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THERMAL DECOMPOSITION OF SODIUM AZIDE

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ABSTRACT

The thermal decomposition of sodium azide has been investigated in the temperature range 240–365°C. Three values for the activation energy, 37.0, 59.0 and 14 kcal mol^{-1} have been obtained depending on the temperature range of study. The mechanism of decomposition seems to involve excited azide ions (through internal conversion) and excitations. The activation energy of 14 kcal mol^{-1} appears to be associated with the promotion of electron in the presence of sodium metal.

INTRODUCTION

A review of the work done on the thermal decomposition of sodium azide (the reported activation energy values are given in Table 1), reveals that, although

TABLE 1

ACTIVATION ENERGY VALUES FOR THE THERMAL DECOMPOSITION OF SODIUM AZIDE

Reference	*Activation energy (kcal mol^{-1})*
Garner and Marke[1]	34.4
Secco[3]	50 ± 5
Jacobs and Kureishy[4]	38
Audubert et al.[2]	40/43
	(below 365°C)
	20/23
	(above 365°C)
Singer and Mueller[5]	36.2 ± 4.8
	36.8 ± 7.1
Eliss and Hall[6]	29.0
	73.4
Torkar et al.[7]	18 ± 2 to 21 ± 1
	41 ± 3 to 47 ± 3

sodium azide has received considerable attention[1-8], there is no coherence in opinion as to its mechanism of decomposition. It has been generally argued that the decomposition involves an electron transfer process as the rate-limiting step[2,5] whereas Torkar et al.[8] have argued that the decomposition of sodium azide is associated with a diffusion-controlled process as the rate-determining step. Their observations that, (1) the activation energies for the thermal decomposition of sodium axide, ~20 and ~40 kcal mol^{-1}, agree well with those obtained from ionic conductivity measurements and (2) the decomposition is sensitised by divalent cations, led them to the above conclusion. In our recent investigations[9] on the effect of divalent cations and anions on the thermal decomposition of sodium azide, we have observed that impurities of different valence, in general, sensitize the decomposition and also that the effect is independent of the charge of the impurity ion. It appears, therefore, that the rate-determining step in the decomposition of sodium azide is associated with electron transfer reactions. In sodium azide, as the band gap is quite large (~8.5 eV), it is unlikely that the promotion of electron occurs to the conduction band. It is probable that electron transfer takes place to the various excitation levels.

In the present work the thermal decomposition of sodium azide has been investigated to determine the kinetic parameters and find out whether any correlation could be established between the activation energy for the decomposition of sodium azide and the thermal energies associated with the promotion of an electron to the excitation levels.

EXPERIMENTAL

Sodium azide used in the present investigation was supplied by Riedel De Haen AG Seelze, Hannover. All the samples were reprecipitated twice from double distilled water by acetone.

The particle sizes studied were in the following ranges: (1) 149–177 μm and (2) 250–297 μm. These particle sizes were obtained by allowing sodium azide samples to pass through stainless-steel sieves.

The kinetic studies of the thermal decomposition were followed in the temperature range 240–365°C in a constant volume vacuum line with an initial pressure of 1×10^{-5} torr. The pressure rise was measured using a McLeod gauge.

RESULTS

The isothermal decomposition of pure sodium azide has been studied in the temperature range 240–365°C as a function of particle size. Figures 1 and 2 show typical plots of the fractional decomposition, α, versus the heating time, t. The kinetic plots have been fitted to the Avrami–Erofeev equation with $n = 2$. Figure 3 represents the Arrhenius plot for the decomposition of sodium azide. The activation energy values are given in Table 2.

At temperatures around 300°C, a metallic mirror of sodium appeared on the

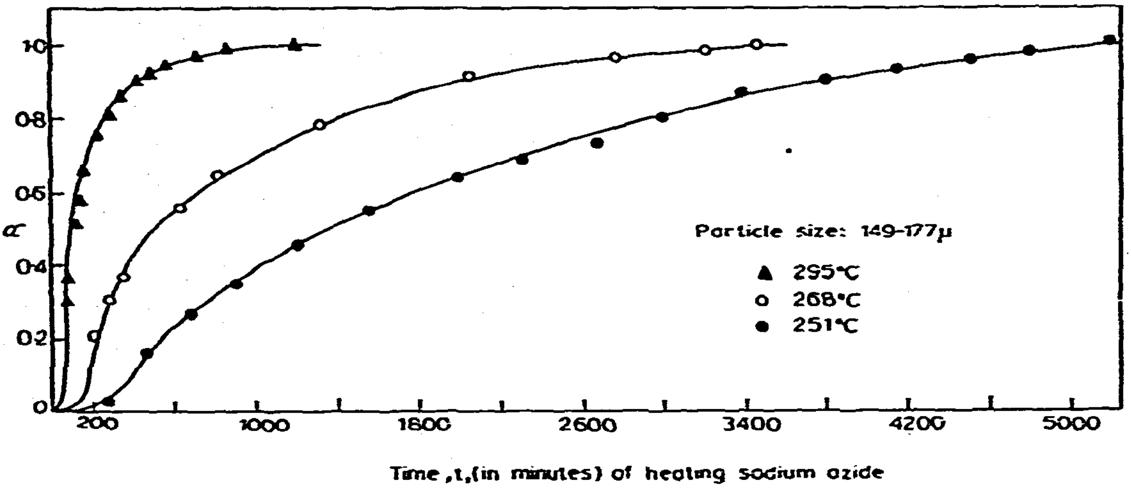

Fig. 1. Plots of the fractional decomposition, α, versus time, t (in min), of heating of sodium azide.

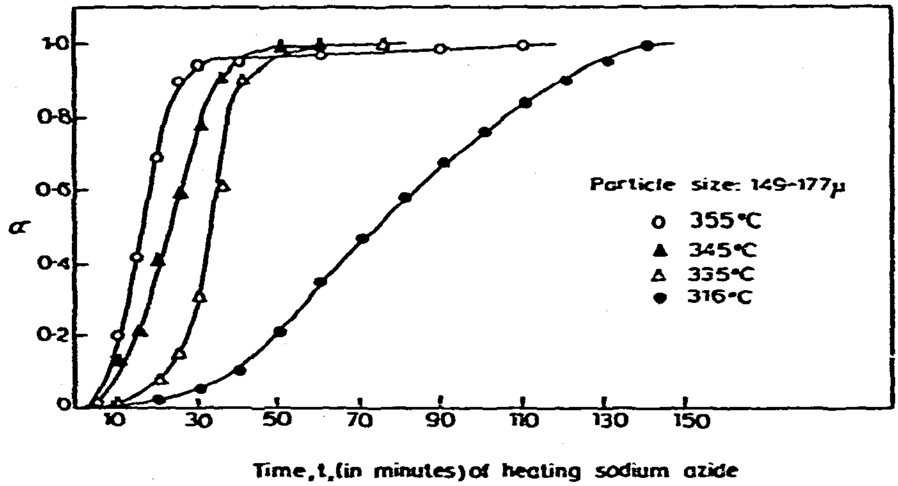

Fig. 2. Plots of the fractional decomposition, α, versus time, t (in min), of heating of sodium azide.

cooler parts of the reaction tube after the decomposition had proceeded to a certain extent.

The thermal activation energies associated with the various electronic transitions in the azide ions have been calculated from the wavelengths corresponding to these processes using the relation $E_{th} = E_{opt} \cdot K_h/K_l$, where E_{th} is the thermal activation energy, E_{opt} is the optical activation energy, K_h and K_l are the high-frequency and low-frequency dielectric constants, respectively. Table 3 gives the activation energies associated with the internal transition of the azide ion and the excitation levels.

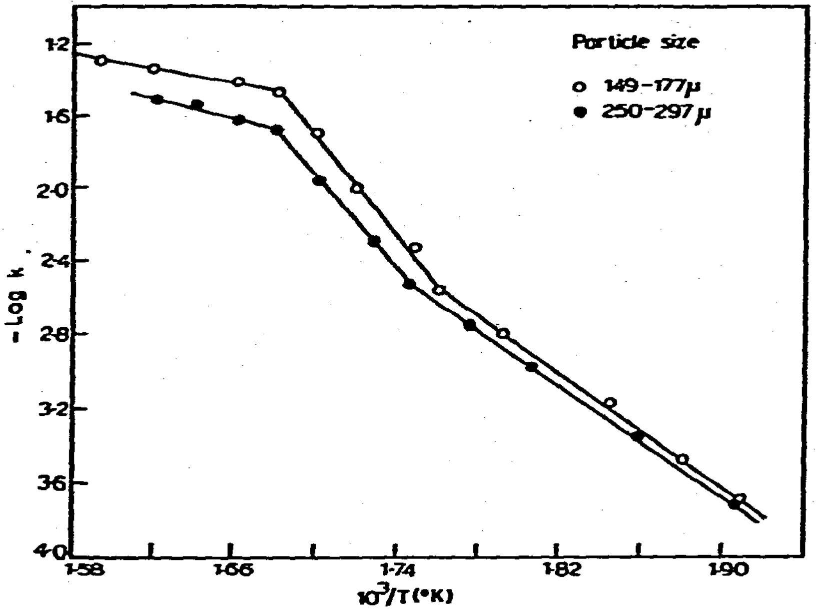

Fig. 3. Arrhenius plots for the decomposition of sodium azide.

TABLE 2

ACTIVATION ENERGY VALUES FOR THE THERMAL DECOMPOSITION OF SODIUM AZIDE

Particle size (μm)	*Temp. (°C)*	*Activation energy (kcal mol^{-1})*
(1) 150–297	251–299 (A)	34.54
	299–315 (B)	58.87
	315–351 (C)	13.81
(2) 149–177	252–295 (A)	36.84
	295–323 (B)	59.87
	323–356 (C)	12.51

TABLE 3

THERMAL ACTIVATION ENERGIES ASSOCIATED WITH VARIOUS EXCITATION LEVELS IN SODIUM AZIDE AND INTERNAL TRANSITION OF AZIDE ION

Quantum No.	*Wavelength*^{a}	*Thermal activation energy (kcal mol^{-1})*
1	1910	51.35
2	1560	62.82
3	1505	65.34
	1465	66.93
Internal transition	2225	43.7

[a] Values taken from S. K. Deb, *J. Chem. Phys.*, 35 (1961) 2122.

DISCUSSION

A comparative analysis of the activation energy values in Tables 2 and 3 shows a correspondence between the activation energies associated with the thermal decomposition of sodium azide in the temperature regions A and B, and the thermal energies required for the excitation of the azide ion via an internal transition and for the promotion of the electron of the azide ion to the second excitation level. The activation energy, 36 kcal mol^{-1}, in the temperature range 251–299 °C (A) is close to 44 kcal mol^{-1}, which is the thermal energy required for the internal transition of the azide ion, while the activation energy, 59 kcal mol^{-1}, in the temperature region 299–315 °C (B) seems to be in good agreement with the energy necessary for the promotion of the electron to the second excitation level. Taking into account the empirical nature of the relation used to calculate the thermal energies, the above agreement between the activation energy values may be considered satisfactory.

In the temperature range 300–350 °C, an activation energy of 14 kcal mol^{-1} has been obtained for the decomposition of sodium azide. This might correspond to the energy required for the removal of an electron from the azide ion in the presence of sodium metal formed as a result of decomposition. Metal particles are known to introduce levels below the conduction band[10]. An approximate calculation of the work, ψ, required to remove an electron from sodium metal into the conduction band of sodium azide gave a value of 0.73 eV. This value has been obtained using the relation[11]

$$\psi = \emptyset - X = \emptyset + h\nu - E - W_1 + 1/2\,\mathrm{eV}$$

where $\emptyset$ = work function of sodium metal; X = work required to remove an electron from the conduction band of the crystal; $h\nu$ = the optical band gap; E = the electron affinity; W_1 = the lattice energy, and eV = the polarisation energy.

It is interesting to point out here that Miller[12] in his investigations on the effect of UV irradiation and heat on sodium azide found that colloidal sodium is formed when the azide was heated at 327 °C as detected by cryoabsorption spectroscopy and ESR. Metallic sodium thus formed, was found to have an optical absorption maximum at 5200 Å. The thermal activation energy associated with this optical absorption is 18.4 kcal mol^{-1}.

Thus, sodium metal formed during the decomposition could considerably alter the energetics of decomposition because alternative routes, which involve lesser activation energy, would be available for the decomposition to proceed.

CONCLUSIONS

The mechanism of the decomposition of sodium azide seems to be quite complex. The decomposition process is associated with three activation energies 37, 59 and 14 kcal mol^{-1}. Agreement of the experimental activation energy values (37 and 59) with the calculated thermal energies associated with internal transition of the azide ion and the promotion of electron to the excitation levels indicates the importance of these processes in the thermal decomposition of sodium azide. Moreover, our activation energy values obtained by pressure measurements are close to those obtained earlier by workers from thermoluminescence and electron emission studies [2, 5], which clearly point towards the role of electron transfer reactions in the decomposition of sodium azide.

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