potential safety hazard, we chose to investigate the thermal stability and reduction of dinitrotoluene in an attempt to define some of the hazardous parameters associated with these reactions.

In a previous, excellent, macro study by Havekoss (9) which inevitably suffered some of the limitations listed above, indications were obtained that dinitrotoluene did react exothermically with tolylenediamine. We wished to investigate this reaction, among the others mentioned above, utilizing the advantages of the DTA technique.

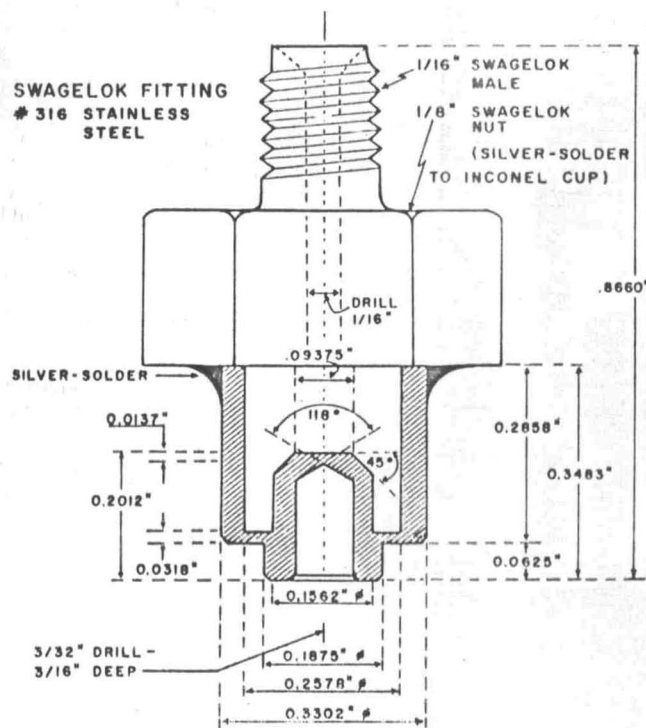


Figure 1. High pressure sample container

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.

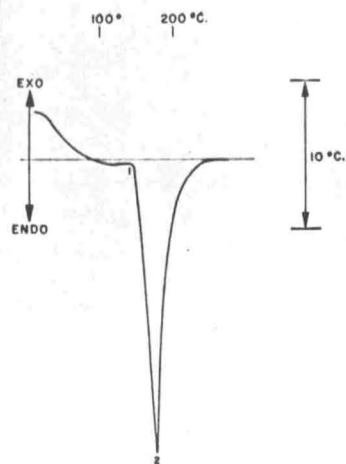


Figure 2. Thermogram of 0.1 gram of H_2O at 50 p.s.i.g. of N_2

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

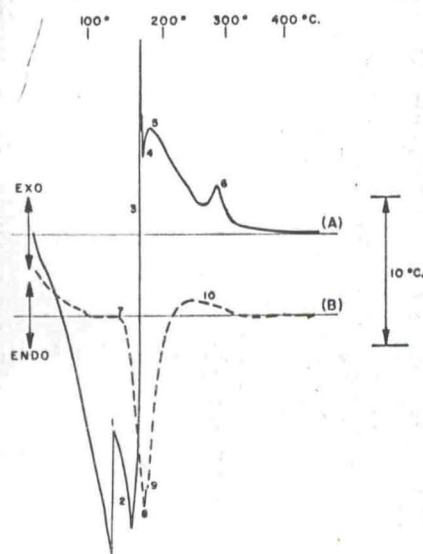


Figure 3. Thermograms of Raney nickel and water

- 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

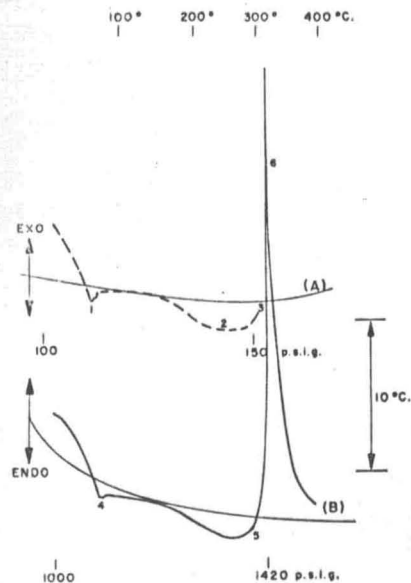


Figure 4. Thermograms of dinitrotoluene

- 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
 - 2, 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

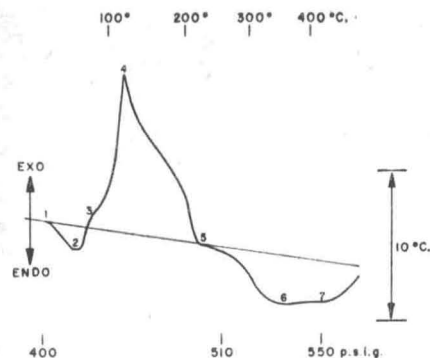


Figure 5. Thermogram of reduction of 0.7530 gram of dinitrotoluene with 0.2333 gram of Raney nickel and water at 400 p.s.i.g. N_2

- 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

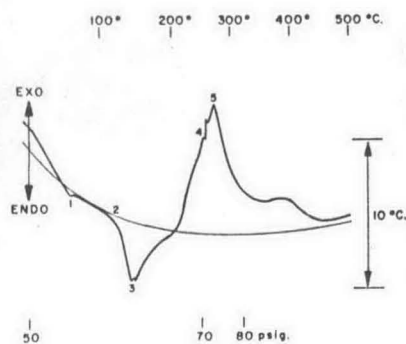


Figure 6. Thermogram showing reaction of 0.1013 gram of dinitrotoluene with 0.0299 gram of tolylenediamine in 0.0768 gram of methanol at 50 p.s.i.g. N₂

1. Dinitrotoluene melting endotherm
2. Methanol boiling
3. Completion of boiling and/or initiation of reaction
4. Initial condensation
5. Exotherm and pressure surge due to decomposition

due to an initial condensation of the tolylenediamine and dinitrotoluene to form unstable compounds which subsequently decompose. Of course, both steps are decomposition and degradation of the starting materials. It is significant that the reaction occurred at a much lower temperature than for dinitrotoluene alone.

Previous workers have shown that nitro compounds react with amines at various dilutions, but the exact mechanism—i.e., oxidation, reduction, or condensation—has not been established (6).

On the other hand, it has been reported that alkaline substances will promote the condensation of certain nitro and amine compounds to *o*- and *p*-nitrophenylamines, azo- and azoxy compounds, and *N*-oxides of phenazine derivatives (19). The presence of acid catalysts such as NiCl₂ and FeCl₃, may catalyze condensation reactions (16).

Under strenuous thermal conditions, the presence of even trace amounts of catalyzing substances may not be necessary to promote these rearrangements and decompositions.

The importance of the investigations of reactions of this type, which may represent a great safety hazard on the macro scale, cannot be overemphasized. The previous reactions also show that a potential safety hazard may exist if the dinitrotoluene is not almost completely reduced, since the tolylenediamine formed is capable of a decomposition reaction with the starting material (dinitrotoluene).

To simulate more closely a reduction condition in which dinitrotoluene is only partially reduced, providing a mixture of amine and nitro compound,

the concentration of Raney nickel was decreased from that used in Figure 5, and dinitrotoluene, Raney nickel, and methanol were introduced into the sample container, as before, but under 250 p.s.i.g. of hydrogen.

In this case we would expect a partial hydrogenation, and subsequently a reaction of the remaining dinitrotoluene with the tolylenediamine formed. This is confirmed in Figure 7. The presence of Raney nickel appears to have intensified the decomposition, causing it to become violent. This can be observed by comparing the decomposition exotherm with that in Figure 6.

The results of this experiment show that the ratio of Raney nickel to the nitro compound as well as contact and agitation may be key features, since these experiments were carried out in a closed unagitated system. This may be especially important during reductions where conditions of segregation may exist and proper hydrogenation may occur in only specific or localized areas.

CONCLUSIONS

The described technique of sample container modifications would permit the investigation of many reactions at high temperatures and pressures, utilizing available equipment with little additional expense.

The investigation of some reactions may prove extremely difficult by methods other than DTA. Since relatively small amounts of samples are utilized, this method provides a much greater safety factor. This is especially important in exploring the types of reactions previously shown, where the extent of personal injury can be great when macro samples are used.

Although this investigation was undertaken primarily from a qualitative viewpoint, by accurate calibration quantitative data could be obtained on heats and yields of certain reactions. This has been demonstrated previously (3, 12).

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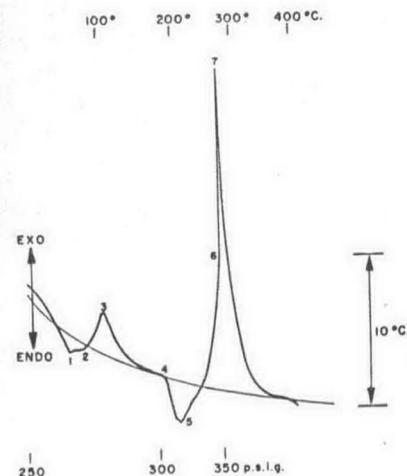


Figure 7. Thermogram showing incomplete reduction of 0.0990 gram of dinitrotoluene with 0.0996 gram of Raney nickel in 0.0348 gram of methanol at 250 p.s.i.g. H₂

1. Dinitrotoluene melting endotherm
2. Hydrogenation starting
3. Peak exotherm of reduction
4. H₂O and/or CH₃OH boiling
5. Completion of boiling and/or initiation of reaction
6. Initial condensation
7. High exotherm and pressure surge due to violent decomposition

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