

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. N_2

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*-nitrodiphenylamines, azo- and azoxy compounds, and *N*-oxides of phenazine derivatives (19). The presence of acid catalysts such as $NiCl_2$ and $FeCl_3$ 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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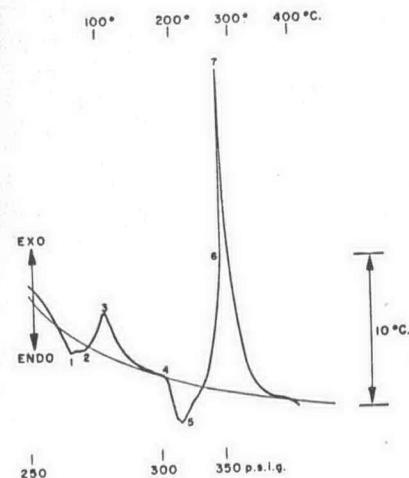


Figure 7. Thermogram showing incomplete reduction of 0.0990 gram of dinitrotoluene with 0.0996 gram of Raney nickel in 0.0348 gram of methanol at 250 p.s.i.g. H_2

1. Dinitrotoluene melting endotherm
2. Hydrogenation starting
3. Peak exotherm of reduction
4. H_2O and/or CH_3OH 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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