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Azidation of Polyvinyl Nitrate & Energy Related Studies

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ABSTRACT

Partially substituted polyvinyl azide (PVAZ) samples were prepared by reacting sodium azide with polyvinyl nitrate (PVN), containing 15.71 per cent *N*, in a solution of dimethyl formamide. Replacement of a large proportion of $-ONO_2$ groups by $-N_3$ groups in polymer chain ('azidation' of PVN) enhanced reactivity, impact sensitivity and energetics, but reduced thermal stability of the products. The thermogravimetric analysis of PVN showed the onset of rapid decomposition at about 171 °C. The kinetic analysis of thermogravimetric results indicated the validity of random nucleation first-order reaction model. A differential scanning calorimetry thermogram of PVAZ showed a peak at 183.9 °C and heat of decomposition of 2732 J/g, which is lower than that for PVN.

1. INTRODUCTION

Polyvinyl azide $\{(C_2H_3N_3)_n\}$ (PVAZ), is a polymeric azide, containing highly reactive azide group attached to the carbon chain. Several inorganic azides like lead azide $Pb(N_3)_2$, are known to be highly sensitive explosives. Similarly, some organic polymers, containing the azide group like glycidyl azide polymer (GAP), are useful as energetic binders in rocket propellant formulations. As an adjunct to our work on the energetics of polyvinyl nitrate (PVN)[1], we decided to study its azide derivative. Although, PVAZ should be an interesting candidate for study as an energetic material, it has not received adequate attention so far. Published literature on PVAZ is rather scanty and superficial. Although, Takeishi and Okawara[2] and Gilbert[3] reported the preparation and general properties of PVAZ, yet they did not dwell upon its energetics and related aspects.

The results of our investigations on the energetics, sensitiveness and thermal stability of PVAZ or, more correctly, PVAZ-PVN complex are presented in this paper.

2. EXPERIMENTAL DETAILS

2.1 Materials

Fibrous PVN, containing 15.71 per cent *N*, was prepared by the controlled nitration of commercial polyvinyl alcohol (Gohsenol NM-11) at a low temperature[1]. The all other materials used at 20 °C were:

Sodium azide (CP grade), specific gravity 1.846.

Dimethyl formamide (DMF, SQ grade, Glaxo), specific gravity 0.9487.

Hydrochloric acid (AR grade), specific gravity 1.18.

Methanol (AR grade, Glaxo), specific gravity 0.889.

2.2 Preparation of PVAZ

The preparation of PVAZ, reported in literature[2,3], involved the reaction of sodium azide (NaN_3) with PVN in dimethyl formamide (DMF) medium, for different time-temperature conditions. A similar procedure was adopted and two batches

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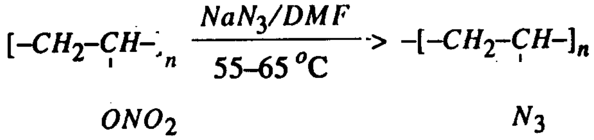
of PVAZ were prepared by reacting NaN_3 with PVN at 55-65 °C for different durations. The reaction scheme was as follows:



$$[-CH_2-\underset{ONO_2}{CH}-]_n \xrightarrow[55-65\,^{\circ}C]{NaN_3/DMF} -[-CH_2-\underset{N_3}{CH}-]_n$$

Polyvinyl nitrate Polyvinyl azide

Five grams of PVN (15.71 per cent N) was dissolved in 95 g DMF at room temperature, in a three-necked pyrex flask. To this mixture, 5.5 g of sodium azide was added gradually with constant stirring. After completion of addition of sodium azide, the reaction mixture was kept for 24 hr in a water bath at 55 °C without stirring. The reaction mixture was then cooled at room temperature and poured into water containing 10 per cent HCl. The resulting brownish-coloured solid mass was filtered. After filtration, the product was washed repeatedly with plenty of distilled water followed by methanol. Finally, the product was wiped with filter paper and dried completely using high vacuum. This product was designated PVAZ-1 for subsequent study.

In a parallel experiment, the reaction mixture was kept on a water bath at 65 °C for 20 hr and then the same procedure was followed. The product so obtained was designated PVAZ-2.

3. RESULTS & DISCUSSION

3.1 Physical Properties

Polyvinyl azide (PVAZ-1 and PVAZ-2) is brownish, soft and fragile when freshly prepared. However, on exposure to air, it darkens and forms a hard mass within a short time. When fresh, it is soluble in tetrahydrofurane (THF), acetone and 1,4-dioxane. However, after storage for a few weeks, it becomes insoluble in all these solvents. These observations suggest the occurrence of air-oxidation of the azide. (Gilbert has reported[3] $C=C$ double bond formation and fairly rapid cross-linkage in his PVAZ samples, without explanation).

3.2 Infrared Spectra

The IR spectra of thin films of freshly prepared PVAZ samples (in THF solution) were taken in a Perkin-Elmer double beam spectrophotometer. A typical IR spectra of PVN (15.71 per cent N) and samples of PVAZ are shown in Fig. 1. The spectra

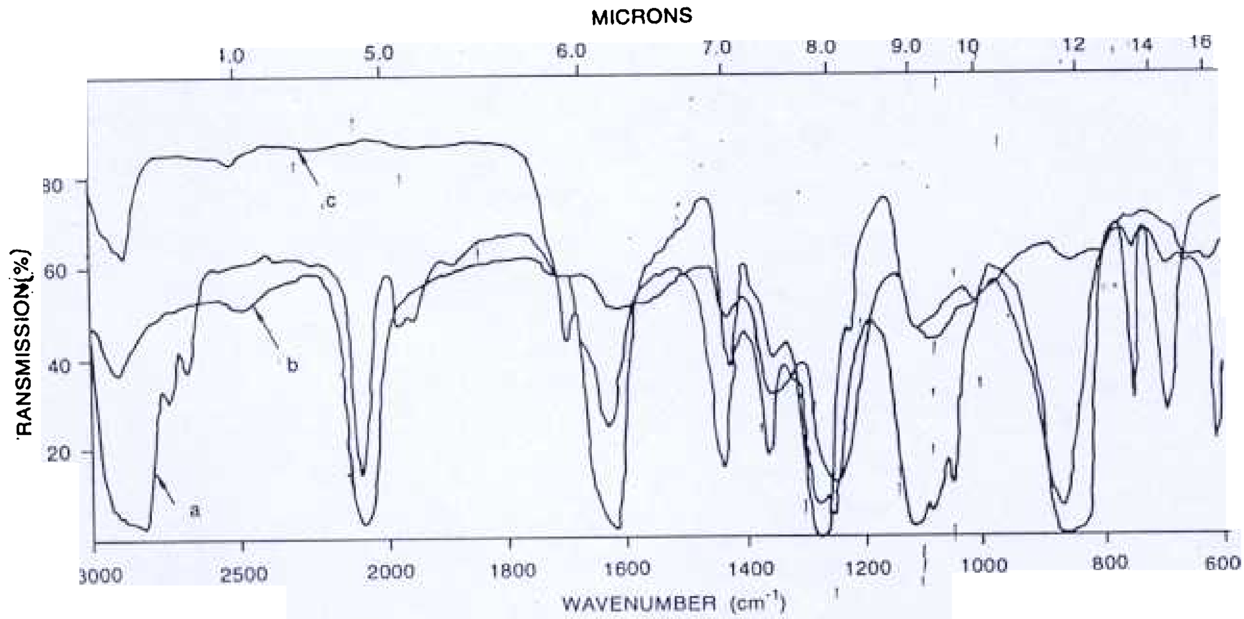


Figure 1. IR spectra (a) PVN (15.71% N) (b) PVAZ-1 (c) PVAZ-2

show absorption peaks at the following frequencies which are assigned to characteristic structural features in accordance with those reported in literature[4,5].

Frequency (cm^{-1})	Relative intensity	Assignments
1675	Strong	$-ONO_2$
1250	Strong	$-ONO_2$, also N_3
1350 & 1430	Weak	$-CH_2$
2100	Very weak	$-N_3$
2920	Weak	$-CH$

The IR spectra show the presence of nitrate as well as azide groups. Therefore, it appears that there is only a partial replacement of nitrate groups by azide groups in the polymer chain under specific conditions.

3.3 Elemental Analysis & Assessment of Azidation

Nitrogen content (% N) in a PVAZ sample would roughly indicate the extent of substitution of nitrate (ONO_2) groups in PVN chains by azide (N_3) groups. The samples of PVAZ-1 and PVAZ-2 were microanalysed at the High Energy Materials Research Laboratory, Pune, using $C, H\ N$ elemental analyser. The results are shown in Table 1.

Table 1. Elemental composition of PVAZ samples

Sample*	Carbon (%)	Hydrogen (%)	Oxygen (%)	Nitrogen (%)
PVAZ-1	49.26	4.96	7.31	38.47
PVAZ-2	48.16	4.92	14.04	32.88

* PVAZ-1 was prepared by reaction at 55 °C for 24 hr.,
PVAZ-2 was prepared by reaction at 65 °C for 20 hr.

Theoretically, PVAZ contains a maximum of 60.87 per cent N (and no oxygen), whereas PVN contains a maximum of 15.73 per cent N (and 53.93 per cent oxygen). Therefore, the presence of 32.88-38.47 per cent N (and 7.3-14.0 per cent oxygen) in the PVAZ samples indicated that the original PVN was only partially converted into PVAZ and/or the samples had undergone some air-oxidation. Thus the PVAZ was actually a combination of PVAZ and PVN.

Simple calculations show the following correlation between the mole ratio $x : y$ in the mixed product $(CH_2\text{-}CH\text{-}N_3)_x.\ (CH_2\text{-}CH\text{-}ONO_2)_y$ and its nitrogen content :

x : y ratio	% N	Significance
		50 per cent azidation (i.e. half the nitrate groups in PVN chain are replaced by azide groups).
2 : 1	43.17	66.66 per cent azidation
3 : 1	47.30	75 per cent azidation
4 : 1	49.86	80 per cent azidation

Calculations also indicate the ratio of vinyl azide to vinyl nitrate repeat units (that is, $x : y$ ratio) in PVAZ-1 and PVAZ-2 is 1.13 : 1 and 0.79 : 1, respectively. In other words, the extent of 'azidation' achieved is a little above 50 per cent in PVAZ-1 and a little below 50 per cent in PVAZ-2. Interestingly, the 'best' sample of PVAZ prepared by Gilbert[3], contained 38.4 per cent C, 4.7 per cent H, 7.3 per cent O and 49.6 per cent N.

3.4 Ignition Delay & Activation Energy

An enclosed Wood's metal bath, with temperature regulator, was used for determination of ignition delay (ID) period. Approximately 5 mg samples of PVAZ (PVAZ-1 and PVAZ-2) were taken in small aluminium capsules, and the ignition delay was noted at bath temperature varying from 453 to 503 K (180 to 230 °C) at intervals of 5 K.

The ignition temperatures, i.e., temperatures corresponding to 5 s ID for PVAZ-1 and PVAZ-2 are 488 K and 498 K, respectively. (For comparison, the ignition temperature of PVN containing 15.71 per cent N is 513 K).

Activation energy of PVAZ samples was calculated by using Semenov equation,

$$D = C\, e^{E/RT}$$

where

D = Ignition delay
E = Activation energy
R = Universal gas constant
T = Absolute temperature
C' = A constant (depending on the composition of the explosive material).

On plotting log D against $1/T$, a straight line was obtained. From the slope of the curve, the following values of activation energy of PVAZ were obtained:

PVAZ-1	13.27 kcal/mol
PVAZ-2	11.30 kcal/mol

Compared to the above values, the activation energy for PVN containing 15.71 per cent N is 16.076 kcal/mol[1].

3.5 Impact Sensitivity

The impact sensitivity measurements on samples of PVAZ were carried out using a standard 'Fallhammer' apparatus[6]. A sample of 20 mg was placed on the anvil and a 2 kg weight was dropped onto it from an arbitrary height. Successive trials were carried out at the height intervals of 5 cm and continued till sufficient data was collected, as per the Bruceton staircase procedure[6]. From the data obtained, the percentage of explosion for each height was calculated.

A graph plotted between the heights of fall and percentage of explosion for PVAZ-1 and PVAZ-2 shows that the median heights of fall for 50 per cent explosion are 50.5 cm and 61 cm, respectively (as compared to 81 cm for PVN containing 15.71 per cent N[1]). Thus, PVAZ was appreciably more sensitive than PVN to impact loads, apparently due to the presence of more reactive and strained azide groups. The sensitivity also increased with increasing 'azidation'.

After repeating the experiments with RDX, the figure of insensitiveness (F of I) of PVAZ and PVN was calculated by the specified procedure[6], with RDX as the reference standard. The F of I values were found to be as follows :

PVAZ-1	79
PVAZ-2	96
RDX (Ref. std	80

Thus, PVAZ-1 is as impact-sensitive as RDX, but PVAZ-2 is less so. (F of I for PVN containing 15.71 per cent N was found[1] to be 127).

3.6 Calorific & Calorimetric Values

Heat of combustion (calorific value) of PVAZ was determined in a Gallenkamp adiabatic bomb calorimeter, using oxygen at 25 atm. Similarly, heat of explosion (calorimetric value) was determined using nitrogen at 25 atm. The following results were obtained :

Specimen	Heat of combustion (cal/g)	Heat of explosion (cal/g)
PVAZ-1	4283	725
PVAZ-2	4293	713

Interestingly, for PVN (15.71 per cent N) the heat of combustion is lower (3023 cal/g), whereas the heat of explosion is higher (987 cal/g)[1]. These differences are explained on the basis of lower fuel (carbon and hydrogen) content and greater oxygen content in PVN than in PVAZ, giving oxygen balance values of -44.9 per cent and -81.1 per cent, respectively.

Heat of formation (ΔH_f) of the two PVAZs (PVAZ-1 and PVAZ-2) was calculated from experimentally determined heat of combustion values by applying the necessary correction, and the following values were obtained :

PVAZ-1	+ 3.76 kcal/mol
PVAZ-2	+ 4.66 kcal/mol

Incidentally, ΔH_f for PVN (15.71 per cent N) is -21.937 kcal/mol. This indicates that PVAZ, having positive ΔH_f, is inherently more energetic than PVN.

3.7 Thermal Analysis

Well-dried PVAZ samples were subjected to thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in Dupont instruments 951 TGA and 910 DSC apparata, respectively, with a view to study their thermal properties like thermal stability, initial decomposition temperature(T_i), final decomposition temperature (T_f), and the heat of decomposition.

A typical non-isothermal TGA thermogram obtained by heating 7 mg sample of PVAZ-1 at a rate of 5 °C/min in nitrogen is shown in Fig. 2. The thermogram shows T_i = 140 °C, onset temperature =171.4 °C, and T_f =182 °C. The rapid decomposition (and weight loss) after the onset temperature culminates in spontaneous ignition. It is also noteworthy that PVAZ-1 is less thermally stable[7] than PVN (15.71 per cent N), for which T_i =176 °C and T_f = 200 °C. This behaviour of PVAZ-1 is due to the presence of a large number of reactive azide groups.

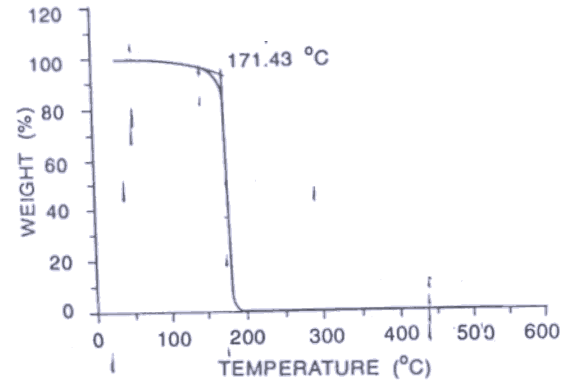


Figure 2. Thermogravimetric plot of PVAZ-1 at heating rate of 5 °C/min.

Kinetic analysis of PVAZ-1 was carried out by fitting its TG data to various kinetic models/equations and using a computer programme[8]. The 'most acceptable set' of kinetic parameters, viz., E and A (consistent with the maximum value of regression coefficient, r) is obtained by applying the random nucleation first order reaction model (Mampel's unimolecular law). The Arrhenius plot for decomposition in the range of 135-145 °C is shown as a typical illustration, in Fig. 3. The computed values of E and ln A as well as r are presented in Table 2.

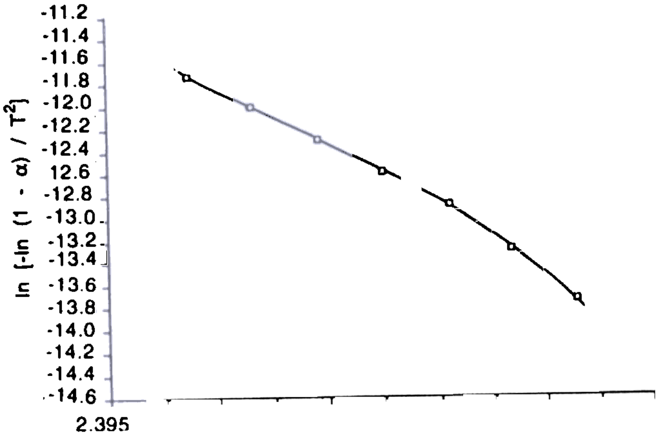


Table 2. Kinetic parameters for PVAZ-1 computed from the TG data using random nucleation (first order) model (heating rate = 5 °C/min, sample size 7 mg)

Temperature range (°C)	Progressive weight loss (%)	Kinetic parameters		Regression coefficient (r)
		E (kJ/mol)	ln A (s^{-1})	
120-130	3.10	360	103.71	0.9827
135-145	4.15	518	146.52	0.9895
148-158	6.32	561	154.07	0.9922
159-171	11.29	517	137.44	0.9874
172-186	99.16	597	155.58	0.9905

From these data, it is observed that with increase in temperature range, the E as well as ln A increase, but this trend is temporarily interrupted by a sudden fall at the range of 159-171 °C.

Also, a DSC thermogram obtained by heating a 2.9 mg sample of PVAZ-1 at a rate of 5 °C/min in nitrogen is shown in Fig. 4. The peak appears at 183.9 °C and the heat of decomposition is 2732 J/g (compared to 196.7 °C and 3068 J/g, respectively, for fibrous[9] PVN containing 15.71 per cent N). The DSC analysis corroborates the conclusion drawn from TGA, viz., PVAZ has lesser thermal stability than PVN. Also, DSC results corroborate the adiabatic bomb calorimetric results in that the enthalpy of explosion of PVAZ is lower than that of PVN.

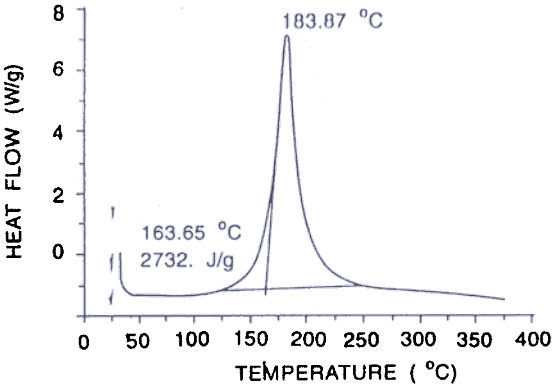


Figure 4. DSC plot of PVAZ-1 at heating rate of 5 °C/min

4. CONCLUSION

The present work shows that the 'azidation' of PVN, i.e., replacement of a significant proportion of -ONO_2 groups by -N_3 groups (thereby increasing the nitrogen content) enhances the reactivity, impact sensitivity and energetics, but reduces the thermal stability.

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