

## A Thermoanalytical Determination of the Activation Energy of the Decomposition of Azodiisobutyronitrile

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### Synopsis

The decomposition of azodiisobutyronitrile (AZDN) has been studied in a simple, robust apparatus specially constructed for simultaneous study of differential thermal analysis and evolved gas detection (DTA/EGD). The results obtained are comparable with those of other thermoanalytic techniques. It is difficult to obtain kinetic results by the DTA technique alone, as the decomposition is confounded with a melting endotherm. This problem does not arise when EGD is used. The apparatus provides a convenient method for research on blowing agents and is being extended to studies of polymer degradation.

### INTRODUCTION

AZDN is used as a blowing agent in the manufacture of foam. The rate of evolution of gas at the working temperature of the polymer determines the type of cell structure. Normally the decomposition is studied by measuring the rate of evolution of gas by displacement of water from a graduated cylinder when the blowing agent is dropped into an inert high-boiling solvent, at a controlled temperature in a sealed system. This method is tedious and has other disadvantages. Some of the gas may remain dissolved in the solvent, and it is difficult to load a powdered sample into the heating liquid inside a sealed system. If more than one gas is evolved simultaneously, no information is obtained on which gas is produced first and at what comparative rate.

Thermoanalytic methods have been used<sup>1,2</sup> to study the decomposition of AZDN. These methods have many advantages. Only one experiment is needed to obtain rates of decomposition over the whole temperature range; the sample can be loaded at leisure; a solvent is not essential; the response of different, simultaneously evolved gases may be separated. In addition, the heat of reaction, whether the reaction is exothermic or endothermic, and information on any subsequent reactions in the residue may be obtained. Differential thermal analysis (DTA), thermogravimetry (TG), and differential thermal analysis with evolved gas detection (DTA/EGD) were used in this study.

Convenient methods are available for calculating kinetic information from the results of these techniques. A further objective was to evaluate the techniques as a means of quality control. If further information is needed, it is simple to convert from EGD to evolved gas analysis (EGA). The only disadvantage of this system is that absolute quantitative data on volume of gas evolved is not available.

## EXPERIMENTAL

### Simultaneous DTA/EGD

The heating arrangements for DTA were dictated by the type of gas detectors used for the EGD. Both the detectors needed two identical supplies of carrier gas, one for the reference stream, and the other, for the sample. Because both must be presented to the detector at the same temperature, especially in the case of the gas density balance, both have to be passed through similar, but entirely separate, paths through the furnace.

No commercial apparatus was available to this specification, so one was designed to satisfy the conditions.

A standard horizontal-tube, 500-watt, 1000°C furnace was employed. Into this was inserted a steel cylinder, drilled longitudinally with two parallel  $\frac{1}{2}$ -in. (15.9-mm) holes, from end to end. Two glass tubes, slightly less than  $\frac{1}{2}$ -in. O.D. (15.5 mm), passed through these holes, and protruded 2 in. beyond each end of the furnace. One end of each of these tubes terminated in a B19 socket, and into these were fitted the holders locating the sample and reference materials in the center of the furnace in ceramic wells. The location of sample is exceedingly reproducible, cleaning is very easy, and the whole holder can simply be unplugged, as it is connected to the recording system with miniature two-pin plugs and sockets.

The furnace was programmed linearly, using an ether proportional temperature controller at 5°C/min (0.083°C/sec). Linear heating rate is especially important for kinetic studies from DTA traces.<sup>3</sup> The steel block had to be earthed to avoid picking up furnace voltage fluctuations on the differential temperature thermocouples. The high thermal conductivity and large thermal mass of this block helped to improve the DTA baseline still further, even though the sample and reference materials were under completely separate controlled atmospheres. Steel was chosen for the block because, as well as being cheaper than copper, it was also better for higher temperature work (up to 600°C), even though suffering from a lower thermal conductivity. The ends of this block, open to the atmosphere, were lagged with ceramic insulators.

Gas was fed in from two independently controlled needle valves and rotameter flowmeters, range 10–100 cc/min ( $1.67 \times 10^{-7}$  to  $16.7 \times 10^{-7}$  m<sup>3</sup>/sec). For the katharometer detector, a flow rate of 50 cc/min ( $8.3 \times 10^{-7}$  m<sup>3</sup>/sec) was used in each stream; for the gas density balance, 70 cc/min ( $1.167 \times 10^{-6}$  m<sup>3</sup>/sec) flowed through the references and 50 cc/min ( $8.3 \times 10^{-7}$  m<sup>3</sup>/sec) through the sample tube. The gas was taken from

the outlet end of the glass furnace tubes directly to the detector with a minimum of tubing. This reduced the possibility of vapor loss by condensation, which was very important in other applications of this apparatus, such as polymer degradation, and did not spoil the baseline of the detector.

In the sample holder there was one chromium-nickel/aluminium-nickel (Cr/Al) thermocouple; the reference holder had two, one being used directly to record the furnace temperature  $T$ , the other being connected back to back with the thermocouple in the sample holder to measure the difference in temperature  $\Delta T$  between sample and reference material. The  $T$  thermocouple output was fed to the  $X$ -axis of a two-pen  $XY_1 Y_2$  chart recorder. The  $\Delta T$  output, amplified by 10 or 100 times, was fed to one  $Y$ -axis; this was adequately sensitive, as blowing agents decompose vigorously. Greater sensitivity was available if necessary. The second  $Y$ -axis of the recorder was fed directly from the output of the gas detector. The sample size was approximately 0.1 g. Solid sample was loaded directly into the ceramic holder. Figure 1 shows how the sample cell and thermocouples are located in each gas tube. Samples used in solution were held in an aluminum dish resting on the thermocouple tip. Much smaller amounts were used for solutions in dibutyl phthalate (DBP) or slurries in silicone oil of viscosity 380 or 1000 centipoises (0.38 to 1.0 Ns/m<sup>2</sup>). The samples were recrystallized from ether and dried in a vacuum oven.

#### du Pont 900 Thermal Analyzer

Experiments were carried out using the differential scanning calorimeter head (DSC) at 5°C/min (0.083°C/sec) from room temperature to 200°C. This is not a true calorimeter, being more correctly a quantitative DTA. Results obtained are similar to those of DSC. Sample sizes used were 5 mg (solid), 1 mg in DBP, and 1 mg in silicone oil.

#### Stanton Thermobalance

The Stanton Model HT-SM thermobalance was used at a heating rate of 6°C/min (0.10°C/sec) with a flat aluminum sample pan 1/2 in. (16 mm) in diameter. The recorded sample temperature was measured with a thermocouple touching the base of the crucible. Sample sizes were 50 mg for the solid, 50 mg of AZDN in DBP, and 50 mg of AZDN in silicone oil.

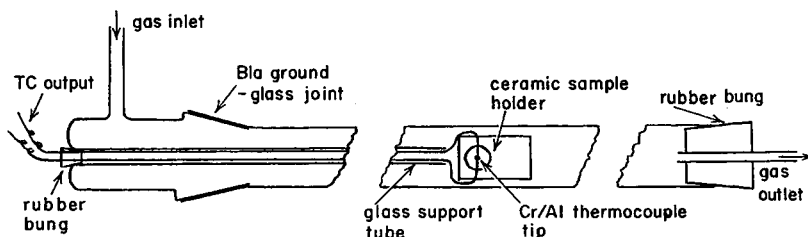


Fig. 1. Gas tube/sample holder arrangements for combined DTA/EGD.

### C. I. Electrobalance

Thermograms of solid AZDN were obtained from a Mark 11B microbalance with a universal attachment. The sample holder was once again a 1/2-in.-(16-mm)-diameter flat aluminum crucible; but in these experiments only 7–8-mg samples for solids and liquids were used, using the balance on the 0–10-mg range. This very small sample spread on a flat crucible minimized the effect of diffusion on the rate of reaction. The temperature thermocouple was situated with its tip 5 mm above the sample surface. The temperature and weight were recorded on a two-pen strip chart recorder in the normal way. Experiments were carried out at 1<sup>1</sup>/<sub>4</sub>, 5, 12, and 20°C/min (0.021, 0.083, 0.20, and 0.33°C/sec).

## RESULTS

The value of the activation energy  $E$  shown in the tables for the DSC, DTA, and EGD results were calculated by the method of Borchardt and Daniels.<sup>4</sup> This method was chosen mainly for convenience. Great accuracy is not to be expected, especially with solid samples, as this method was derived for stirred homogeneous solutions. It was also applied to the EGD traces as the rate of gas evolution is also a quantitative measure of the rate at which a reaction is proceeding.

The method of Horowitz and Metzger<sup>5</sup> was chosen for the TG as a direct parallel to the method of Borchardt and Daniels, in that it takes the rate constant as being proportional to the rate of weight loss as a function of weight remaining. For the calculation of  $E$  from the Arrhenius plot, the proportionality constants need not be known. The reaction was taken to be first order.<sup>1</sup>

The results in Table I show fair agreement between the results from

TABLE I  
Activation Energy for the Decomposition of AZDN, using TG, DSC, and EGD

Sample	Activation energy $E$ , kcal/mole				Ref. 6
	EGD	DSC	TG (Stanton)	TG (C.I. Electro- balance)	
AZDN solid	33.2	31.7	31.9	30.5	
AZDN solution or slurry	32.6	30.5	25.1	34.6	30.8
Solvent or dispersant	DBP; 380 cp Si oil; 1000 cp Si oil	DBP	1000 cp Si oil	1000 cp Si oil	

classical techniques<sup>6</sup> (the value quoted is the mean of several different workers and techniques) and the thermoanalytic methods. EGD analysis on excessive amounts of solid samples gives results that are much too high

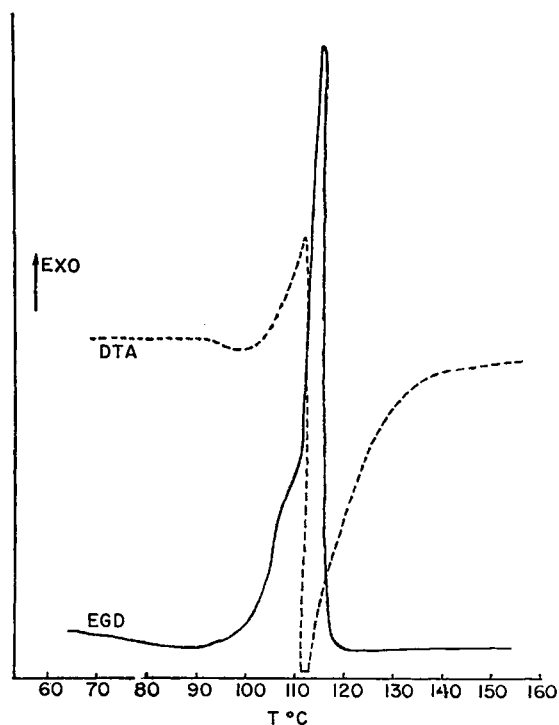


Fig. 2. AZDN, solid sample in DTA/EGD apparatus.  $\Delta T$ : 6.5°C/in.

(Table II). This was attributed to overloading of the detectors, which were extremely sensitive. Another difficulty with solid samples and slurries was that the melting point overlapped the temperature range in which decomposition occurred (Fig. 2). The DTA results obtained in the DTA/EGD equipment were unreliable. The ceramic cell used has a low thermal conductivity, thus the melting endotherm is so wide that it completely obliterates the last part of the decomposition exotherm.

TABLE II  
Effect of Sample Size on EGD Results for Solid Samples

Sample weight, mg	$E$ , kcal/mole
1.0	33.3
2.0	30.8
3.0	32.2
4.0	33.2
9.5	56.2
21.5	97.2
45.0	108.9
50.0	108.5
60.0	109.0

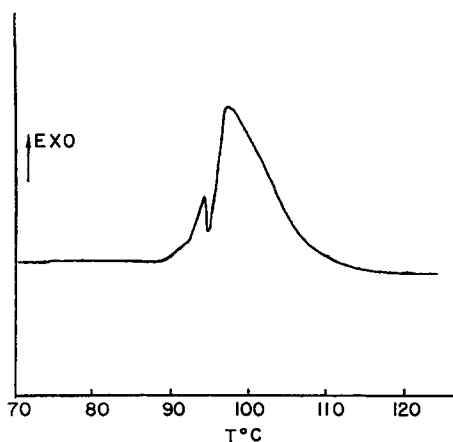


Fig. 3. Solid sample in DSC apparatus.  $\Delta T$ :  $0.5^\circ\text{C}/\text{in}$ .

When the DSC cell is used at slow heating rates, the endotherm is very narrow (Fig. 3), and a fair estimate of the area of the exotherm can be made. This of course can only be an approximation, and the closeness of the result in Table I may be fortuitous.

Thermogravimetric results for solutions are poor, due to a continuing slow weight loss well after the completion of the AZDN decomposition. This was initially thought to be due to solvent loss, but a thermogram of pure solvent showed no weight loss till well above the decomposition temperature of AZDN. This loss is now attributed to nitrogen dissolved in the solvent being slowly expelled as the temperature is raised. This is one instance where TG can pick up a phenomenon which appears only as a gently endothermic drift on the DTA, and may be easily missed.

The results from the Stanton thermobalance are in general less reliable than the TG results from the C. I. electrobalance because the Stanton chart is less easy to read accurately.<sup>7</sup>

The rate of diffusion affects the value of  $E$  obtained (Table III), probably

TABLE III  
Effect of Viscosity

Solvent or dispersant	$E$ , kcal/mole
DBP	31.6
380 cp Silicone oil	31.9
1000 cp Silicone oil	34.2
Mean	32.6

because in less viscous solutions the removal of nitrogen is comparatively more rapid, with a consequent increase in the ease with which the reaction proceeds. In the case of solid specimens, however, the rate of diffusion

is much slower and causes the reaction to be recorded over a wider temperature range, giving an apparent fall in the value of  $E$  as the heating rate rises (Table IV). In mobile solvents at low concentrations, it seems

TABLE IV  
Effect of Heating Rate on TG Results (Solid Samples)

Heating rate, °C/min	$E$ , kcal/mole
1 <sup>1</sup> / <sub>4</sub>	34.8
5	32.5
12	30.8
20	29.4

the diffusion rate is sufficiently rapid to have no apparent effect on the value of  $E$ .<sup>1</sup>

## DISCUSSION

The values obtained for activation energies of AZDN vary according to whether the specimen is a powder or is in solution or slurry. All the thermoanalytic techniques are in fair agreement with each other and with the literature values. These techniques cover the whole range of temperature in one experiment, and are rapid. Further information is also available on reactions, e.g., transitions, that occur during the heating of the sample that would be missed when using volumetric methods. Thermoanalytic methods are therefore particularly applicable for research purposes and for screening potential blowing agents.

Techniques for the determination of activation energies, especially sampling techniques, must be carefully chosen. Conventional methods of measuring the rate of AZDN decomposition rely on the reaction taking place in solution. This is obviously not applicable when a blowing agent is used. When solid AZDN particles are distributed throughout the polymer to be foamed, thermoanalytic techniques should be considered in conjunction with kinetic data obtained from experiments performed on solid samples. In general, the solution results are somewhat lower than the solid results, presumably because of the more rapid removal of gas from the vicinity of the reaction. They are more applicable to the use of AZDN for initiating polymerization, as in this case the AZDN molecules are well separated from each other. When choosing the technique of examination, the environment of the sample must approximate as closely as possible to the conditions of use.

### Thermogravimetry

The TG results were fairly good, especially with the C. I. thermobalance, where the chart is large and clear. Thermogravimetry with AZDN in solution was not so accurate as for solid AZDN. This is due to the slow diffusion of dissolved nitrogen.

### Differential Thermal Analysis

The DTA results on solid AZDN are poor because the AZDN melting and decomposition overlap. This causes a very large endotherm to be superposed on the decomposition exotherm (Fig. 2).

Better results are seen using the DSC cell, where the metal sample pan with high thermal conductivity, together with a slow heating rate, causes the endotherm to be rendered very narrow, so that a reasonable approximation may be obtained (Fig. 3). Results for AZDN in solution are good.

### Evolved Gas Detection

This technique does not appear to possess the high accuracy expected which should be its chief advantage over DTA and TG. The detector used was designed for gas chromatography where minimal quantities are used. Although DTA may be performed on microquantities, it is much more convenient to use larger quantities.

The present design, using milligrams of material, is a convenient compromise. In Table II the errors introduced by excessive sample are shown.

We thank Mr. G. McFarlane for his experimental assistance and Mr. D. P. Sondhi for the construction of the DTA/EGD apparatus.

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Received July 7, 1971

Revised November 19, 1971