

THE THERMAL DECOMPOSITION OF AZODICARBONAMIDE

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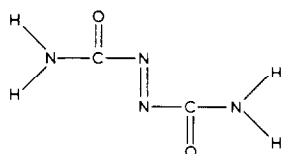
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ABSTRACT

The work presented here was designed to investigate various aspects of the decomposition of azodicarbonamide, an organic solid used as a chemical blowing agent in the plastics industry. The decomposition was studied by TG and DTA experiments, and the heat of reaction calculated to be 1046 kJ mol^{-1} also the activation energy was found by experiments to be 77 kJ mol^{-1} . The reaction products were analyzed by IR spectroscopy and the products identified, to postulate a reaction sequence.

INTRODUCTION

Azodicarbonamide



is used extensively in the production of expanded polymer films, particularly PVC. Polyvinyl chloride foams are essentially standard formulations containing a blowing agent for expansion of the composition. Of the many chemical blowing agents available, azodicarbonamide is used almost exclusively in the production of expanded PVC. In the pure state, this compound decomposes at temperatures above 215°C . However, by the correct choice of activator, azodicarbonamide may be made to decompose at temperatures ranging from 150 to 200°C [1]. Compounds of cadmium, lead and zinc, such as stearates, octoates, naphthenates and benzoates, lower the decomposition temperature of azodicarbonamide into the temperature range normally used in the processing of PVC.

The practice of expanding rubber and plastics originated over forty years ago and since then great changes have occurred in the type of compounds used for this purpose [2]. Originally, rubber was expanded using nitrogen, nitrous oxide or carbon dioxide at about 200 atm and elevated temperatures. Other compounds proposed are ammonia, methane, dichlorofluoromethane, ammonium nitrite and ammonium nitrate. All the inorganic compounds and mixtures suffered from dispersion difficulty and, eventually, but surprisingly slowly, attention was turned to organic compounds which evolved nitrogen, nitrous oxide or carbon dioxide on decomposition by heat.

As a definition, a blowing agent is any compound, organic or inorganic, that releases gas on heating to a definite minimum temperature. Differing ranges of temperature are permissible since not all substances are in a fit condition to accept expansion at the same temperature.

From studies on azodicarbonamide [1], the following conclusions have been reached.

(1) Cadmium, lead and zinc compounds lower the decomposition temperature.

(2) When optimum foam expansion is not obtained, it may be due to (i) inadequate activation of the blowing agent; (ii) loss of gas prior to reaching optimum fusion of the PVC compound; (iii) too low a melt viscosity following fusion which may result in gas loss.

(3) At any given temperature, the rate of decomposition is increased by an increase in activator concentration.

(4) At any given concentration of activator, the rate of decomposition is increased by an increase in temperature. Thus, the level of activator must be correlated to the temperature of processing.

(5) Activator performance is influenced by the anion structure and acidity of the activator.

(6) The decomposition products may function as heat stabilizers for PVC in the presence of the activator material.

Solid organic compounds are characterized by molecular lattices in which the molecules are arranged in some fairly close-packed form in the crystal. The forces holding the molecules together are mainly Van der Waals. The intermolecular forces are small compared with the energies of bond dissociation and the distances between molecules in the crystal large compared with the intermolecular distance within the single molecule.

A consequence of this is that liquefaction or sublimation occurs at such relatively low temperatures that one or both of these physical changes occurs before thermal decomposition.

The detailed mechanism of such solid decompositions that do occur in organic solids is very much determined by an accurate knowledge of the lattice structure of the crystal.

Differences between organic and inorganic decomposition are that in organic decompositions:

(1) there is no clear establishment of the existence of a reaction interface or of the existence of nuclei;

(2) decomposition is usually accompanied by the formation of a liquid phase and a consequent rapid increase in reaction rate.

However the α - t (α -fraction decomposed) curves are often similar to those obtained for inorganic systems, e.g.

$$\frac{dp}{dt} = kp$$

$$\frac{dp}{dt} = k \left(1 - \frac{P}{P_f} \right)$$

$$\log \frac{P_f}{P_f - P} = Kt$$

where P = gas pressure at time t and P_f = final gas pressure. These expressions have been given in terms of pressure because it is often found convenient to observe these reactions in organic materials by noting the pressure changes that take place.

EXPERIMENTAL

Thermogravimetric (TG) experiments were performed using the Stanton-Redcroft thermobalance, sample weights of 0.1 g were used. After a series of experiments using the rising temperature method, it was found more useful to carry out experiments isothermally using a range of temperatures.

Differential Thermal Analysis (DTA) experiments were carried out on the Netzsch DTA unit using dead burnt alumina as the reference material.

MATERIALS

The different types of available azodicarbonamide studied are listed in Table 1, together with some of the known properties of the reaction.

RESULTS

Rising temperature thermograms obtained, from the TG experiments, were found to be of little use other than to indicate the presence of a sudden, complete reaction with a weight loss of 65–70%. A comparison of Genitron AC4 and Azocel 504 showed the Azocel 504 to be reactive at a lower temperature than the Genitron AC4 for a heating rate of $4.7^\circ\text{C min}^{-1}$, the

TABLE 1

Types of azodicarbonamide and some of their known properties

Property	Genitron AC			Genitron AC4	Azocel 504
	Reed [1]	Lally and Alter [2]	Reed [3]	Whiffen [4]	Fairmount Chemicals [5]
Molecular weight			116.1		
Heat of combustion (kJ mol ⁻¹)			1096	1066.9	
Gas evolution	300 ml at 199°C over 30 min		438 ml at 209°C	230 ml at 220°C in 6 min	
Decomposition temperature (°C)	235–240	> 215	230	210–220	196–202
Specific heat (°C)			0.26	0.26 (23–60)	
Specific gravity	1.66			1.66	1.65
Solubility					DMF and diethylene glycol
Bulk density (lbs./cu.ft.)				30	13–16

following threshold temperatures were obtained (see Fig. 1)

Genitron AC4 209.5°C

Azocel 504 193.5°C

Corroboration of this type of reaction was obtained by the use of DTA. Thermograms plotted at a heating rate of 5°C min⁻¹ yielded the following information (see Fig. 2).

(1) A sudden exothermic reaction, for Azocel 504, at 190°C.

(2) A heat of reaction of 1046 kJ mol⁻¹ (literature value of 1067 kJ mol⁻¹).

(3) Liquefaction of the residue at 225°C.

In further thermogravimetric determinations, at later dates, the effect of sample weight variations and ageing were investigated. Sample weight was seen to affect the reaction drastically. Below a "critical weight" the reaction ceased to be instantaneous and a slow decomposition was observed (Fig. 3). However, when this critical weight was exceeded, no variations in the period of reaction initiation (initiation time) were observed. Hence, it was con-

cluded that, within reasonable limits, variations in sample weight would not affect the reaction when the critical weight had been exceeded (Fig. 4).

Ageing of the azodicarbonamide had no effect on the main reaction. Initiation time was unaffected both by heat ageing at 120°C (Fig. 5) and UV irradiation (Fig. 6). However, heat ageing did affect the total weight loss to the extent that after 6.5 h ageing at 120°C the percentage decomposition had decreased from 74 to 61% by weight. Hence, it was also concluded that

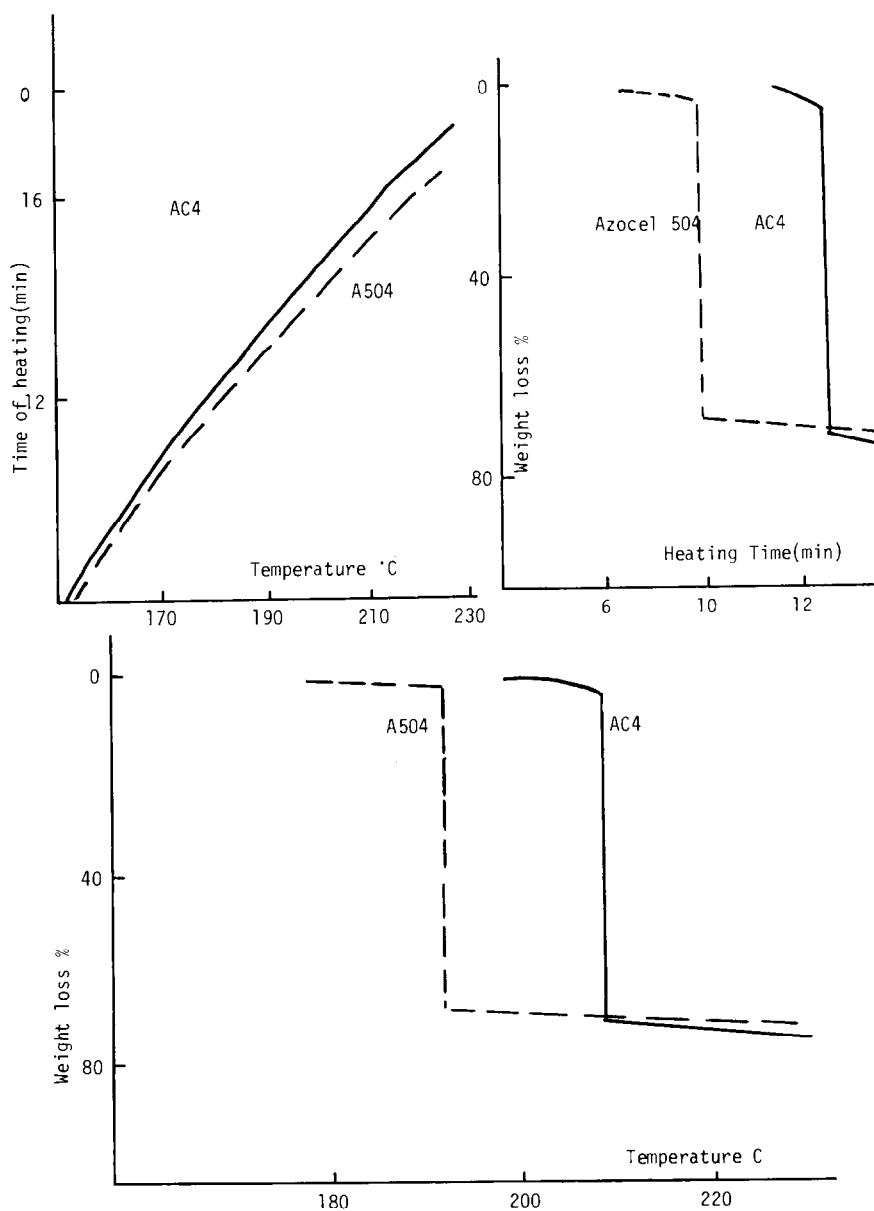


Fig. 1. Weight loss % vs. temperature.

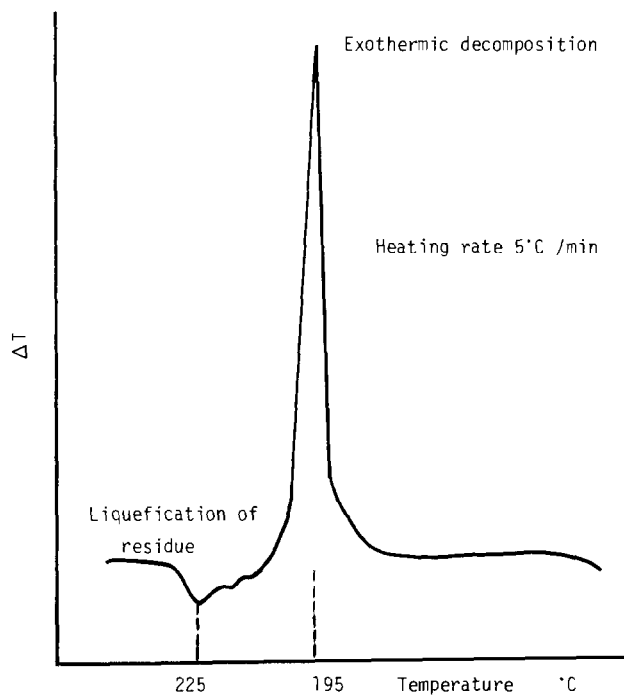


Fig. 2. DTA trace of azodicarbonamide decomposition.

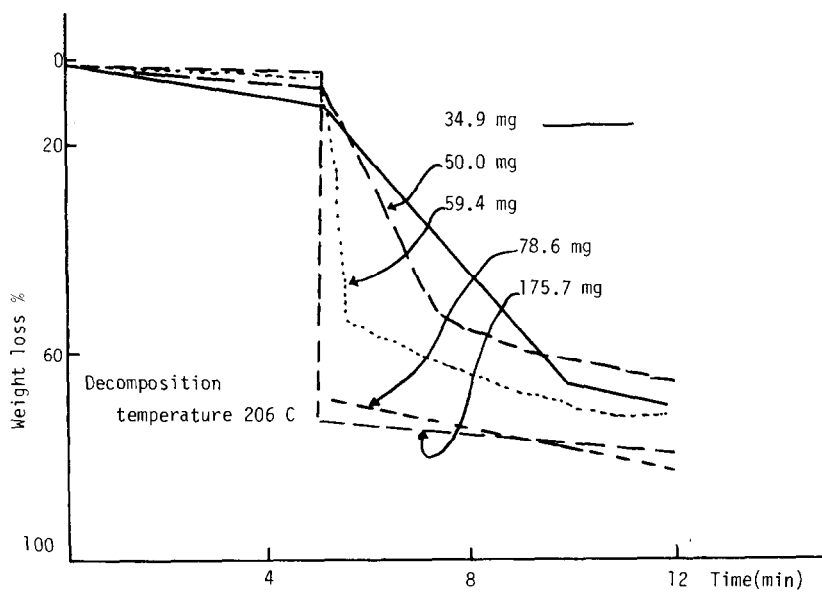


Fig. 3. Azodicarbonamide decomposition. Variation in sample weight Azocel 504 in nitrogen.

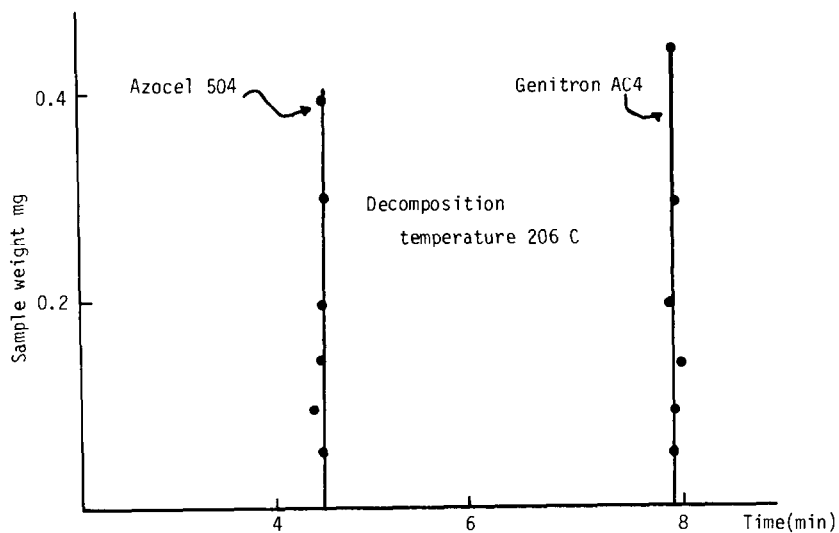


Fig. 4. Sample weight vs. initiation time.

experiments carried out at a later date would not be significantly affected by the ageing of the azodicarbonamide.

In an attempt to evaluate the free energy of the system, ΔG , from the expression

$$\Delta G = -RT \ln p$$

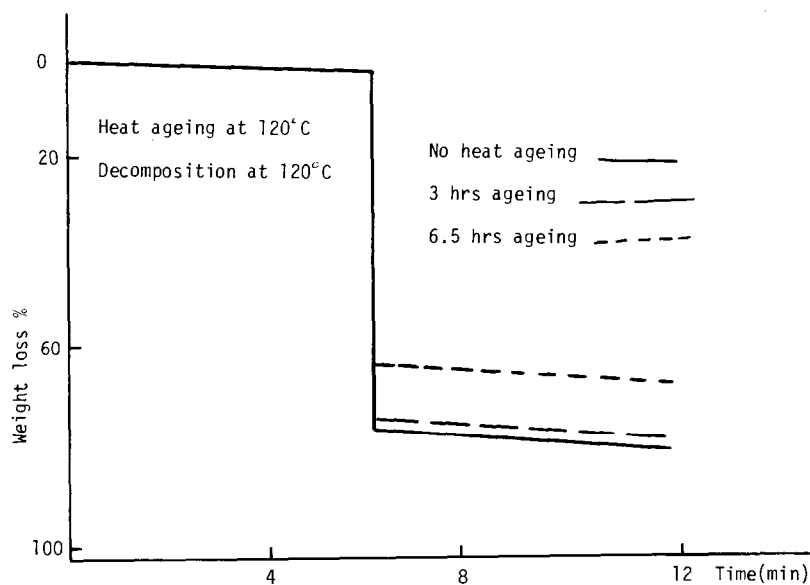


Fig. 5. Ageing of azodicarbonamide Genitron AC4.

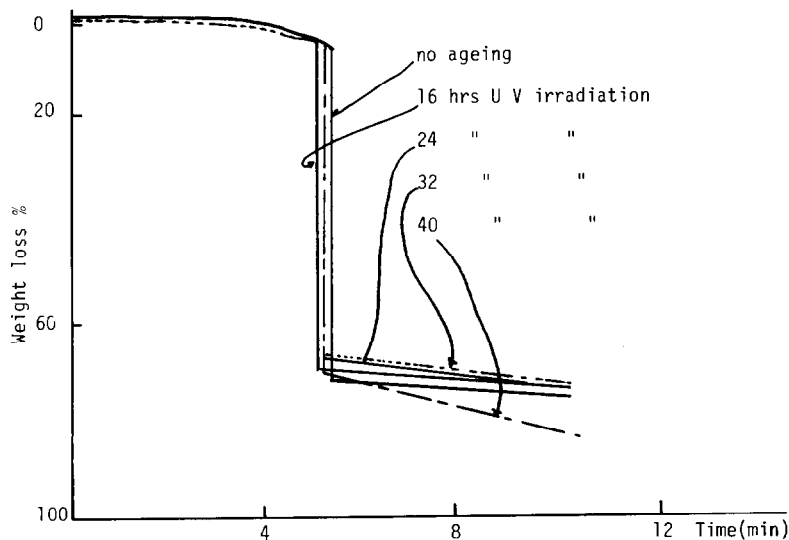


Fig. 6. Light ageing of Genitron AC4.

experiments using varying partial pressures of nitrogen were carried out, the temperature of decomposition being measured. However, no sequence or pattern of results were obtained and hence the graph of $\ln p$ against $1/T$ could not be drawn, and ΔG could not be evaluated.

The process of decomposition was also followed using IR spectroscopy. Samples were evaluated at various points along the thermogram. No reaction was observed during the initiation period but after the instantaneous reaction several products were isolated. These could be split into two groups:

- (a) sublimate. This comprised essentially cyanuric acid, with slight traces of cyamelide;
- (b) residue. This comprised essentially urazole (1,3-dihydroxy-2,4,6-triazole), with a small amount of biuret.

Using TG analysis, samples were evaluated at constant temperature, over a range of temperatures both in nitrogen and in air. Comparisons were made and it was found that there were no differences in the initiation times. However, it was noticed that Azocel 504 reacted much quicker than Genitron AC4 (Figs. 7, 8 and 9). Consistency and reproducibility of the results is shown in Fig. 10 which gives initiation time vs. temperature. The results have been obtained over a period of nine months in atmospheres of nitrogen and air. From the linear reaction rate and this graph, values of the activation energy (E_a) of the initial reaction have been calculated from the Arrhenius equation (see Fig. 11)

$$K = Ae^{-E_a/RT}$$

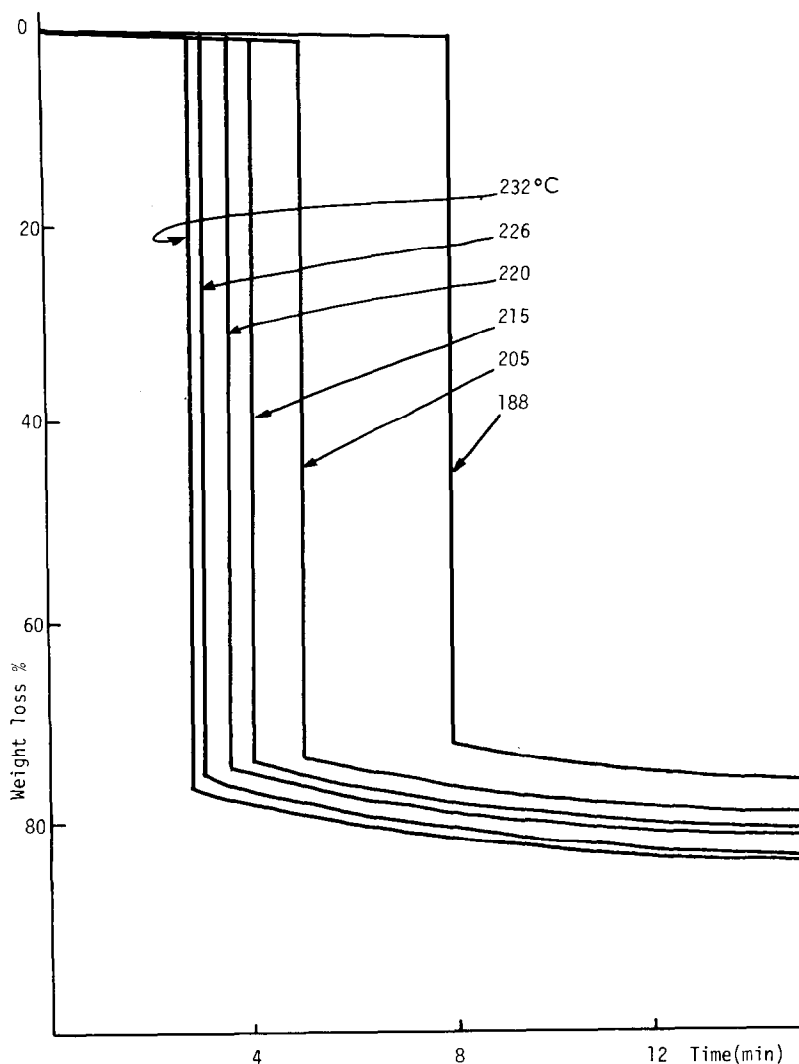


Fig. 7. Azodicarbonamide decomposition Azocel 504 in nitrogen.

where K = rate constant; A = constant; E_a = activation energy; R = gas constant; T = temperature. In these investigations and using the linear law, the induction time can be used in place of K . Activation energies determined in this way gave the following results:

Genitron AC4	74.47	kJ mol^{-1}
Azocel 504	79.92	kJ mol^{-1}

Dilution of the azodicarbonamide with activated alumina produced a graph whose form indicated a gradual weight loss (Fig. 12), and activation

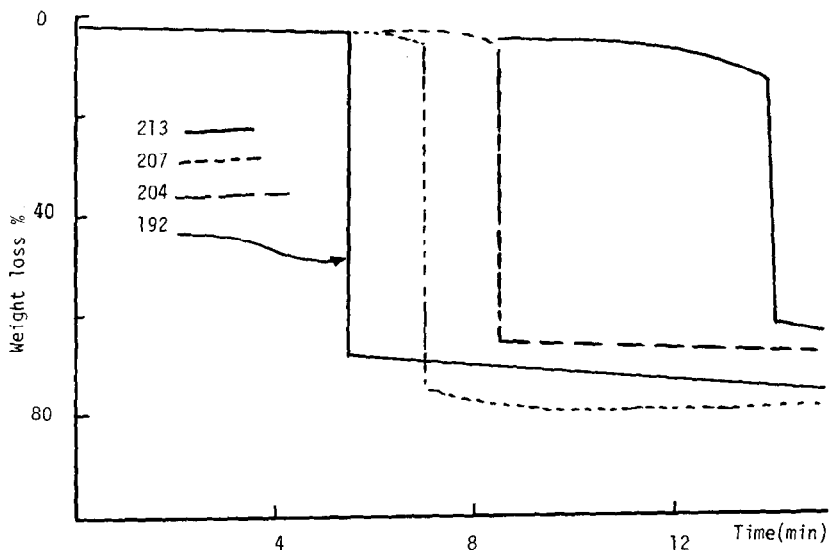


Fig. 8. Azodicarbonamide decomposition in air. Genitron AC4.

energy in this case was determined by plotting the slope of this graph against $1/T$. This gave a direct plot of rate constant vs. temperature and an activation energy for Genitron AC4 of $67.57 \text{ kJ mol}^{-1}$ (Fig. 13). This value and the one obtained previously are of the same magnitude and would, therefore, indicate a similar process or reaction mechanism.

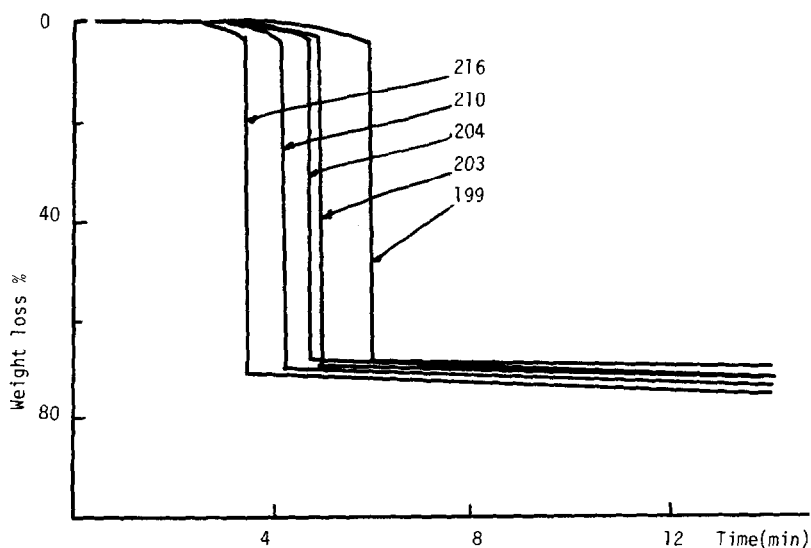


Fig. 9. Azodicarbonamide decomposition in air. Azocel 504.

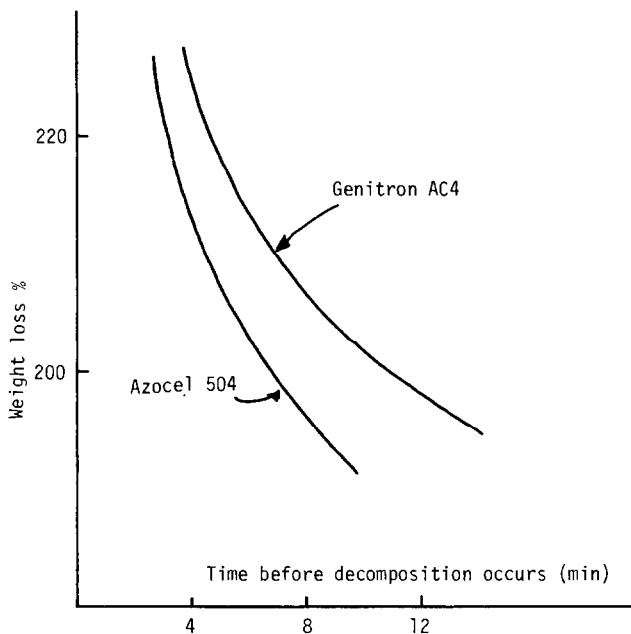


Fig. 10. Azodicarbonamide decompositions. Weight loss % vs. time before decomposition occurs.

DISCUSSION

In our experiments it was observed that ageing of the azodicarbonamide both by heat and UV irradiation did not affect the reaction kinetics: a

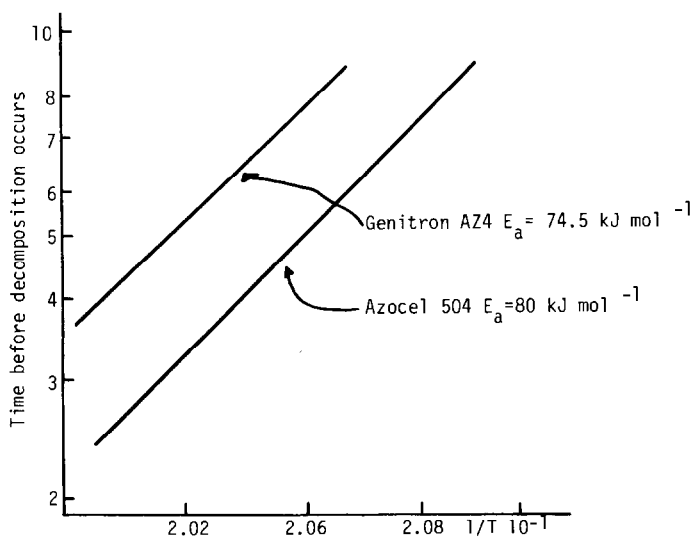


Fig. 11. Azodicarbonamide decompositions, Arrhenius plot.

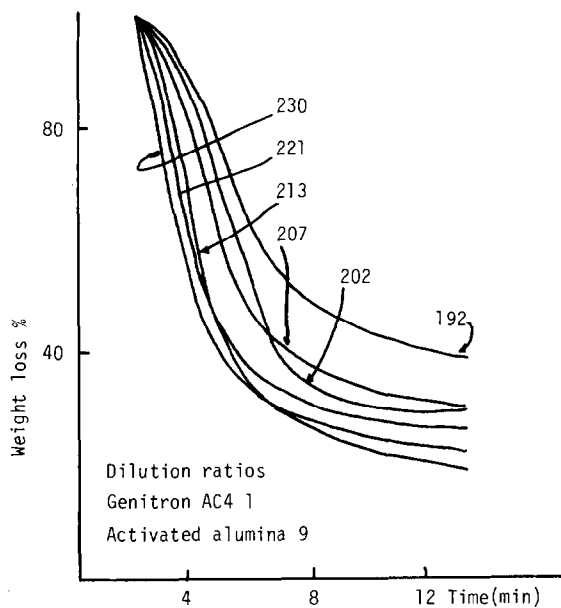


Fig. 12. Azodicarbonamide decompositions. Dispersions in activated alumina under nitrogen.

similar pattern of reaction being observed both before and after ageing. However, heat ageing may be a significant factor from an industrial viewpoint in that the total weight loss or gas evolution decreases with heat ageing. Thus, difficulty may be encountered when working near the upper limits of expansion.

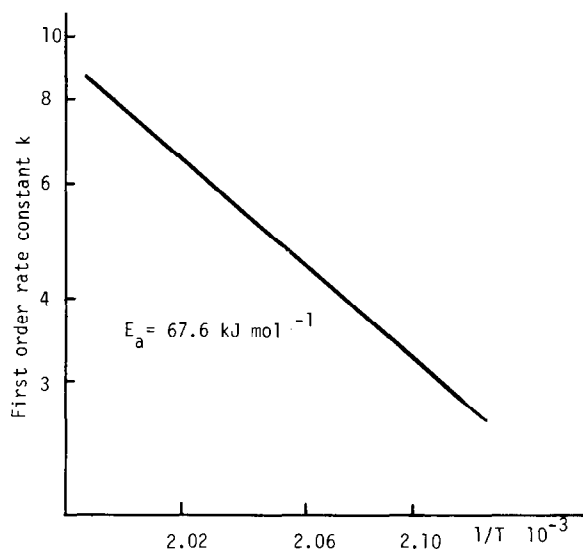


Fig. 13. Azodicarbonamide decompositions in activated alumina. Arrhenius plot.

From a mechanistic point of view the thermograms indicate two types of reaction:

(1) an initiation time in which 1–2% weight loss is observed, but no trace of reaction when followed by IR spectroscopy, followed by a sudden complete decomposition resulting in a total weight loss of 65–70%.

(2) a slower reaction, again with an initiation period, resulting in a similar total weight loss of 65–70%.

Hence, decomposition experiments in general show two mechanisms for which an activation energy may be calculated. Mechanism (i) is clearly associated with a process occurring in the induction or initiation period and in promotor catalyzed reactions, and has an activation energy of $125.5 \text{ kJ mol}^{-1}$; whereas (ii) has an activation energy of $146.5 \text{ kJ mol}^{-1}$ and occurs in those experiments where the material is decomposing in a non-explosive manner.

The existence of “periods of induction” was first realized by Cruickshank (1801) when he found that certain reactions were characterized by an initial period during which the process appeared to be quiescent. Periods of induction are sometimes associated with autocatalysis or processes involving chain mechanisms. The induction due to autocatalysis may be regarded as a result of successive reactions; in each case there is a slow stage followed by one or more rapid ones in which a product of the first stage is concerned. This is not thought to be likely in this case.

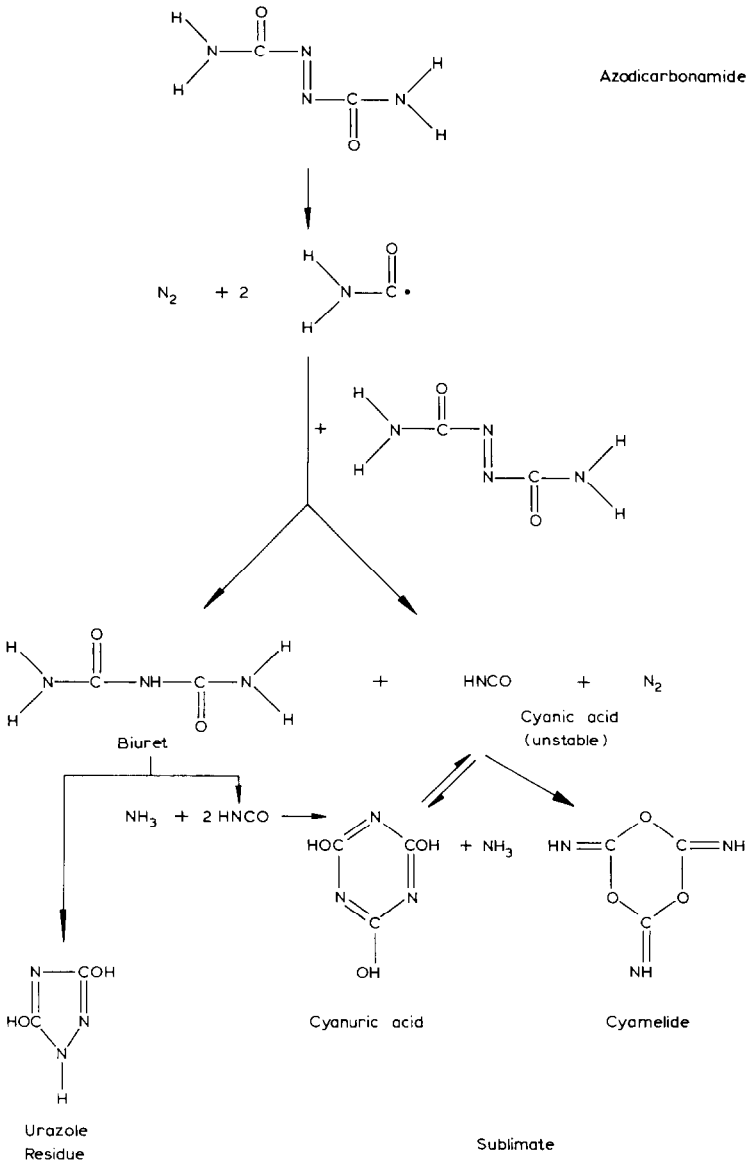
However, a process involving a chain mechanism, i.e., a nucleation process, is more likely and several arguments have been put forward to substantiate this type of mechanism. The concept of reaction chains was first postulated in connection with the photochemical combination of hydrogen and chlorine, but it has proved of great value in the interpretation of many other reactions, both thermal and photochemical. The chain carriers are usually atoms or radicals, and the resulting chains are referred to as atomic or radical chains. The possibility has been considered that chains may be propagated by molecules of the product carrying an excess of energy, obtained from the heat evolved in the reaction, which they transfer to molecules of reactant. Such energy chains, however, are apparently uncommon.

From a physical viewpoint the reaction is brought about by the formation of reaction sites within the particle. These sites grow and branch out into chains. However, one particle can only contain a certain number of growing chains and it is the coalescence of these chains between particles which is responsible for the explosive reaction. Isolation of the individual particles would produce a slower reaction, the rate being probably governed by the particle size.

Also, from an organic standpoint an examination of the structure of azodicarbonamide and the products formed on reaction, the following observations can be made:

- (1) azodicarbonamide is basically an unstable molecule containing six lone pairs of electrons;
- (2) reaction would be favored by an electron deficient surface, which would increase the rate of molecular breakdown;
- (3) the mechanism of the azodicarbonamide reaction is probably bimolecular with the formation of radicals.

The reaction, therefore, now appears to adopt the following pattern, the breakdown into radicals and the subsequent reaction of another molecule of azodicarbonamide being the chain mechanism or nucleation mentioned above. The sequence is



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